# The theory of equilibrium critical phenomena

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Abstract. The theory of critical phenomena in systems at equilibrium is reviewed at an introductory level with special emphasis on the values of the critical point exponents  $\alpha, \beta, \gamma, ...,$  and their interrelations. The experimental observations are surveyed and the analogies between different physical systems-fluids, magnets, superfluids, binary alloys, etc.-are developed phenomenologically. An exact theoretical basis for the analogies follows from the equivalence between classical and quantal 'lattice gases' and the Ising and Heisenberg-Ising magnetic models. General rigorous inequalities for critical exponents at and below  $T_c$  are derived. The nature and validity of the 'classical' (phenomenological and mean field) theories are discussed, their predictions being contrasted with the exact results for plane Ising models, which are summarized concisely. Padé approximant and ratio techniques applied to appropriate series expansions lead to precise critical-point estimates for the three-dimensional Heisenberg and Ising models (tables of data are presented). With this background a critique is presented of recent theoretical ideas: namely, the 'droplet' picture of the critical point and the 'homogeneity' and 'scaling' hypotheses. These lead to a 'law of corresponding states' near a critical point and to relations between the various exponents which suggest that perhaps only two or three exponents might be algebraically independent for any system.

# 1. Introduction

# 1.1. Phases and critical points

Change of phase—the boiling of water, the melting of iron—is one of the most striking aspects of the macroscopic physical world. In many cases the various phases of matter seem quite dissimilar and separate, and transitions between them are abrupt and unheralded. Nevertheless, by varying the temperature or other thermodynamic parameters, two distinct phases can frequently be made more and more similar in their properties until, ultimately, at a certain critical point, all differences vanish. Beyond this point only one homogeneous equilibrium phase can exist and all changes are continuous and smooth. The most familiar example of such a critical point is (i) that which terminates the coexistence curve of a liquid and its vapour at a characteristic temperature, pressure and density,  $T_{\rm e}$ ,  $p_{\rm e}$  and  $\rho_{\rm e}$ . Other examples are as follows: the critical point of phase separation in (ii) a binary fluid mixture or (iii) a binary metallic alloy, which marks the temperature above which (or sometimes below which) the components mix homogeneously in all proportions; (iv) the Curie point or critical point of a ferromagnetic crystal at which the spontaneous magnetization, and hence the difference between two differently oriented magnetic domains, goes continuously to zero; (v) the Néel point at which the alternating spin order of an antiferromagnet goes to zero so that two counterphase domains become indistinguishable; (vi) the ordering temperature  $T_{\rm e}$  of a

homogeneous binary crystal such as beta-brass (Cu–Zn), above which the two species have no preference for one or the other crystal sublattice, but below which one sublattice is predominantly occupied by one species; (vii) the lambda point of liquid helium 4 below which there exist macroscopically distinct régimes of superfluid flow but above which superfluidity vanishes; (viii) the critical point of a metallic superconductor below which the electrical resistance vanishes and various permanent currents may flow but above which dissipation always occurs.

More formally those transitions in which one or more first derivatives of the relevant thermodynamic potentials change discontinuously as a function of their variables may be called *first-order transitions*. For a fluid it is appropriate to consider the Gibbs free energy G as a function of p and T; the specific volume  $v = (\partial G/\partial p)_T$  and the entropy  $S = -(\partial G/\partial T)_p$  are discontinuous across the vapour pressure curve. In a ferromagnet the equilibrium magnetization  $M = -(\partial F/\partial H)_T$ , where F is the Helmholtz free energy and H the magnetic field, changes abruptly as the field passes through zero when T is less than  $T_c$ .

On the other hand, transitions in which the first derivatives of the thermodynamic potential remain continuous while only higher-order derivatives such as the compressibility, the specific heat or the susceptibility are divergent or change discontinuously at the transition point may conveniently be termed continuous transitions.<sup>†</sup> It is for such transitions that we use the term 'critical point'. It might be argued that the word 'point' may not always be appropriate unless one considers the variation of only a single thermodynamic parameter. Thus the transition from antiferromagnetic to paramagnetic phases as a function of temperature probably remains continuous for a range of magnetic fields about zero, and the lambda line of liquid helium is a line of continuous transition points over its whole length. Although this distinction will often be an important one in the discussion of particular systems (see below) the theoretical and experimental questions remain much the same for all critical points. In particular a dominant characteristic is the large increase of the microscopic fluctuations in the vicinity of a critical point which herald the approaching transition. Fluctuations of density, energy, magnetization, etc., can reach effectively macroscopic magnitudes and, correspondingly, the related second thermodynamic derivatives (specific heats, susceptibilities, etc., as mentioned above) and the intensities for the scattering of waves off the system become very large or even tend to infinity at certain wavelengths.

Consequently a problem of central interest in the study of critical phenomena, both experimentally and theoretically, is the determination of the asymptotic laws governing the approach to a critical point. Some of these, notably the 'one-third' power law for the vanishing of the density discontinuity  $\rho_{\rm L} - \rho_{\rm G}$  between coexisting liquid and gas as a function of  $T_{\rm c} - T$ , strikingly demonstrated in figure 1, have a fairly long history; others, such as the logarithmic divergence of the specific heat  $C_p$  of helium at the lambda point and the near-logarithmic divergence of  $C_V$  for argon at its critical point, are more recent discoveries. Theories competent to make

<sup>&</sup>lt;sup>†</sup> The original classification of transitions, due to Ehrenfest, which essentially recognized only discontinuities in thermodynamic derivatives, rather than divergencies, is inappropriate in the light of present theoretical and experimental knowledge. It seems best, therefore, to discard terminology such as 'second order' or 'third order' which is often confusing or uninformative.

significant predictions about critical-point behaviour have, however, developed mainly in the past decade or two and have been a focal point of activity in the last few years.

The purpose of this article is to review at an introductory level the theory of critical phenomena as it stands today. While the limitations of space (and of the author's competence) do not allow the presentation of full details or the discussion of all theoretical aspects (in particular dynamic phenomena will not be discussed except briefly in the concluding section), it is hoped that the main features will be clearly outlined so that both the strengths and weaknesses of the present position will be evident.



Figure 1. Plot of the cube root of  $\Delta T = T_c - T$  against  $\Delta \rho = \rho_L - \rho_G$  for CO<sub>2</sub> demonstrating the validity of the 'one-third' law to high accuracy over three decades in temperature. (After Lorentzen 1965.)

The layout of the article is as follows. The underlying philosophy and some statistical-mechanical and mathematical background are sketched in the remainder of this section. Section 2 contains an introductory survey of the experimental situation, mainly in regard to fluids and magnetic systems; this serves to establish the definitions of the various critical exponents  $\alpha, \beta, \gamma, ...$ , and leads to the phenomenological development of the close analogies between different physical systems. (The definitions and values of the critical exponents are collected in a fold-out table at the end of the article for easy reference.) Rigorous inequalities which the critical-point exponents must satisfy are proved in §3. The phenomenological analogies find a firm theoretical foundation in the equivalence of classical-lattice gases and Ising-model ferromagnets and of quantal-lattice gases and anisotropic

Heisenberg-Ising ferromagnets as shown in §4. The basic 'classical' approaches to the theory of critical points are reviewed briefly, and their validity discussed, in §5. The deficiencies of the classical theories are now evident, particularly by comparison with the exact results for plane Ising models which are reviewed in §6. The use of series expansions to obtain numerical information about critical points when exact theories have not been discovered is discussed in §7; the results for the Ising and Heisenberg models found from the series using the Padé approximant and ratio techniques are surveyed in §8. (Fairly extensive tables of critical data are presented.) We return to the problem of our general theoretical understanding in §9 and review the various relations and 'laws' which have been derived from the 'droplet' picture of the critical point and from various 'homogeneity' and 'scaling' hypotheses. The article is summarized in the concluding section, and, with a view to future developments, various special aspects are mentioned and some of the problems confronting the theory of *non*-equilibrium critical phenomena are sketched. A reader familiar with the subject but interested in recent developments might wish to read only §§ 6.2, 6.3, 8, 9 and 10.

Although our exposition is self-contained, greater emphasis on the experimental situation would have been appropriate were it not for a companion article by Heller (1967) which presents a critique of the wide range of pertinent experimental data and techniques.

### 1.2. The task of theory

Before embarking on an exposition of the theory of critical phenomena it is appropriate to ask what the main aim of theory should be. This is sometimes held (implicitly or explicitly) to be the calculation of the observable properties of a system from first principles using the full microscopic quantum-mechanical description of the constituent electrons, protons and neutrons. Such a calculation, however, even if feasible for a many-particle system which undergoes a phase transition need not and, in all probability, would not increase one's *understanding* of the observed behaviour of the system. Rather, the aim of the theory of a complex phenomenon should be to elucidate which general features of the Hamiltonian of the system lead to the most characteristic and typical observed properties. Initially one should aim at a broad qualitative understanding, successively refining one's quantitative grasp of the problem when it becomes clear that the main features have been found.

To achieve these ends the study of 'model systems' has been increasingly rewarding. The ideal model should provide as realistic a description as possible of those features of a physical system believed to be important for the phenomena under study but, at the same time, should be tractable mathematically. Without this second characteristic, theoretical discussion frequently adds little more to one's understanding than that gained directly from experiments. Conversely one should always attempt to refine a model in order to test how far its defects as a true microscopic description affect the conclusions drawn.<sup>†</sup>

The recent history of the study of critical phenomena has, in the main, followed the course of simplifying the physical models while improving and strengthening

 $\dagger$  The philosophy advanced here has been vividly expounded by Frenkel (1946 a, quoted by Tamm 1962).

the mathematical techniques to the stage where, at last, fairly accurate theoretical treatments can be given for models which, while gross oversimplifications of reality in many respects, do certainly embody a number of the vital features of the particles and interactions leading to phase transitions and critical points. The first part of this article will be devoted to sketching some of these models and to exploring the analogies between different physical systems that can be drawn on the basis of their mathematical structure.

Given a model one must choose the theoretical approach. We shall concentrate attention on physical systems in thermodynamic equilibrium (or, sometimes, suffering infinitesimal departures from equilibrium). The appropriate method is then that of statistical mechanics, classical or quantum-mechanical according to the dictates of the model. We stress here that if the real system is not in true equilibrium but is in some non-equilibrium or, perhaps, semi-metastable state, normal statistical mechanics is not appropriate and one must think again. Conversely, in performing experiments to check equilibrium theories care must be taken to maintain equilibrium. This may not always be easy since time constants can become very long (of the order of days) even in quite simple systems when near their critical points, and first-order transitions are often intimately associated with hysteresis and unstable or metastable states.

# 1.3. Basis in statistical mechanics

For a system of N identical particles of mass m confined in a domain  $\Omega$  of volume  $V(\Omega)$  the fundamental relation of classical statistical mechanics is

$$Q(T, N, \Omega) = \frac{1}{N!} \int_{\Omega} d\mathbf{r}_1 \dots \int_{\Omega} d\mathbf{r}_N \exp\left(-\beta U_N\right)$$
(1.3.1)

where  $\beta = 1/k_{\rm B} T$  and  $U_N = U_N(\mathbf{r}_1, ..., \mathbf{r}_N)$  is the total potential energy. From this expression for the configurational partition function the connection with thermodynamics is established by

$$-\frac{F_N}{Nk_{\rm B}T} = \frac{1}{N} \ln \left\{ Q(T, N, \Omega) \right\} - d \ln \Lambda$$
(1.3.2)

where  $F_N$ , the total Helmholtz free energy, is regarded as a function of T and of the specific volume

$$v = \frac{1}{\rho} = \frac{V(\Omega)}{N} \tag{1.3.3}$$

and where d is the dimensionality and

$$\Lambda^2 = \frac{h^2}{2\pi m k_{\rm B} T} \tag{1.3.4}$$

h being Planck's constant. Alternatively, one may form the grand canonical partition function

$$\Xi(T,Z;\,\Omega) = \sum_{N=0}^{\infty} z^N Q(T,N,\Omega)$$
(1.3.5)

where, in d dimensions, the activity z is related to the chemical potential  $\mu$  by

$$z = \frac{\mathrm{e}^{\beta\mu}}{\Lambda^d} \tag{1.3.6}$$

and then derive thermodynamic properties from

$$\frac{p}{k_{\rm B}T} = \pi_{\Omega}(T, z) = \frac{1}{V(\Omega)} \ln \{\Xi(T, z, \Omega)\}.$$
(1.3.7)

For quantum-mechanical systems one must, of course, replace (1.3.1) by

$$Z(T; N, \Omega) = \Lambda^{-dN} \mathcal{Q}(T; N, \Omega) = \operatorname{Tr}_{\Omega} \{ \exp\left(-\beta \mathscr{H}_{N,\Omega} \right) \}$$
(1.3.8)

where  $\mathscr{H}_{N,\Omega}$  is the total Hamiltonian operator for N particles in the domain  $\Omega$  and the trace is taken with a set of states complete in  $\Omega$  (and of appropriate symmetry).

Now it is easy to see that the (intensive) thermodynamic properties computed from these formulae will depend (i) on the size or volume  $V(\Omega)$  of the system, (ii) for a given size, on the shape of the domain  $\Omega$ , and (iii) for given  $\Omega$ , on which ensemble, canonical or grand canonical, is employed. Furthermore, for no system of finite volume in any ensemble can a sharp (or true) phase transition or critical point occur.<sup>†</sup>

It is now generally appreciated that the paradoxes posed by these observations disappear if one always considers the 'thermodynamic' (or 'bulk') limit in which the volume of the system becomes infinite. The canonical free energy *per particle* and the grand canonical pressure are defined by

$$-\frac{F(T,v)}{k_{\rm B}T} = \lim_{V(\Omega)\to\infty} \frac{1}{N} \ln \left\{ Q(T; N, \Omega) \right\} - d\ln\Lambda$$
(1.3.9)

with  $N/V(\Omega) \rightarrow \rho = 1/v$ , and

$$\frac{p}{k_{\rm B}T} = \lim_{V(\Omega) \to \infty} \frac{1}{V(\Omega)} \ln \{ \Xi(T, z; \Omega) \}.$$
(1.3.10)

In this limit all thermodynamic properties may be computed in *either* ensemble with the *same* results and these satisfy the standard thermodynamic stability criteria (e.g. positivity of the isothermal compressibility  $K_T$  and of the specific heat at constant volume  $C_V$ ). The sequence of domains used in constructing the limit may have widely varying shapes (subject, essentially, only to the requirement that the fraction of the total volume which lies close to the surface of  $\Omega$  vanishes in the limit). Rigorous proofs of these theorems for all densities, pressures and (non-zero) temperatures and for both classical and quantum-mechanical systems have been given recently by Ruelle (1963 a, b) and Fisher (1964 a, b, c) (see also Griffiths (1964 a, 1965 a) for a discussion of spin systems and the microcanonical ensemble). The most important conditions used in the existing proofs are that the interaction potentials have a sufficiently repulsive core (to prevent collapse) and do not decay too slowly at infinity. For pure pair-interaction potentials it is sufficient

<sup>†</sup> This is simply because the integrand in (1.3.1) is a bounded analytic function of  $\beta$  and the domain of integration is finite. Similarly the trace in (1.3.8) is merely the absolutely convergent sum of simple exponentials in  $\beta > 0$ .

that

$$|\phi(\mathbf{r})| \leq \frac{C}{r^{3+\epsilon}} \quad \text{as} \quad r \to \infty$$
 (1.3.11)

and

$$\phi(\mathbf{r}) \ge \frac{C'}{r^{3+\epsilon'}} \quad \text{as} \quad r \to 0$$
 (1.3.12)

where C, C',  $\epsilon$  and  $\epsilon'$  are positive constants. (For more general and complete statements see the references cited.)

Unfortunately these conditions exclude systems with long-range dipole-dipole or Coulomb interactions. In these cases the theoretical definition and uniqueness of the thermodynamic potentials, and hence of any phase transition, is still something of an open question. (The problem of a residual shape dependence obviously arises in ferromagnetic systems where it is customary to make a 'demagnetization' correction to remove the main effects of the dipolar forces.)

Taking the thermodynamic limit also allows the free energy or pressure to 'grow' mathematical singularities (non-analytic points) so that *in the limit* a system can exhibit a perfectly sharp phase transition and a well-defined critical point. For this reason we shall always presuppose the thermodynamic limit. Considerable illumination of the mathematical mechanism by which such singularities might develop has been gained in a fundamental analysis by Yang and Lee (1952 a). They introduced the zeros of the grand canonical function in the *complex* z plane and thereby opened a fascinating chapter in the study of phase transitions which is likely to develop further as mathematical techniques improve. As yet, however, it had led to no conclusions regarding critical phenomena and so we shall not discuss it. (For recent introductions see Uhlenbeck and Ford (1963) and, including an extension to the complex temperature plane, Fisher (1965 a, §§ 12, 13).)

While theoretically it is satisfying that a unique prescription for calculating thermodynamic properties can be given, it remains true that all systems studied in a laboratory are finite in size. The standard answer to this objection is that one studies macroscopic systems with  $N \simeq 10^{20} - 10^{24}$  particles and that fluctuations in bulk properties are of relative order  $N^{-1/2} \simeq 10^{-10} - 10^{-12}$  and so are undetectable in most direct experimental measurements. This argument, however, must be re-examined near a critical point since it assumes that specific heats, susceptibilities, compressibilities, etc., are bounded<sup>†</sup> and this is not generally true at a critical point. Indeed, one knows from Onsager's work on the plane Ising model (see below) that the height of the specific-heat peak of a finite system may grow as slowly as  $\ln N$  so that accurate experiments could conceivably detect the finiteness of even quite large systems. More general theoretical arguments advanced recently suggest that one may typically see departures from ideal limiting behaviour at temperature deviations from  $T_{\rm c}$  given roughly by  $\Delta T/T_{\rm c} \sim N^{-1/3}$  (see Domb 1965 a, b, c, and Ferdinand and Fisher 1967). However, present-day experiments are probably limited close to  $T_{\rm e}$  by inhomogeneities, gravitational fields and other interfering factors, rather than by finite size. In favourable cases, such as illustrated in figure 1,

<sup>†</sup> The argument also neglects surface and boundary terms which are of relative order  $N^{-1/3}$  and so are larger than the fluctuations. In principle, however, one can distinguish such terms (away from a critical point) by studying systems of varying size and shape.

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from three to six decades of change in  $\Delta T$  (or other variables) may be accessible to experiment, and comparison with calculations based on the thermodynamic limit are certainly quite appropriate. Nevertheless, in pressing data close to a critical point the ultimate limiting factors must be borne in mind and further research will doubtless be conducted on this question.

#### 1.4. Critical-point exponents

Since much of our discussion will concern the way in which various physical quantities (specific heats, susceptibilities, peak scattering intensities, etc.) diverge to infinity or converge to zero as the temperature or other variable approaches its critical-point value, it is appropriate to present a few mathematical definitions which enable critical behaviour to be characterized numerically. Speaking loosely, we may say a positive (or non-negative) function f(x) varies as  $x^{\lambda}$  when x approaches zero from above, or we may write

$$f(x) \sim x^{\lambda}$$
 as  $x \to 0+$ . (1.4.1)

More precisely this will mean that

$$\lim_{x \to 0+} \left\{ \frac{\ln f(x)}{\ln x} \right\} = \lambda. \tag{1.4.2}$$

Of course the existence of the exponent  $\lambda$  does not mean that f(x) is simply proportional to  $x^{\lambda}$ . One must always expect correction terms of higher order. In what might be termed the simple case one may hope that these will be of the form

$$f(x) = Ax^{\lambda}(1 + ax + ...) \quad (x \to 0 +)$$
(1.4.3)

where A is the *amplitude* of the singularity (using 'singularity' in a physical sense), while a is the amplitude of the leading correction term. In practice (1.4.3) frequently seems to apply and in such cases, as we shall discuss below, it is not difficult to estimate  $\lambda$  (and A) from numerical data on f(x). In particular cases, however, the correction term may be large (on the appropriate dimensionless scale) or might be of a more singular form, such as  $1 + ax^{1/4}$  for example, so that the leading asymptotic behaviour is less easily resolved.

In the non-simple case, however, complexities such as

$$f(x) = A |\ln x|^{\mu} x^{\lambda} \{1 + ax^{\nu} + ...\}$$
  
$$f(x) = A |\ln|\ln x|^{\mu} x^{\lambda} \{1 + a(\ln x)^{-\nu} + ...\} \quad (\nu > 0)$$
(1.4.4)

might arise without contradiction of (1.4.1) or (1.4.2). If this occurs it may be very difficult, if not virtually impossible, to estimate the leading exponent  $\lambda$  from numerical data unless more or less detailed knowledge about the higher-order terms is available. (Indeed, in practice, a logarithmic factor will 'look like' a small algebraic power of degree  $\Delta\lambda \simeq -0.2$  to -0.1 for typical ranges of x.)

The special value  $\lambda = 0$  merits a further remark. It is rather natural to associate this with the *simple case* of a pure logarithmic divergence, namely

$$f(x) = A \ln x + B + \dots$$
(1.4.5)

as may be seen by taking the limit  $\mu \rightarrow 0$  in

$$f(x) = \frac{A}{\mu}(x^{\mu} - 1) + B.$$
(1.4.6)

In practice (1.4.5) does quite often seem appropriate. Clearly, however, this is not the only possibility and, in particular, if f(x) approaches a constant at x = 0 then  $\lambda$ , as defined by (1.4.2), is always zero, for example in (1.4.6)  $\lambda \equiv 0$  for all  $\mu > 0$ . In such circumstances it may be desirable to *extend* the definition of  $\lambda$  to apply to the 'singular part' of f(x). This may be done by the following device, which can be tested on the example (1.4.6). Firstly, we find the smallest integer k such that  $f^{(k)}(x) = d^k f/dx^k$  diverges to infinity as  $x \to 0 + .\dagger$  We then define the exponent  $\lambda_s$ for the singular part of f(x) as

$$\lambda_{\rm s} = +k + \lim_{x \to 0+} \left( \frac{\ln f^{(k)}(x)}{\ln x} \right). \tag{1.4.7}$$

Because of the differentiations required in this definition it is clear that the accurate determination of  $\lambda_s$  from numerical data will normally be quite hard.

Finally, as a complement to (1.4.7), we note that  $f(x) \sim x^{\lambda}$  rigorously implies that

$$f^{(-1)}(x) = \int_0^x f(x') \, dx' \sim x^{1+\lambda}. \tag{1.4.8}$$

We have, perhaps, laboured over-heavily on these simple mathematical points, but they have not always been recognized very clearly or kept in mind in the analysis of experimental data or in the discussion of theoretical proposals.

# 2. Survey of phenomena and analogies

In the introduction  $(\S1.1)$  we listed some seven distinct types of physical system which exhibit critical phenomena. The realization of the close theoretical analogies between these, at first sight, contrasting systems has played an important part in the development of a general and coherent viewpoint. For reasons of space, however, we cannot study all these interrelations in the detail they deserve. Rather, we shall focus attention chiefly on two groups of critical phenomena, namely those occurring at the critical point for condensation of a simple fluid and those occurring in a ferromagnet at its Curie point. In this section we shall review the analogies from a mainly phenomenological and *ad hoc* viewpoint, returning later to a deeper study of their theoretical significance. Part A is devoted to simple fluid systems, part B to magnetic systems and part C to binary systems, superfluids, etc.

#### A. Fluid systems

#### 2.1. Gas-liquid critical point

From below the critical temperature  $T_c$  the critical point of a fluid is characterized most directly by the vanishing of the difference between the densities of gas and

<sup>†</sup> If k does not exist, i.e. is infinite, then f(x) might be termed non-singular at x = 0. The example  $f(x) = \exp(-1/x)$ , which is by no means purely academic, shows that this does not mean that f(x) is mathematically an *analytical* function at x = 0, although for 'experimental purposes' this may be effectively true.

liquid coexisting at a chemical potential  $\mu_{\sigma}(T)$  and pressure  $p_{\sigma}(T)$ . In accordance with §1.4, we define the exponent  $\beta$  by<sup>†</sup>

$$\rho_{\rm L} - \rho_{\rm G} \sim (T_{\rm c} - T)^{\beta} \quad (T \to T_{\rm c} -).$$
(2.1.1)

The evidence of figure 1 for CO<sub>2</sub> suggests  $\beta \simeq \frac{1}{3}$ . An analysis of the data for xenon (Weinberger and Schneider 1952, Fisher 1964 b) indicated

$$\beta = 0.345 \pm 0.015 \simeq 1/2.9$$

Most simple gases obey a law of corresponding states quite well and this value of  $\beta$ is quite general<sup>‡</sup> (Guggenheim 1945). This suggests that the values of the critical exponents do not depend sensitively on the details of the intermolecular interactions.

From above, the critical point is most readily characterized by the divergence of the isothermal compressibility

$$K_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_T.$$
(2.1.2)

On the critical isochore  $\rho = \rho_c$  this divergence may be described by

$$K_T \sim \frac{1}{(T_c - T)^{\gamma}} \quad (T \to T_c + ).$$
 (2.1.3)

(The maximum of  $K_T$  on an isotherm most probably diverges similarly with temperature.) For a general review of the experimental evidence on the values of the critical exponents we refer to Heller's (1967) article. Here we draw attention only to Habgood and Schneider's (1954) data on xenon from which one may conclude  $\gamma > 1.1$ , and, rather uncertainly,  $\gamma \simeq 1.2 - 1.3$  (see Fisher 1964 b). Below T<sub>c</sub> one may measure the compressibility of gas or liquid at the condensation (or boiling) point and define, correspondingly, two further exponents  $\gamma_{G}$  and  $\gamma_{L}$ . Most theories predict  $\gamma_{G}' = \gamma_{L}' = \gamma'$  and, indeed, very little evidence suggesting a difference between  $\gamma_{\rm G}'$  and  $\gamma_{\rm L}'$  has been advanced. Consequently we shall usually drop the distinction between gas and liquid sides. One might, similarly, distinguish exponents  $\beta_{\rm L}$  and  $\beta_{\rm G}$  for  $\rho_{\rm L} - \rho_{\rm c}$  and  $\rho_{\rm c} - \rho_{\rm G}$ , but the law of rectilinear diameter, namely

$$\frac{1}{2}(\rho_{\rm L} + \rho_{\rm G}) = \rho_{\rm e} \left\{ 1 + \frac{a(T_{\rm e} - T)}{T_{\rm e}} \right\}$$
(2.1.4)

which is quite well obeyed experimentally near  $T_{\rm c}$  indicates  $\beta_{\rm G} = \beta_{\rm L} = \beta$ .

Since  $K_T$  becomes infinite at the critical point, the critical  $(p, \rho)$  isotherm should become horizontal at  $\rho = \rho_c$ . To describe its shape we may define an exponent  $\delta$  by

$$p - p_{\rm c} \sim \operatorname{sgn} \left\{ \rho - \rho_{\rm c} \right\} \left| \rho - \rho_{\rm c} \right|^{\delta} \tag{2.1.5}$$

where again one could (and, in principle, should) distinguish a  $\delta_L$  and  $\delta_G$ . From a theoretical standpoint the chemical potential is in some ways more fundamental than the pressure but the thermodynamic relation

$$\rho = \left(\frac{\partial p}{\partial \mu}\right)_T \tag{2.1.6}$$

<sup>†</sup> No confusion should arise, in practice, with  $\beta = 1/k_B T$ . <sup>‡</sup> Close analysis generally indicates  $\beta$  slightly exceeding  $\frac{1}{3}$ . On present evidence one seems justified in discarding Rice's (1950) suggestion that fluid-coexistence curves have a 'flat top'.

shows their behaviour is similar. In particular at  $T = T_{c}$  we have

$$p - p_{\rm e} \simeq \rho_{\rm e}(\mu - \mu_{\rm e}).$$

An analysis of a number of simple gases by Widom and Rice (1955) indicated  $\delta \simeq 4.2 \pm 0.2$ . It has recently been suggested that more complete data close to  $\rho_{\rm e}$  might lead to the somewhat higher value  $\delta \simeq 5$  (Larsen and Levelt Sengers 1965) but at present there is no very strong evidence for this (see Heller 1967).

Finally, the specific heats at constant volume  $C_V$  of various gases, most notably argon and nitrogen, have been found to increase rapidly near  $T_c$ , apparently diverging to infinity in a roughly logarithmic manner (Bagatskii *et al.* 1962, Voronel' *et al.* 1963, 1964, 1966, Fisher 1964 c, Moldover and Little 1965). We may write

$$C_{\nu}(\rho = \rho_{\rm c}, T) \sim (T - T_{\rm c})^{-\alpha} \quad (T > T_{\rm c})$$
  
 
$$\sim (T_{\rm c} - T)^{-\alpha'} \quad (T < T_{\rm c}) \quad (2.1.7)$$

where, below  $T_c$ ,  $C_V$  refers to the overall two-phase specific heat at constant *total* volume (and particle number). For argon and nitrogen below  $T_c$  one can conclude that  $\alpha'$  probably exceeds zero by no more than 0.1 (but see §3.3); above  $T_c$  the data are less clear cut (see, for example, Fisher 1964 c), although  $\alpha$  is always much smaller than  $\gamma$  and might well be zero.

It is appropriate here to note the thermodynamic relations

$$\frac{1}{K_S} = \frac{1}{K_T} + \frac{Tv(\partial p/\partial T)_V^2}{C_V}$$
(2.1.8)

$$C_p = C_V + Tv \left(\frac{\partial p}{\partial T}\right)_V^2 K_T$$
(2.1.9)

and

$$\frac{C_p}{C_V} = \frac{K_T}{K_S} \tag{2.1.10}$$

from which one can see that the adiabatic compressibility  $K_S$  diverges with exponent  $\alpha$  or  $\alpha'$  while  $C_p$  diverges like  $K_T$ . Measurements of the velocity of sound

$$u = (\rho K_S)^{-1/2} \tag{2.1.11}$$

yield values of  $K_s$  and hence estimates for  $\alpha$  and  $\alpha'$  (see Sette (1966) and, especially, Chase *et al.* (1964), Chase and Williamson (1966)).

There have been some experimental indications<sup>†</sup> that the true (or limiting) critical exponents may differ for gases such as <sup>3</sup>He and <sup>4</sup>He which are of low molecular weight so that de Boer's dimensionless quantum parameter

$$\Lambda^* = \frac{h}{(m\epsilon\sigma^2)^{1/2}} \tag{2.1.12}$$

is relatively large. (Here h is Planck's constant, and m,  $\epsilon$  and  $\sigma$  measure the molecular mass, potential-well depth and collision diameter.) Although recent experiments on

<sup>†</sup> For details see Sherman (1965), Edwards (1965), Chase and Zimmerman (1965) and, for some discussion, Sherman and Hammel (1965) and Fisher (1966 a, b, c). For quantal critical-point behaviour with 'infinite-range' forces see § 5.4 and Burke *et al.* (1966).

<sup>4</sup>He (Roach and Douglass 1966) yield  $\beta \simeq 0.35$ , so casting doubt on the previous suggestions, it is certainly true, as can be seen from figure 2, that the normalized amplitude of the singularity in  $\rho_{\rm L} - \rho_{\rm G}$  changes significantly with  $\Lambda^*$ .



Figure 2. Plots of  $R^3 = \{(\rho_L - \rho_G)/2\rho_c\}^3$  against  $T/T_c$  for: A, <sup>3</sup>He; B, <sup>4</sup>He; C, parahydrogen; and D, the classical limit  $\Lambda^* = 0$  approximated by xenon. (From Fisher 1966 a.)

#### 2.2. Critical scattering

When radiation, for example light, x rays or neutrons, of incident wave vector  $\mathbf{k}_0$  is scattered quasi-elastically off an ideal (i.e. low-density) gas one observes a scattering intensity  $I_0(\mathbf{k})$  which depends only on the properties of individual isolated molecules or atoms. (The wave vector  $\mathbf{k}$ , or reduced 'momentum transfer', is defined in terms of the wave vector  $\mathbf{k}'$  of the scattered radiation by  $\mathbf{k} = \mathbf{k}' - \mathbf{k}_0$ . For three-dimensional systems one has

$$k = \left| \mathbf{k} \right| = \frac{4\pi}{\lambda} \sin \frac{1}{2}\theta$$

where  $\theta$  is the scattering angle and  $\lambda$  the wavelength.) As the density increases, however, the observed scattering intensity  $I(\mathbf{k})$  deviates from  $I_0(\mathbf{k})$  and, in particular, near the critical point the reduced scattering intensity

$$\hat{\chi}(\mathbf{k}) = \frac{I(\mathbf{k})}{I_0(\mathbf{k})} \tag{2.2.1}$$

becomes very large, especially at low angles (small k). This is the phenomenon of 'critical opalescence'.

Because  $\hat{\chi}(\mathbf{k})$  becomes large it is customary experimentally (and convenient theoretically) to plot the reciprocal intensity (or  $\hat{\chi}^{-1}$ ) against  $k^2$  (spherical symmetry

in  $\mathbf{k}$  space is observed in the critical region). Some results from Thomas and Schmidt's (1963) x-ray studies on argon are shown in figure 3. Away from the critical point such plots are roughly linear and it appears that one may write

$$\frac{I}{I_0} = \hat{\chi}(\mathbf{k}) = \frac{\hat{\chi}(0)\kappa_1^2}{\kappa_1^2 + k^2 + O(k^4)} = \frac{\hat{\chi}(0)}{1 + \Lambda^2 k^2 + O(k^4)}$$
(2.2.2)

which is of 'Lorentzian form' if the terms higher than first order in  $k^2$  are neglected.



Figure 3. Critical scattering from argon: a plot of reciprocal scattering intensity against θ<sup>2</sup>
(θ is the scattering angle) for various temperatures on an isobar close to critical (p ≃ p<sub>c</sub>).
A, T<sub>c</sub>+2 °K, 5V; B, T<sub>c</sub>+1 °K, 4V; C, T<sub>c</sub>+0.45 °K, 3V; D, T<sub>c</sub>+0.25 °K, 2V;
E, T<sub>c</sub>+0.05 °K, V. (From Thomas and Schmidt 1963.)

If (2.2.2) is valid for small k (its theoretical justification will be discussed in §2.3) the parameter  $\kappa_1 = \kappa_1(\rho, T)$  may be defined more formally by

$$\kappa_1^2 = \Lambda^{-2} = \lim_{k \to 0} \frac{k^2}{\{\hat{\chi}(0)/\hat{\chi}(\mathbf{k})\} - 1}$$
(2.2.3)

which shows that  $1/\kappa_1 = \Lambda$  is a characteristic state-dependent *length* for the system.

It also appears generally that the (extrapolated) zero-angle scattering intensity  $\hat{\chi}(0)$  will diverge *at* the critical point (see below for the theoretical reason). To describe the critical-point scattering we thus introduce an exponent  $\eta$  by

$$\frac{I_{\rm c}(\mathbf{k})}{I_0(\mathbf{k})} = \hat{\chi}_{\rm c}(\mathbf{k}) \sim \frac{1}{k^{2-\eta}} \quad (k \to 0).$$
(2.2.4)

If one could always neglect the higher-order terms in (2.2.2) one would conclude that  $\eta \equiv 0$ . However, this is not justified in general, although experimental evidence (which is at present rather inadequate) does suggest that  $\eta$  is quite small (say < 0.2) and is certainly non-negative (see Heller 1967, Fisher 1964 b).

It follows from (2.2.3), from the divergence of  $\hat{\chi}(0)$  at the critical point, and from (2.2.4) that  $\kappa_1 \rightarrow 0$  as the critical point is approached so that the characteristic length  $\Lambda$  becomes infinite. We may accordingly introduce an exponent  $\nu_1$ , for the behaviour on the critical isochore, by

$$\kappa_1(\rho = \rho_c, T) \sim (T - T_c)^{\nu_1} \quad (T \to T_c +)$$
(2.2.5)

with similar definitions of  $\nu_{1,L}$  and  $\nu_{1,G}$  for  $\rho = \rho_L$  and  $\rho_G$  respectively below  $T_c$ . Existing experimental evidence on the values of these exponents is again rather meagre, especially below  $T_c$ , but one may conclude that  $\nu_1$  lies in the range 0.55 to 0.70.

The foregoing discussion is purely phenomenological. However, it is well known that scattering experiments are essentially direct measurements of the microscopic fluctuations and correlations. It is therefore appropriate at this stage to present the relevant general theory (which is not special to critical phenomena) so as to reveal more clearly the significance of the exponents  $\eta$  and  $\nu$ . This is done in §2.3 which might, however, be omitted on a first reading, although it will be referred to later.

#### 2.3. Fluid correlations and fluctuations

The pair density or distribution function  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$  for a particle system measures the joint probability of finding two particles in volume elements  $d\mathbf{r}_1$  and  $d\mathbf{r}_2$  (see, for example, de Boer 1949). In a large uniform system (i.e. with no spatially varying external potentials)  $\rho_2$  will be a function only of  $\mathbf{r} = \mathbf{r}_{1,2} = \mathbf{r}_2 - \mathbf{r}_1$ , except near the walls. This is true even if two phases are present since the denser phase, say, is equally likely to occupy any part of the total domain. In a single phase, however, the fluctuations at macroscopically distant points should be independent so that the distribution functions for large separations should factorize, i.e.

$$\rho_2(\mathbf{r}) \to \rho^2 = v^{-2} \quad \text{as} \quad r \to \infty \text{ (one phase).}$$
(2.3.1)

Evidently it is useful to define the net pair correlation function by

$$G(\mathbf{r}) = g_2(\mathbf{r}) - 1 = v^2 \rho_2(\mathbf{r}) - 1$$
(2.3.2)

where  $g_2(\mathbf{r})$  is the 'radial distribution function'. In a one-phase region

$$G(\mathbf{r}) \to 0 \quad \text{as} \quad r \to \infty \tag{2.3.3}$$

and one may define the Fourier transform

$$\widehat{G}(\mathbf{k}) = \int \exp\left(i\mathbf{k}\cdot\mathbf{r}\right)G(\mathbf{r})\,d\mathbf{r}.$$
(2.3.4)

This will be finite at k = 0 provided the correlations decay sufficiently rapidly for  $G(\mathbf{r})$  to be integrable; otherwise  $\hat{G}(\mathbf{k})$  will diverge as  $k \to 0$ .

Now, in terms of  $\hat{G}(\mathbf{k})$ , the reduced scattering intensity is given simply by

$$\frac{I}{I_0} = \hat{\chi}(\mathbf{k}) = 1 + \rho \hat{G}(\mathbf{k}).$$
(2.3.5)

This expression is valid under the following assumptions:

(i) The first Born approximation is valid so that only single scattering occurs. If the scattering is too intense, multiple scattering will be present and must be corrected for experimentally or theoretically.

(ii) The scattering takes place 'quasi-elastically' so that the energy exchanged between the radiation and the system (which by conservation of energy and momentum cannot vanish identically if scattering occurs) is small compared with the energy of the incident radiation. Equivalently the frequency of the radiation must be high compared with the natural frequencies of the molecular motions. When this condition is not fulfilled, the scattered radiation is, in general, shifted in frequency and, correspondingly, one must also consider the time dependence of the correlation functions. This is often the case for neutron scattering as discussed by Van Hove (1954 a) but in this article we shall not have space to consider such time and frequency dependence (see  $\S10$  and Heller 1967,  $\S5$ ).

The zero-angle scattering  $\hat{\chi}(0)$  is evidently related to  $\hat{G}(0)$  and hence to the integral of  $G(\mathbf{r})$  over all space. This in turn is related to the compressibility by the *fluctuation theorem* 

$$k_{\rm B} T \rho K_T = \frac{K_T}{K_T^{\rm ideal}} = 1 + \rho \int G(\mathbf{r}) \, d\mathbf{r}$$
(2.3.6)

which is a fairly general consequence of statistical mechanics.<sup>†</sup> Combination of these observations yields the important relation

$$\frac{I(0)}{I_0(0)} = \hat{\chi}(0) = \frac{K_T}{K_T^{\text{ideal}}}.$$
(2.3.7)

This implies that the zero-angle scattering intensity must diverge in just the same way as the compressibility when the critical point is approached (e.g. with exponent  $\gamma$  for  $\rho = \rho_c$ ,  $T > T_c$ ) and so justifies the previous phenomenological conclusion. (It might, however, be mentioned that (2.3.7) has not so far been checked experimentally with any accuracy.)

The divergence of  $\int G(\mathbf{r}) d\mathbf{r}$  at the critical point implies a slow decay of  $G_{c}(\mathbf{r})$  at infinity. Indeed, Fourier inversion of the relation (2.2.4), which defined the exponent  $\eta$ , yields, in d dimensions,

$$G_{\rm e}(r) \sim \frac{1}{r^{d-2+\eta}} \quad (r \to \infty) \tag{2.3.8}$$

which can be viewed as an alternative, more theoretical, definition of  $\eta$ .

One may similarly find a more direct definition of the characteristic length parameter  $\Lambda = 1/\kappa_1$  and hence of the corresponding exponent  $\nu_1$ . Formal expansion

 $<sup>\</sup>dagger$  The fluctuation relation (2.3.6) can be established formally in the grand canonical ensemble quite easily, although there are difficulties in the canonical ensemble. Nothing approaching a rigorous proof for the thermodynamic limit has yet been given but, at least for sufficiently short-range interactions, there seems no reason to doubt its general validity.

of exp  $(i\mathbf{k}.\mathbf{r})$  in powers of k in (2.3.4) and comparison of (2.3.5) with (2.2.2) yields the identification

$$\Lambda^{2} = \kappa_{1}^{-2} = \frac{\frac{1}{2}c\rho\int r^{2}G(\mathbf{r})\,d\mathbf{r}}{1+\rho\int G(\mathbf{r})\,d\mathbf{r}}$$
(2.3.9)

where c is a constant. (When  $G(\mathbf{r})$  is spherically symmetric or is appropriately averaged  $c = \frac{1}{2} \langle \cos^2 \theta \rangle$  which has the value  $\frac{1}{6}$  for d = 3.) Evidently  $\Lambda$  is a root mean square or *effective range of correlation*. From (2.3.8) one sees that  $\kappa_1 \rightarrow 0$  at the critical point (assuming  $\eta \ge 0$ ), hence justifying the definition (2.2.5) of  $\nu_1$ .

Of course the existence of  $\Lambda$  depends on the finiteness of the second moment  $\int r^2 G(\mathbf{r}) d\mathbf{r}$  away from the critical-point and two-phase region. For short-range forces this is to be expected quite generally† (although it might be in doubt if long-range forces play a significant role). Indeed, the general theoretical expectation for a one-phase system not at a critical point is that the asymptotic correlations will decay with an *exponential* envelope<sup>‡</sup>, i.e.

$$|G(\mathbf{r})| \sim e^{-\kappa r} \quad (r \to \infty) \tag{2.3.10}$$

where  $\kappa = \kappa(\rho, T)$  may be termed the *true* (or exponential) *inverse range of the correlation*.§ From (2.3.8) it follows that  $\kappa$  also vanishes at the critical point and we may define corresponding exponents, for example

$$\kappa(\rho = \rho_{\rm c}, T) \sim (T - T_{\rm c})^{\nu} \quad (T \to T_{\rm c} + ).$$
 (2.3.11)

It is natural to expect that near the critical point there is essentially only one important temperature-dependent length which approaches infinity. If this is so,  $\kappa \sim \kappa_1$  and we have

$$\nu \equiv \nu_1. \tag{2.3.12}$$

Indeed, if one neglects the  $O(k^4)$  terms in the denominator of (2.2.2) and performs the Fourier inversion one finds, for fixed  $\kappa_1 > 0$ ,

$$G(\mathbf{r}) \simeq \frac{C_{d} \exp(-\kappa_{1} r)}{r^{\frac{1}{2}(d-1)}} \quad (r \to \infty)$$
(2.3.13)

which, for d = 3, is the famous result of Ornstein and Zernike (Zernike 1916) which leads to the complete identification of  $\kappa$  and  $\kappa_1$  near  $T_c$ . In fact, however, the question of the uniqueness of the correlation range near the critical point is quite profound and we shall return to it. Nevertheless for the present, and most of this article, we shall accept the identity (2.3.12) and use the exponent  $\nu$  for both  $\kappa$  and  $\kappa_1$ . (One must note that even if  $\kappa$  and  $\kappa_1$  do become proportional close to  $T_c$  they will still differ appreciably outside the critical region.)

<sup>&</sup>lt;sup>†</sup> In the region of low density it is a consequence of existing proofs of the convergence of the virial and activity expansions (Ruelle 1963 b, 1964 a, b, Penrose 1963, Ginibre 1965).

<sup>&</sup>lt;sup>‡</sup> For forces of strictly finite range this again can be proved in the region of known convergence of the virial series (Ruelle 1964 a, b).

<sup>§</sup> By the general theory of the Fourier integral the parameter  $\kappa$  may be defined analytically as the imaginary part of the singularities of  $G(k\mathbf{e})$ , where  $\mathbf{e}$  is a unit vector, which lie nearest to the real axis in the complex k plane.

Finally, in discussing the general theory of the correlation functions, the behaviour in the two-phase region should be mentioned (see, for example, Fisher 1965 b). If  $\rho_{\rm G} \leq \rho \leq \rho_{\rm L}$ , the independence and macroscopic extent of the two phases implies that

$$G_{\text{tot}}(\mathbf{r},\rho) = \left(\frac{\rho_{\text{L}}}{\rho}\right)^2 \frac{\rho - \rho_{\text{G}}}{\rho_{\text{L}} - \rho_{\text{G}}} G_{\text{L}}(\mathbf{r}) + \left(\frac{\rho_{\text{G}}}{\rho}\right)^2 \frac{\rho_{\text{L}} - \rho}{\rho_{\text{L}} - \rho_{\text{G}}} G_{\text{G}}(\mathbf{r}) + \frac{(\rho_{\text{L}} - \rho)(\rho - \rho_{\text{G}})}{\rho^2}.$$
(2.3.14)

From this it is clear that the *existence* of two distinct phases can be detected from the pair correlation function which no longer vanishes at infinity but rather approaches

$$G_{\rm tot}(\infty,\rho) = \frac{\frac{1}{4}(\rho_{\rm L} - \rho_{\rm G})^2 - (\rho - \bar{\rho})^2}{\rho^2}$$
(2.3.15)

where  $\bar{\rho} = \frac{1}{2}(\rho_{\rm L} + \rho_{\rm G})$ . Evidently the density discontinuity  $\rho_{\rm L} - \rho_{\rm G}$  cannot be found from this 'long-range order' at one value of  $\rho$  (unless, say,  $\bar{\rho}$  is known). Note that the non-zero limiting value  $G_{\rm tot}(\infty)$  implies that the Fourier transform  $\hat{G}(\mathbf{k})$ will have a delta-function singularity at the origin of  $\mathbf{k}$  space.

#### B. Magnetic systems

#### 2.4. Ferromagnets

In the previous sections we characterized the phenomenological behaviour of fluids at their critical points in terms of a number of exponents, principally  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ,  $\gamma'$ ,  $\delta$ ,  $\eta$ ,  $\nu$  and  $\nu'$ . For convenience these definitions are summarized in a fold-out table at the end of this article. We turn now to magnetic systems and give analogous definitions of critical exponents.

Let us consider firstly ferromagnets which are characterized by the existence of a *spontaneous magnetization* 

$$M_0(T) = \lim_{H \to 0^+} M(H, T)$$
(2.4.1)

below the Curie temperature  $T_c$ , where H will always denote the 'true' or 'internal field' acting on the system (i.e. the 'applied field' corrected for demagnetization). As H passes through zero the equilibrium magnetization will change discontinuously to  $-M_0(T)$ . Above  $T_c$  in the 'paramagnetic region' the magnetization varies continuously as H changes sign. At all temperatures there is no transition or sharp anomaly in any non-zero field.

This behaviour is quite analogous to that of a fluid if changes of M and H are identified with changes of  $\rho$  and p respectively. Figure 4 illustrates the consequent analogy between the phase diagrams of fluid and ferromagnet. In accordance with (2.1.1) we thus define the magnetic exponent  $\beta$  by

$$M_0(T) \sim (T - T_c)^{\beta}.$$
 (2.4.2)

<sup>†</sup> We shall always assume, as normal, that magnetic systems are invariant under  $\mathbf{H} \rightarrow -\mathbf{H}$ . In all ferromagnets two or more 'easy directions' for the magnetization vector  $\mathbf{M}_0$  are favoured to at least some extent. It is convenient to take the z axis along one of these directions and, unless otherwise specified,  $\mathbf{M}$  and  $\mathbf{H}$  will be supposed parallel to this axis. How is this analogy borne out by experiment? Again we refer to Heller (1967) for a critical discussion of the evidence, but we shall list some results which illustrate the surprising degree to which the analogy seems to hold. From experiments on the insulating ferromagnets EuS and CrBr<sub>3</sub> Heller and Benedek (1965) and Senturia and Benedek (1966) have concluded that  $\beta \simeq 0.330$  and  $0.365 \pm 0.015$  respectively, although the data go only to within 0.7 to 1% of  $T_{\rm e}$ . These values are just in the range found for fluid critical points.<sup>+</sup>



Figure 4. Comparison of (a) the (p, T) phase diagram of a simple fluid, with (b) the (H, T) diagram for a simple ferromagnet. The dotted lines above  $T_c$  represent the critical isochore  $(\rho = \rho_c)$  and critical isomomental (M = 0), respectively. The arrows suggest the predominant spin configurations in the different regions of the phase diagram.

Above  $T_{\rm c}$  the isothermal susceptibility in zero field

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_{H=0} \tag{2.4.3}$$

diverges as  $T_{\rm c}$  is approached. The analogy indicates that we should characterize

<sup>†</sup> Experiments on Ni, a metallic conductor, tend to indicate a slightly higher value, around 0.4. Indeed Dash *et al.* (1966) have suggested that the limiting value of  $\beta$  close to  $T_c$  might be 0.5, rather as suggested for quantal gases (§ 2.1). However, the interpretation of their (resonance) data is not clear-cut and Noakes and Arrott (1967), on the basis of direct measurements in the same region, have concluded that  $\beta = 0.36 \pm 0.04$  which is probably more reliable. Even for the *dilute* ferromagnetic alloy Fe<sub>2.65</sub>Pd<sub>97.35</sub> Craig *et al.* (1965) found definite evidence for  $\beta \leq 0.35$ .

this behaviour as

$$\chi_T \sim (T - T_c)^{-\gamma} \quad (T \to T_c +).$$
 (2.4.4)

Symmetry with respect to H below  $T_c$  means we need only define a single exponent  $\gamma'$  for the divergence of the initial susceptibility by

$$\chi_T = \lim_{H \to 0} \left( \frac{\partial M}{\partial H} \right)_T \sim (T_c - T)^{-\gamma'} \quad (T \to T_c - )$$
(2.4.5)

(rather than distinguish  $\gamma_{\rm G}'$  and  $\gamma_{\rm L}'$ ). Experimentally, values for  $\gamma$  around  $1.35 \simeq \frac{4}{3}$  have been determined for Ni, Fe, Gd, YtFeO<sub>3</sub> and various alloys and copper salts<sup>†</sup> which compare with the fluid values of 1.2 to 1.3 (§2.1).

The analogous definition for the critical magnetic isotherm is clearly

$$H \sim \text{sgn}\{M\} |M|^{\delta} \quad (T = T_{c}).$$
 (2.4.6)

The first analysis of a ferromagnet, namely nickel, gave  $\delta = 4.2 \pm 0.1$  (Kouvel and Fisher 1964), in surprisingly close agreement with Widom and Rice's (1955) analysis for simple fluids. Graham (1965) has also reported  $\delta \simeq 4$  for gadolinium. More recently, from a study of nickel at somewhat lower fields, Noakes and Arrott (1967) have tentatively concluded  $\delta = 4.66 \pm 0.34.\ddagger$ 

For specific heats the analogous definitions are

$$C_{H=0}(T) \sim (T - T_c)^{-\alpha} \quad (T > T_c)$$
 (2.4.7)

$$\sim (T_{\rm c} - T)^{-\alpha'}$$
 (T < T<sub>c</sub>). (2.4.8)

(It might be asked why the analogous specific heat is not  $C_M$  since

$$M = \text{const.'} \leftrightarrow \rho = \text{const.'}$$
?

In fact above  $T_c H = 0$  implies  $M = M_c = 0$ , while below  $T_c$  the 'two-phase' M = 0 specific heat also corresponds to H = 0 since only then can two oppositely magnetized domains coexist in the same specimen to yield a total zero magnetization.)

Experimentally, ferromagnetic specific heats do exhibit lambda anomalies at  $T_{\rm c}$  (see figure 5). So far few materials have been studied closely. Some of the best data are for EuO (Teaney 1966) which exhibits a very roughly logarithmic anomaly. For reasons that are not clear, however, this is significantly rounded over a range  $\Delta T/T_{\rm c} \simeq 3 \times 10^{-3}$ .

#### 2.5. Magnetic scattering

Magnetic scattering can be observed by using neutrons which interact with the electron spin density. The basic theory has been expounded by Van Hove (1945 b). As in all scattering from a regular periodic crystal the total intensity  $I_{tot}(\mathbf{k})$  will be periodic in  $\mathbf{k}$  space and one must distinguish between (i) coherent scattering (or Bragg) peaks due to stationary long-range periodic order and (ii) incoherent

<sup>†</sup> See Miedema *et al.* (1963), Kouvel and Fisher (1964), Noakes and Arrott (1964), Arajs and Colvin (1964), Arajs (1965), Graham (1965), Gorodetsky *et al.* (1966) and Noakes *et al.* (1965) who found  $\gamma = 1.333 \pm 0.015$  for iron. It should also be remarked that a lower value  $\gamma \simeq 1.25$  has been reported for Co by Colvin and Arajs (1965) and a higher value  $\gamma \simeq 1.6$  for CrO<sub>2</sub> by Kouvel and Rodbell (1967 a, b).

<sup>‡</sup> For CrO<sub>2</sub> Kouvel and Rodbell (1967 a, b) find  $\delta \simeq 5.75$  which is probably associated with the atypical value of  $\gamma$  (but see figure 18 in § 9, below).

or diffuse scattering due to fluctuations. Ideally the coherent peak intensities are proportional to delta functions  $M^2 \delta(\mathbf{k} - \mathbf{K})$ , where M is the overall magnetization density and  $\mathbf{K}$  is a reciprocal lattice vector, but in practice they have a definite width due to instrumental factors and to the finite, albeit macroscopic, size of magnetic and crystalline domains, etc. Evidently in zero field below  $T_c$  we shall have

$$I_{\rm coh}(\mathbf{0}, T) \sim M_0^2(T) \sim (T_{\rm c} - T)^{2\beta}$$
 (2.5.1)

which gives an alternative way of measuring the exponent  $\beta$ . Above  $T_c$  the coherent peak is absent in zero field.



Figure 5. Specific heat of EuO and EuS showing the magnetic lambda anomaly superimposed on the lattice contributions to the specific heat. (From Teaney 1966.)

For a ferromagnet in the critical region the diffuse scattering  $I(\mathbf{k})$  also peaks around  $\mathbf{k} = 0$  (and corresponding points in reciprocal space).<sup>†</sup> The zero-angle  $(k \rightarrow 0)$  scattering intensity apparently diverges at the critical point and one may write, as for a fluid,

$$I_{\rm c}(\mathbf{k}) \sim \frac{1}{k^{2-\eta}} \quad (k \to 0).$$
 (2.5.2)

Present experimental evidence, notably on iron (Jacrot *et al.* 1962, Passel *et al.* 1965), indicates only  $0.2 > \eta \gtrsim 0$ .

By fitting to the Lorentzian scattering curve (2.14) for small  $k^2$  one may, as in the fluid case, define an inverse range parameter  $\kappa_1(T)$  which measures the slope of  $1/I(\mathbf{k}, T)$  against  $k^2$  as  $k \to 0$ . This again vanishes at the critical point; in zero field  $M = M_c = 0$ ) we may write

$$\kappa_1(T) \sim (T - T_c)^{\nu} \quad (T \to T_c +)$$
(2.5.3)

with a similar definition of  $\nu'$  below  $T_{\rm e}$ . (We no longer distinguish a  $\nu_1$  from  $\nu$ .) From the cited experiments on iron one finds  $\nu \simeq 0.67$ .

<sup>†</sup> Below  $T_c$  the diffuse scattering is *superimposed* on the Bragg peak and near  $T_c$  it can be difficult experimentally to distinguish the two components unambiguously.

# M. E. Fisher

The microscopic theoretical interpretation is simplified if we assume that the electronic spins are sufficiently well localized on lattice sites that they may be described by a set of spin vectors  $\mathbf{S}_{\mathbf{r}}$ . This is open to question for conducting ferromagnets but should be a good approximation for magnetic insulators. Of the net spin-pair correlation functions

$$\Gamma_{\alpha\beta}(\mathbf{r}, H, T) = \frac{\langle S_{\mathbf{0}}^{\alpha} S_{\mathbf{r}}^{\beta} \rangle - \langle S_{\mathbf{0}}^{\alpha} \rangle \langle S_{\mathbf{0}}^{\beta} \rangle}{\frac{1}{3}S(S+1)} \quad (\alpha, \beta = x, y, z)$$
(2.5.4)

one may usually concentrate attention on the longitudinal (with respect to the easy axis) correlation function

$$\Gamma(\mathbf{r}) = \Gamma_{zz}(\mathbf{r}). \tag{2.5.5}$$

In a non-zero field, or in a single domain, all these correlation functions vanish as  $r \to \infty$  since  $\langle S_0^{\alpha} S_r^{\beta} \rangle$  factorizes asymptotically as the fluctuations become independent. The fluctuation relation for the longitudinal susceptibility then states

$$\frac{\chi_T}{\chi_T^{\text{ideal}}} = 1 + \sum_{\mathbf{r} \neq 0} \Gamma(\mathbf{r})$$
(2.5.6)

where

$$\chi_T^{\text{ideal}} = \frac{\frac{1}{3}S(S+1)g^2\beta_B^2}{k_BT}$$
(2.5.7)

in which it is assumed that each spin interacts with the field via a term in the Hamiltonian  $-g\beta_{\rm B}H_z S_z$  which commutes with the total Hamiltonian. The relation (2.5.6) is easily derived *formally* by differentiating the expression for the free energy of a (finite) magnetic system twice with respect to  $H_z$  (and recalling that operators may be cyclically permuted under a trace).

The longitudinal quasi-elastic scattering intensity can, in Bornap proximation, be written

$$\frac{I(\mathbf{k})}{I_0(\mathbf{k})} = \hat{\chi}(\mathbf{k}) = 1 + \hat{\Gamma}(\mathbf{k})$$
(2.5.8)

where  $I_0(\mathbf{k})$  is the form factor for non-interacting spins and where the Fourier transform is

$$\widehat{\Gamma}(\mathbf{k}) = \sum_{\mathbf{r}\neq 0} \exp\left(i\mathbf{k} \cdot \mathbf{r}\right) \Gamma(\mathbf{r}).$$
(2.5.9)

In the interpretation of experimental data it must be remembered that the transverse spin fluctuations will generally also give rise to some scattering so that (2.5.8) may not be directly applicable.<sup>†</sup>

It is worth remarking that if one introduces a spatially varying field

$$H_z(\mathbf{r}) = \mathscr{R}\{H_z^0 \exp\left(i\mathbf{k} \cdot \mathbf{r}\right)\}$$
(2.5.10)

one finds (on neglecting certain, in general non-zero, commutators that are probably unimportant near  $T_c$ ) that  $\hat{\chi}(\mathbf{k})$  can also be interpreted as a wave-number dependent susceptibility measuring the magnetic response to the varying field.

 $\dagger$  For a completely isotropic magnet in zero field the transverse scattering intensity will be the same as the longitudinal intensity.

From (2.5.8) and (2.5.6) we see that the zero-angle scattering intensity is essentially proportional to the isothermal susceptibility and so

$$I(\mathbf{0}) \sim \chi_T \sim (T - T_c)^{-\gamma} \quad (H = 0, T > T_c).$$
(2.5.11)

The experiments of Passel *et al.* (1965) on iron do serve to check this (see also Bally *et al.* 1967). At the critical point the correlations must decay slowly and comparing (2.5.8) and (2.5.2) yields (in *d* dimensions)

$$\Gamma_{\rm c}(\mathbf{r}) \sim \langle S_0^z S_{\mathbf{r}}^z \rangle \sim \frac{1}{r^{d-2+\eta}}$$
(2.5.12)

by analogy with (2.3.8). Similarly, by expanding the Fourier transforms,  $\kappa_1$  may be expressed directly in terms of the second moment of  $\Gamma(\mathbf{r})$ :

$$\kappa_1^{-2} = c \hat{\chi}^{-1}(0) \sum_{\mathbf{r}} r^2 \Gamma(\mathbf{r})$$
(2.5.13)

with c an appropriate constant. Finally, one may anticipate that, provided dipolar and other long-range interactions are not significant,  $\Gamma(\mathbf{r})$  will decay as  $e^{-\kappa r}$  where  $\kappa$  is the 'true' inverse range of correlation. By the arguments given in the fluid case one expects that *near* the critical point (but not elsewhere)  $\kappa$  will become proportional to  $\kappa_1$  and hence in zero field will also vanish with exponents  $\nu$  and  $\nu'$  above and below  $T_c$  respectively.

The definitions of the magnetic critical-point exponents are also summarized in the fold-out table at the end of the article.

#### 2.6. Antiferromagnets

In a simple uniaxial antiferromagnet below its critical (or Néel) temperature in small or zero fields the spins on alternate lattice sites point predominantly parallel and antiparallel to the easy axis (the 'c axis'). This is readily detected in neutron scattering by the appearance of a coherent 'superlattice' peak centred, not at  $\mathbf{k} = \mathbf{0}$  as for a ferromagnet, but at a wave vector  $\mathbf{k} = \mathbf{k}_0$  appropriate to the larger magnetic unit cell implied by the alternating order. The intensity of this coherent peak is proportional to the square of what may be termed the spontaneous sublattice magnetization  $M_0'(T)$ .

The sublattice magnetization may be defined theoretically either via scattering theory from the long-range spin correlations as

$$\lim_{r \to \infty} \left| \langle S_0^z S_r^z \rangle \right| = (\langle S_0 \rangle')^2 \propto (M_0')^2$$
(2.6.1)

or by introducing a 'staggered magnetic field'

$$H(\mathbf{r}) = H' \exp (i\mathbf{k}_0 \cdot \mathbf{r})$$
  
= + H' for **r** on one sublattice  
= -H' for **r** on the second sublattice. (2.6.2)

Such a field (which probably cannot be generated experimentally) will produce an alternating magnetization

$$M'(\mathbf{r}, H', T) = M'(H', T) \exp(i\mathbf{k}_0 \cdot \mathbf{r}).$$
(2.6.3)

Above  $T_c$  this magnetization will vanish as  $H' \rightarrow 0$  but below  $T_c$  a spontaneous staggered magnetization

$$M_0'(T) = \lim_{H' \to 0^+} M'(H', T)$$
(2.6.4)

will remain. Evidently one may also define a corresponding staggered susceptibility  $\chi_T^{\dagger}$ .

By analogy with a ferromagnet we now expect

$$\{I_{\rm coh}(\mathbf{k}_0, T)\}^{1/2} \sim M_0'(T) \sim (T_{\rm c} - T)^{\beta}$$
(2.6.5)

and in terms of the *diffuse* scattering peak centred at  $\mathbf{k} = \mathbf{k}_0$  (rather than at  $\mathbf{k} = \mathbf{0}$ )

$$I(\mathbf{k}_0, T) \sim \chi_T^{\dagger}(T) \sim (T - T_c)^{-\gamma} \quad (T > T_c)$$

$$(2.6.6)$$

with a similar definition of  $\gamma'_{\mathbf{k}}$  below  $T_{\mathbf{c}}$ . By considering the diffuse scattering as a function of small  $|\mathbf{k} - \mathbf{k}_0|^2$  we may clearly define the range parameter  $\kappa_1$  and the



Figure 6. Schematic phase diagram of an anisotropic antiferromagnet. A finite *staggered* field destroys the transition but a uniform field does not. The broken lines indicate that the nature of the transition(s) may change at sufficiently high fields and sufficiently low temperatures, but note that the antiferromagnetic phase is completely enclosed by transition lines.

exponents  $\eta$ ,  $\nu$  and  $\nu'$  as previously. Precisely the same definitions (2.4.7) and (2.4.8) for the specific-heat exponents apply as for a ferromagnet. However, the exponent  $\delta$  is essentially unmeasurable since one would need to apply a real *finite* staggered field at  $T = T_{\rm e}$ .

In the case of a ferromagnet a finite external field destroys the transition (see figure 3) essentially because the coexistence of oppositely magnetized domains becomes infinitely improbable thermodynamically. Equally an antiferromagnet in a *finite* staggered field would not have a (sharp or true) transition. In practice, however, one can only observe an antiferromagnet in a uniform (parallel) field. This in turn corresponds to a ferromagnet in a staggered field which would act quite similarly on oppositely magnetized domains and so would have little tendency to destroy their coexistence. Thus the ferromagnetic transition should remain sharp for at least a range of staggered fields. By analogy we must expect, and it is confirmed by experiment (e.g. Schelling and Friedberg 1967), that the *anti*ferromagnetic transition will remain sharp in a finite uniform field, the critical point being drawn out into a 'critical line' (or 'lambda line') (see figure 6). Correspondingly the initial (H = 0) susceptibility  $\chi_T$  of an antiferromagnet does *not* exhibit a divergence

at  $T_{\rm c}$ . (However,  $\partial \chi_T / \partial T$  generally becomes large at  $T_{\rm c}$  and displays an anomaly closely mirroring the specific heat.<sup>†</sup>)

Experimental confirmation of the analogy of antiferromagnets to ferromagnets and hence to fluids is good. Most striking are the classic nuclear magnetic resonance experiments of Heller and Benedek (1962) on the sublattice magnetization of the antiferromagnetic crystal MnF<sub>2</sub>. They approached  $T_c$  to within a few parts in 10<sup>5</sup> and concluded that  $\beta = 0.335 \pm 0.003.$ ; Furthermore, specific-heat measurements on MnF<sub>2</sub> (Teaney 1965) which approached  $T_c$  to 1 part in 10<sup>4</sup> revealed an anomaly closely matching that in argon (see figure 7). Heat-capacity measurements on other



Figure 7. Magnetic specific heat of  $MnF_2$  near the Néel or critical temperature  $T_N$  (Teaney 1965). The closed squares represent the specific-heat density for argon (Bagatskii *et al.* 1962). The broken curve is for  $\alpha = 0.1$ .

antiferromagnets (notable examples are those of Skalyo and Friedberg (1964) on  $CoCl_2.6H_2O$ ) yield very similar results, although an ill-understood rounding is often observed close to  $T_c$  (as mentioned for EuO, see also Teaney (1966)). Cooper and Nathans (1966) have studied neutron scattering from KMnF<sub>3</sub> with the conclusions that  $\gamma \simeq 1.33$ ,  $\nu \simeq 0.67$  and  $\eta \simeq 0$ , which closely resemble the results for iron (see also experiments by Okazaki *et al.* (1965) and Tuberfield *et al.* (1965) on MnF<sub>2</sub>).

#### C. Other systems

#### 2.7. Binary fluids and alloys

In this section we briefly sketch some of the analogies and experimental results for binary fluid and alloy systems which undergo (i) phase separation (when AA and BB contacts are favoured energetically over AB contacts) or (ii) ordering (when AB

‡ See Heller (1966, 1967) for details and for a critical discussion.

<sup>&</sup>lt;sup>†</sup> For a theoretical discussion indicating that  $\chi_{T,anti}$  should rather generally have a singular part with exponents  $1-\alpha$  for  $T > T_c$  and  $1-\alpha'$  for  $T < T_c$  see Fisher (1962, 1965 a). A striking experimental confirmation has been presented by Wolf and Wyatt (1964).

contacts are most favourable). In case (i) the mole fraction of, say, the A component  $x_A$  is analogous to the density in a one-component fluid system. Below  $T_c$  (and sometimes *above* a lower critical point) the mixture will separate into an A-rich and a B-rich phase.

Clearly the exponent  $\beta$  should now describe how the concentration differences  $x_A^{(i)} - x_A^{(ii)}$  or  $x_B^{(ii)} - x_B^{(i)}$  between the two phases vanish with  $T_c - T$ . Indeed, most binary fluid separation curves are well described by a  $\beta$  close to  $\frac{1}{3}$  as analogy would suggest (see Rowlinson 1959). One should refer in particular to excellent measurements by Thompson and Rice (1964) who went to within 1 part in 10<sup>6</sup> of  $T_c$  for CCl<sub>4</sub> + C<sub>7</sub>F<sub>16</sub> and found  $\beta = 0.33 \pm 0.02$ .

The significance of the other exponents can be found by realizing that composition changes (at constant pressure) correspond to density changes in a pure fluid. As regards  $\alpha$  and  $\alpha'$  there are some data showing that  $C_{p,x}(T)$  displays an anomaly but these are not very precise (see Rowlinson 1966). The exponents  $\gamma$  and  $\delta$  are not very accessible experimentally since they require accurate measurements of the Gibbs free energy or chemical potentials. Although many light- and x-rayscattering studies have been performed on binary solutions (usually of small organic molecules, for a review see Brumberger (1966)) results are not yet very clear-cut. It appears probable that  $\gamma > 1.1$  and it should be mentioned that Chu and Kao (1965) and Brady *et al.* (1966) have found definite evidence that  $\eta \gtrsim 0.1$  (see Heller 1967, § 5.1).

Case (ii) of an ordering crystalline binary alloy such as beta-brass ( $\simeq 50\%$  CuZn) is most directly analogous to an antiferromagnet since the phase transition is signalled by the appearance below  $T_{\rm c}$  of a coherent superlattice scattering line at  $\mathbf{k} = \mathbf{k}_0$ . This corresponds to a long-range preferential occupancy of one sublattice by one species while the other species preferentially occupies the second equivalent interlacing sublattice. The intensity of the coherent peak at  $\mathbf{k}_0$  is proportional to the square of the disparity of occupation between the sublattices and is hence analogous to  $M_0'(T)$ , the sublattice magnetization of an antiferromagnet. (For a review of the basic theory see Münster (1966).)

As regards experimental data we note that the existence of a marked lambda anomaly in the specific heat of beta-brass has been well known for some time (see, for example, Nix and Shockley 1938). More recently Als-Nielsen and Dietrich (1967) have made accurate neutron-scattering measurements from which they conclude that  $\beta = 0.305 \pm 0.010$ ,  $\gamma = 1.25 \pm 0.02$  and  $\nu = 0.647 \pm 0.022$ . As we shall see later when we discuss numerical results for the Ising model, the value of  $\beta$ is significant not only because it is quite close to  $\frac{1}{3}$  (as now expected) but also because it is definitely slightly lower than  $\frac{1}{3}$ .

# 2.8. Superfluid helium

The (p, T) phase diagram of <sup>4</sup>He is shown schematically in figure 8. Unlike the liquid or gas phase, the superfluid phase is entirely enclosed by transition lines. This is like an antiferromagnetic phase in the (H, T) plane (see figure 6). While the transitions to gas and crystal are first order, the transition across the 'lambda line' between the normal-fluid and superfluid phases is apparently continuous along its whole length and so may be compared to the antiferromagnetic (H, T) transition

line (at least in sufficiently small fields). Furthermore, the specific heat  $C_p$  for helium, which is analogous to  $C_H$  for an antiferromagnet, displays a closely logarithmic anomaly. (From (2.1.9) one sees that  $K_T$  and/or  $C_V$  must have a similar behaviour; the anomaly in  $K_T$  has been detected by Grilly (1966).) The logarithmic nature of the specific-heat singularity is particularly striking on the vapour-pressure line (see figure 8) where the measurements of Fairbank *et al.* (1957) (see also Fairbank and Kellers 1966) accurately fit the simple formulae

$$\frac{C_{\sigma}}{k_{\rm B}} = A^{+} \ln\left(\frac{T}{T_{\rm c}} - 1\right) + B^{+} \quad (T \ge T_{\rm c}) 
= A^{-} \ln\left(1 - \frac{T_{\rm c}}{T}\right) + B^{-} \quad (T \le T_{\rm c})$$
(2.8.1)

over more than four decades of  $\Delta T/T_c$  with  $A^- = A^+$  but  $B^- > B^+$ . Evidently one can, by analogy, define specific-heat exponents and conclude that  $\alpha = \alpha' = 0$  with an accuracy probably better than to  $\pm 0.03$ .



Figure 8. Phase diagram of <sup>4</sup>He (not to scale) illustrating the 'enclosed' nature of the superfluid state:  $\lambda$  denotes the lambda line, c the gas-liquid critical point, and  $\sigma$  the vapourpressure line.

It is not, however, clear how to define exponents  $\gamma$ ,  $\gamma'$  and  $\delta$  since there seems to be no appropriate 'external field'. Again the situation is analogous to an antiferromagnet where the required 'staggered magnetic field' is not physically realizable. Scattering experiments on helium are also not helpful since neither for  $\mathbf{k} = \mathbf{0}$  nor any other value is a critical scattering peak associated with the transition.<sup>†</sup> This indicates, as is well known, that the 'ordering' in the superfluid state is intrinsically different from that in systems discussed previously.

Penrose (1951) and Penrose and Onsager (1956) (see also Yang 1962) suggested that the long-range order characterizing a superfluid is in the off-diagonal part of the quantum-mechanical *one*-body density matrix  $\rho_1(\mathbf{r}, \mathbf{r}')$  (or singlet correlation function) rather than in a two-particle or two-spin correlation function. In a

<sup>&</sup>lt;sup>†</sup> Attention should be drawn, however, to a recent suggestion by Hohenberg and Platzman (1966) indicating that high-energy inelastic neutron scattering might yield a direct measure of  $n_0$  as defined in equation (2.8.3).

second quantized formulation we have†

$$\rho_1(\mathbf{r},\mathbf{r}') = \langle \boldsymbol{\psi}^{\dagger}(\mathbf{r}) \, \boldsymbol{\psi}(\mathbf{r}') \rangle \tag{2.8.2}$$

and then  $|\psi|$ , the modulus of the 'order parameter', may be defined  $\ddagger$  by

$$\lim_{\mathbf{r}-\mathbf{r}'|\to\infty}\rho_1(\mathbf{r}-\mathbf{r}') = n_0 = |\psi|^2$$
(2.8.3)

which should be compared with the definition (2.6.1) of the antiferromagnetic sublattice magnetization  $M_0'$ . The parameter  $n_0$  is usually termed the 'density of the condensate' by analogy with condensation in an ideal Bose-Einstein fluid.

Evidently the exponent  $\beta$  should now be defined by

$$\{n_0(T)\}^{1/2} = |\psi(T)| \sim (T - T_c)^{\beta}$$
(2.8.4)

but, unfortunately, no way of observing  $n_0$  or  $|\psi|$  has yet been demonstrated.§ One can, however, observe the superfluid density  $\rho_s(T)$ . Although this is really a hydrodynamical property it is not implausible that near  $T_c$  it might vary roughly as  $n_0$ . (Proportionality of  $\rho_s$  to  $n_0$  is asserted in the simpler phenomenological theories of superfluidity but this has been seriously questioned by Josephson (1966).) At any rate it should be mentioned that recent observations by Clow and Reppy (1966) and Tyson and Douglass (1966) have shown that

$$\rho_{\rm s}(T) \sim (T_{\rm c} - T)^{\zeta} \quad (T \to T_{\rm c} -)$$
(2.8.5)

with  $\zeta = 0.666 \pm 0.010$ . This is surprisingly close to the value  $2\beta \simeq \frac{2}{3}$  that the naïve analogies with magnetic systems would suggest.

We shall return to magnetic analogies for helium in discussing model systems (§4.3) where the nature of the appropriate 'external field' will be seen.

# 2.9. Superconductors, ferroelectrics, etc.

Among other systems exhibiting critical points which we shall not consider in any detail are superconductors, ferroelectrics and antiferroelectrics. The values of the observed critical exponents for these systems seem to indicate that they are not so closely analogous to fluids and magnets. In particular the specific heat of a superconductor under normal experimental resolution displays, not a lambda-type anomaly, but only a finite (and slightly rounded) discontinuity at  $T_c$  (Cochran 1962). This difference of behaviour is probably due to the overwhelming importance of

† In terms of the N-body Schrödinger wave functions  $\Phi_{N,m}(\mathbf{r}_1, ..., \mathbf{r}_N)$  for the level  $E_{N,m}$  normalized in a domain  $\Omega$  the singlet density matrix is defined grand canonically by

$$\rho_1(\mathbf{r},\mathbf{r}';z,T;\Omega) = \sum_{N,m} NW_{N,m} \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \Phi_{N,m}^*(\mathbf{r},\mathbf{r}_2,\dots,\mathbf{r}_N) \Phi_{N,m}(\mathbf{r}',\mathbf{r}_2,\dots,\mathbf{r}_N)$$

where the grand canonical weight function is

$$W_{N,m} = z^N \exp\left(rac{-E_{N,m}/k_{
m B}T}{\Xi(z,T)}
ight)$$

in which  $\Xi$  is the grand canonical partition function.

 $\ddagger$  The order parameter is generally complex and hence also has a phase  $\phi$  which plays a significant role in the theory. We shall not discuss this except to point out that spiral spin orderings in metamagnets equally require the introduction of a phase.

§ See footnote to p. 641.

Fermi statistics for electrons in metals as evidenced by the large (of order 10<sup>3</sup> to 10<sup>4</sup>) ratio of the Fermi temperature  $T_{\rm F}$  (=  $E_{\rm F}/k_{\rm B}$ ) to the critical temperature. It is possible that if the specific heat of a superconductor could be measured on a scale  $\Delta T/T_{\rm c} \simeq 10^{-10}$ , then a more or less logarithmic anomaly would again be observed (Thouless 1960).

The specific heats of a number of ferroelectric crystals are known to exhibit pronounced lambda anomalies although present data are not very precise (see, for example, Grindlay 1965 a, b). However, the exponents  $\gamma$  and  $\gamma'$  for the initial electric susceptibility seem to be close to unity (rather than greater than 1.2 as for other systems). Recent measurements have been made by Craig (1966) and, with greater precision for triglycine sulphate, by Gonzalo (1966) who found

$$\gamma = \gamma' = 1.00 \pm 0.05.$$

For the spontaneous polarization  $P_0(T)$  Gonzalo found  $\beta = 0.51 \pm 0.05$ . However, for the hydrogen-bonded ferroelectric potassium dihydrogen phosphate  $d(P_0)^2/dT$ seems divergent at  $T_c$  (von Arx and Bantle 1943), which implies that  $\beta < \frac{1}{2}$ . For this class of ferroelectrics the critical phenomena, in particular the specific-heat anomaly, are confined to a narrow region around  $T_c (\Delta T/T_c \simeq 2\%)$  which prevents one determining  $\beta$  from the existing data more precisely than, say,  $\beta = 0.4 \pm 0.1$ . The narrow 'critical region' is somewhat analogous to that expected theoretically for a superconductor in that one can similarly divine two significant energy parameters of contrasting magnitudes (see, for example, Uehling 1963). Although there are a variety of different physical mechanisms which give rise to ferroelectricity (Jona and Shirane 1962, Uehling 1963) it is possible that the very-long-range nature of the Coulomb forces, which is presumably relevant in all cases, may be the reason why these transitions apparently have a critical-point behaviour markedly different from those discussed previously.

In this connection it is interesting to note, as pointed out by Egelstaff and Ring (1967), that the coexistence curves for the gas-liquid critical points of the alkali metals are apparently characterized by  $\beta \simeq 0.42-0.45$ , although existing data do not go very close to  $T_c$ . Here again longer-range and specifically Coulomb forces probably play an important role.

#### 3. Exponent inequalities

In the previous section we defined the basic critical-point exponents  $\alpha$ ,  $\alpha'$ ,  $\beta$ , ... for a number of systems. Apart from results for the two-dimensional Ising model (§ 6) and in the limit of infinitely weak, infinitely long-ranged forces (§ 5.4) there are essentially no rigorous results for the values of the exponents or for relations between them. Recently, however, it was discovered<sup>†</sup> that certain quite general *inequalities* can be proved between the exponents  $\alpha'$ ,  $\beta$ ,  $\gamma'$  (below  $T_c$ ) and  $\delta$ . Because these results are rigorous and of wide application (although of course they leave much to be desired) we present them fairly carefully before discussing more specific theories or models.

<sup>†</sup> On the grounds of a model calculation Essam and Fisher (1963) (see § 9.1) suggested the validity of the *equality*  $\alpha' + 2\beta + \gamma' = 2$ . Shortly afterwards Rushbrooke (1963) showed this could be proved thermodynamically as an *inequality* with  $\geq$  replacing =.

#### 3.1. Stability and convexity

Let us consider a particle system. Standard thermodynamic arguments (see, for example, Guggenheim 1950) based on the minimization of the Helmholtz free energy F(T, v) establish the stability relations

$$C_{\nu} = T \left( \frac{\partial S}{\partial T} \right)_{\nu} = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{\nu} \ge 0$$
(3.1.1)

and

$$\frac{1}{K_T} = -v \left(\frac{\partial p}{\partial v}\right)_T = v \left(\frac{\partial^2 F}{\partial v^2}\right)_T \ge 0.$$
(3.1.2)

As mentioned in §1.3 these also follow rigorously from the statistical mechanics of the canonical ensemble where one can prove (Ruelle 1963 a, Fisher 1964 a) the rather more general convexity relations

$$F[\frac{1}{2}(T_1 + T_2), v] \ge \frac{1}{2}F(T_1, v) + \frac{1}{2}F(T_2, v)$$
(3.1.3)

and

$$F[T, \frac{1}{2}(v_1 + v_2)] \leq \frac{1}{2}F(T, v_1) + \frac{1}{2}F(T, v_2)$$
(3.1.4)

which have an obvious graphical interpretation.

If for a magnetic system one assumes that the magnetization (density) M is a 'good' thermodynamic variable and considers the corresponding free energy A(T, M) one equally concludes

$$C_M = T \left( \frac{\partial S}{\partial T} \right)_M = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_M \ge 0$$
(3.1.5)

and

$$\frac{1}{\chi_T} = \left(\frac{\partial H}{\partial M}\right)_T = \left(\frac{\partial^2 A}{\partial M^2}\right)_T \ge 0.$$
(3.1.6)

A precisely analogous rigorous statistical-mechanical proof of (3.1.5) and the corresponding convexity relation can be given provided (i) the magnetization (as an operator) commutes with the total Hamiltonian. Similarly a proof of (3.1.6) and (3.1.5) can be given (independent of (i)) provided (ii) the magnetic field H enters only linearly into the Hamiltonian  $\mathcal{H}$  (Griffiths 1964 and private communication). This condition means strictly that any diamagnetic terms in  $\mathcal{H}$  (proportional to  $H^2$ ) must be ignored. Despite these restrictions we expect (3.1.5) to be of rather general validity. (We assume throughout, of course, that true equilibrium is always established.)

# 3.2. Inequality for $\alpha'$ , $\beta$ and $\gamma'$

Using the stability-convexity relations of the last section we shall first give thermodynamic proofs of the inequality (Rushbrooke 1963)

$$\alpha' + 2\beta + \gamma' \ge 2 \tag{3.2.1}$$

for a ferromagnet and of the corresponding analogy for a fluid (Fisher 1964 b). For this purpose it is convenient (and more rigorous) to redefine the exponent  $\beta$  by

$$\frac{dM_0}{dT} \sim (T_c - T)^{\beta - 1}$$
(3.2.2)

which, using the general exponent definition (1.4.2), rigorously implies the original definition (2.4.2) (see equation (1.4.8)).

Now by standard thermodynamic manipulations one has

$$\frac{C_H}{T} = \left(\frac{\partial S}{\partial T}\right)_M + \left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H$$
(3.2.3)

and

$$\left(\frac{\partial S}{\partial M}\right)_T = -\frac{\partial^2 A}{\partial M \partial T} = -\left(\frac{\partial H}{\partial T}\right)_M = \left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H.$$
(3.2.4)

Combination of these with the definitions (3.1.5) and (3.1.6) yields

$$C_{\mathcal{H}} = C_{\mathcal{M}} + T \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}^2 \chi_T^{-1}$$
(3.2.5)

which is the magnetic analogue of the well-known relation between  $C_p$  and  $C_V$ . For  $T < T_c$  consider now the limit  $H \rightarrow 0$ . By the definition of a ferromagnet we have

(i) 
$$\lim_{H \to 0^+} \left( \frac{\partial M}{\partial T} \right)_H = \frac{dM_0}{dT} \quad (T \le T_c)$$
(3.2.6)

and we may assume

(ii) 
$$\lim_{H \to 0} \chi_T(H, T) = \chi_T(0, T) < \infty \quad (T \le T_c).$$
(3.2.7)

This last condition is not obviously correct since  $\chi_T(H)$  might diverge as  $H \to 0$  as it does for certain models (such as the Berlin-Kac (1952) spherical model and the system of non-interacting spin waves in an isotropic d = 3 ferromagnet, in both of which cases  $\chi_T(H) \sim H^{-1/2}$  as  $H \to 0$ ). However,  $\gamma'$  is only defined if  $\chi_T$  does exist at H = 0.

Combination of these observations and the inequality (3.1.5) yields finally

$$C_{H=0} \ge T \left(\frac{dM_0}{dT}\right)^2 \chi_T^{-1} \quad (H=0).$$
 (3.2.8)

On taking logarithms, dividing by  $-\ln|T_c - T|$  and using the general exponent definition (1.4.2) one obtains

$$\alpha' \ge 2(1-\beta) - \gamma' \tag{3.2.9}$$

which is equivalent to (3.2.1). (If  $\gamma'$  does not exist one finds only  $\alpha' \ge 0$  which is trivial.)

For a fluid the argument is a little more complicated (Fisher 1964 b) since in the two-phase region ( $\rho = \rho_c, T < T_c$ ) the total entropy is a sum of the entropies for the two phases whose proportions, in general, change as the temperature is altered at constant total volume.

In terms of the mole fractions

$$x_{\rm L} = \left(\frac{\rho_{\rm L}}{\rho_{\rm c}}\right) \frac{\rho_{\rm c} - \rho_{\rm G}}{\rho_{\rm L} - \rho_{\rm G}}$$

$$x_{\rm G} = 1 - x_{\rm L}$$
(3.2.10)

and

of coexisting phases at the critical density one finds (Fisher 1964 b)

$$C_{\mathcal{F}_{a}}(T) = x_{\mathrm{L}} C_{\mathcal{F}}^{\mathrm{L}} + x_{\mathrm{G}} C_{\mathcal{F}}^{\mathrm{G}} + \frac{x_{\mathrm{L}} T}{\rho_{\mathrm{L}}^{3} K_{T}^{\mathrm{L}}} \left(\frac{\partial \rho_{\mathrm{L}}}{\partial T}\right)^{2} + \frac{x_{\mathrm{G}} T}{\rho_{\mathrm{G}}^{3} K_{T}^{\mathrm{G}}} \left(\frac{\partial \rho_{\mathrm{G}}}{\partial T}\right)^{2}$$
(3.2.11)

where  $C_{\nu}^{L}$ ,  $K_{T}^{L}$  and  $C_{\nu}^{G}$ ,  $K_{T}^{G}$  are the constant-volume specific heats and isothermal compressibilities of the liquid and gas phases respectively in the limit that the coexistence curve  $p = p_{\sigma}(T)$  is approached from the respective single phases. We now assume

(iii) 
$$0 < x_{\rm L}(T_{\rm c}) = \lim_{T \to T_{\rm c}^-} x_{\rm L}(T) = 1 - x_{\rm G}(T_{\rm c}) < 1.$$
 (3.2.12)

This implies  $\beta_{\rm L} = \beta_{\rm G}$  and would be assured by the law of the rectilinear diameter (2.1.4). Weaker or slightly different assumptions are possible, leading to effectively the same conclusions (see Griffiths 1965 c). Using (3.1.5) to drop the first two terms in (3.2.11) and dropping one or another of the last two leads to inequalities analogous to (3.2.8). If we take logarithms and the limit  $T \rightarrow T_c$  as before we obtain finally

$$\alpha' + 2\beta + \min\{\gamma_{\rm L}', \gamma_{\rm G}'\} \ge 2. \tag{3.2.13}$$

As one illustration of the practical utility of this inequality we note that from  $\beta < 0.36$  and  $\alpha' < 0.1$ , which seem to be implied by the experimental data on pure fluids (§2.1), one can conclude

$$\gamma_{\rm L}', \gamma_{\rm G}' > 1.17.$$
 (3.2.14)

This is valuable since  $K_T^{L}$  and  $K_T^{G}$  are both hard to measure accurately. If  $\beta = 0.345$  and the specific heat below  $T_c$  is logarithmic one would have

$$\gamma_{\rm L}', \gamma_{\rm G}' > 1.31.$$
 (3.2.15)

#### 3.3. Inequality for $\delta$ and use of convexity

Griffiths (1965 b) has derived the important inequality

$$\alpha' + \beta(1+\delta) \ge 2 \tag{3.3.1}$$

by direct use of the convexity properties of the free energy. We shall present an extension of his argument which also yields an alternative derivation of the first inequality (3.2.1). More recently Rushbrooke (1965) has given a thermodynamic derivation of this inequality for  $\delta$ .

Let us consider the free energy A(T, M) of a ferromagnet. Below  $T_c$  the field  $H = (\partial A / \partial M)_T$  vanishes identically for M less than the spontaneous magnetization  $M_0(T)$ , and so

$$A(T, M) = A(T, 0) = A_0(T) \quad M \le M_0(T).$$
(3.3.2)

(We suppose  $M \ge 0$  here and below.) If we assume the existence of the *initial* susceptibility  $\chi_T$  (see previous section, condition (ii)) we further have

$$A(T,M) = A(T,0) + \frac{1}{2}\chi_T^{-1} \{M - M_0(T)\}^2 \{1 + o(M - M_0)\} \text{ for } M \ge M_0(T).$$
(3.3.3)

Now let us suppose  $T_1 \leq T_2 \leq T_c$  so that

$$M_1 = M_0(T_1) \ge M_2 = M_0(T_2). \tag{3.3.4}$$

(We assume  $M_0(T)$  is monotonic decreasing sufficiently close to  $T_c$ .) The convexity of A(T, M) in T means that the graph of A against T for fixed M always lies on or below any tangent (which in turn has a slope  $(\partial A/\partial T)_M = -S$ ). A tangent at  $(T_i, M_1)$  thus yields

$$A(T_2, M_1) \leq A(T_1, M_2) - (T_2 - T_1) S(T_1, M_1)$$
(3.3.5)

while a tangent at  $(T_2, M_2)$  yields

$$A(T_1, M_2) \leq A(T_2, M_2) - (T_1 - T_2) S(T_2, M_2).$$
(3.3.6)

From (3.3.2) and (3.3.3) we have

and

$$A(T_1, M_1) = A(T_1, M_2) = A_0(T_1)$$
  

$$S(T_1, M_1) = S_0(T_1) \quad S(T_2, M_2) = S_0(T_2)$$
(3.3.7)

where the zero subscripts denote M = H = 0. Substituting and adding the two inequalities yields the basic inequality

$$A(T_2, M_1) - A(T_2, M_2) \leq (T_2 - T_1) \{ S_0(T_2) - S_0(T_1) \}.$$
(3.3.8)

We now divide by  $(T_2 - T_1)^2$  and rearrange using (3.3.3) to obtain

$$\frac{S_0(T_2) - S_0(T_1)}{T_2 - T_1} \ge \frac{1}{2} \chi_T^{-1} \left(\frac{M_1 - M_2}{T_2 - T_1}\right)^2 \{1 + o(M_1 - M_2)\}.$$
(3.3.9)

On taking the limit  $T_2 \rightarrow T_1 = T < T_c$  we rediscover the thermodynamic inequality (3.2.8) except for an additional factor  $\frac{1}{2}$  on the right-hand side. From this the original inequality for  $\alpha'$ ,  $\beta$  and  $\gamma'$  follows as before.

To derive (3.3.1) from (3.3.8) we put  $T_1 = T$ ,  $M_1 = M_0(T)$  and let  $T_2 \rightarrow T_c$  so that  $M_2 \rightarrow 0$ . Then for the free energy on the critical isotherm one finds

$$A(T_{\rm c}, M_0) - A_{\rm c} \leq (T_{\rm c} - T) \{S_{\rm c} - S_0(T)\}.$$
(3.3.10)

Now integration of the definitions of  $\alpha'$  and  $\delta$  shows by (1.4.8) that the right-hand side varies as  $(T_c - T)^{1+1-\alpha'}$  while the left-hand side varies as  $M_0^{1+\delta} \sim (T_c - T)^{\beta(1+\delta)}$ . Accordingly (3.3.10) implies the new exponent relation (3.3.1).

An application of this inequality to the data for fluids (§2.1) is a little disquieting. (The proof for the fluid case (see Griffiths 1965 c) is somewhat more involved because of the lack of symmetry.) The upper limits  $\beta \leq 0.36$  and  $\delta \leq 4.4$ yield

$$\alpha' \ge 2 - 0.36 \times 5.4 = 0.05 \tag{3.3.11}$$

which is not inconsistent with the specific-heat data although it rules out a simple logarithmic divergence. However, the central values  $\beta = 0.345$  and  $\delta = 4.2$  yield

$$\alpha' \ge 0.20 \tag{3.3.12}$$

which seems to contradict present interpretations of experiment quite violently (Voronel' *et al.* 1963, 1964, 1966) although it remains possible that the true specific heats close to  $T_{\rm c}$  are in fact sharper than suspected. The resolution of this discrepancy is an important experimental problem.

For a fluid the condensation or vapour-pressure line  $p_{\sigma}(T)$  may (and probably does) have a singularity of the form

$$\frac{d^2 p_{\sigma}}{dT^2} \sim (T_{\rm c} - T)^{-\alpha^*} \quad (T \to T_{\rm c} - ).$$
(3.3.13)

Griffiths (1965 b, c) has shown generally that such a singularity is restricted by

$$\alpha^* - \alpha' \leqslant \beta. \tag{3.3.14}$$

This is probably rather a weak inequality since the small amount of evidence available suggests  $\alpha^* \simeq \alpha'$ . We may also note that since the specific heat must be integrable we have  $\alpha' < 1$  so that from (3.2.1) and (3.3.1) we can conclude generally

$$\gamma' > 1 - 2\beta$$
 and  $1 + \delta > 1/\beta$ . (3.3.15)

By making some quite plausible but more special and less fundamental assumptions, Griffiths (1965 c) has derived a variety of further inequalities involving, in particular, the variation of the entropy on the critical isotherm and of the field and magnetization on the critical isentrope ( $S = S_c$ ) (see also Liberman 1966).

# 4. Models and analogies

Before taking up the discussion of theoretical arguments that lead to explicit numerical values for the critical exponents and amplitudes we shall review the definitions and general properties of those theoretical models which are most useful in the study of critical phenomena.<sup>†</sup> This will lead to a more precise and clear theoretical understanding of the analogies between the various systems which we have developed phenomenologically in the previous sections.

#### 4.1. Lattice gases

To understand the critical behaviour of a fluid *including* possible quantum effects one must study a quantum-mechanical model. The standard gas-liquid model is, of course, the continuum gas of identical point particles interacting with pairwise potentials  $\phi(\mathbf{r})$  and obeying quantum mechanics with appropriate statistics. With suitable  $\phi(\mathbf{r})$  this model is quite realistic (although the existence of internal molecular structure and three- or more-body potentials must not be forgotten altogether), but it is quite intractable as regards critical behaviour except in the unrealistic case of infinitely weak, infinitely long-range forces (see §5.4). By adopting classical mechanics the mathematics simplifies and the model should still be good for the heavier gases, for example xenon, krypton and argon. Although appreciable progress on the classical gas problem has been made in recent years, mainly based on virial expansions or integral equations which are most accurate at low density (see, for example, Rowlinson 1965), no significant results regarding the behaviour of the critical specific heat, isotherm or compressibility have been achieved, nor do such results yet seem in sight.

<sup>†</sup> Space prevents us from considering a number of worthwhile models, in particular the spherical model (Berlin and Kac 1952, Joyce 1966), already alluded to, and Stillinger and Helfand's (1964) binary fluid model with Gaussian Mayer-function interactions.

A more powerful simplification is achieved by the *lattice gas model*<sup>†</sup> in which all position vectors **r** are restricted to the sites of a regular space lattice  $\mathscr{L}$ . If  $v_0$  is the cell volume then, in the definition of partition functions etc., integrals over the continuum are simply replaced by sums over the lattice, i.e.

$$\int d\mathbf{r} \to v_0 \sum_{\mathbf{r}}.$$
(4.1.1)

To formulate the *classical lattice gas model* it is convenient to introduce occupation variables

$$t_{\mathbf{r}} = 1$$
 if site **r** is occupied  
= 0 if site **r** is vacant. (4.1.2)

(We always assume, in accord with (1.3.12), that  $\phi(0) = +\infty$  so that double occupation of a site is forbidden.) From the usual definitions (1.3.1) and (1.3.5) it is then not difficult to see that the grand partition function of the system is

$$\Xi(T,z;\mathscr{L}) = \sum_{t_{\mathbf{r}}=0,1} \exp\left\{\beta\bar{\mu}\sum_{\mathbf{r}} t_{\mathbf{r}} - \sum_{(\mathbf{r},\mathbf{r}')} \beta\phi(\mathbf{r}-\mathbf{r}') t_{\mathbf{r}} t_{\mathbf{r}'}\right\}$$
(4.1.3)

where  $\beta = 1/k_{B}T$  and

$$\bar{\mu} = k_{\rm B} T \ln \left( z v_0 \right) = \mu - k_{\rm B} T \ln \left( \frac{\Lambda^d}{v_0} \right) \tag{4.1.4}$$

and where the second and third sums run over all sites **r** and pairs of sites (**r**, **r**') of  $\mathscr{L}$ . The first sum represents the sum over all configurations for all values of N. (For brevity we shall often label the lattice sites  $\ddagger i, j = 1, 2, ..., N_{\mathscr{L}}$ .) Externally varying fields may be included by allowing z to depend on **r** (and taking  $\ln(z_r v_0)$  inside the corresponding summation).

As apparently first noted by Matsubara and Matsuda (1956, 1957), one may also construct a *quantum-mechanical lattice gas* in essentially the same way. Since the many-body wave functions  $\Phi_N(\mathbf{r}_1, ..., \mathbf{r}_N)$  are now defined only at discrete lattice points, differential operators must be converted into their finite-difference analogues. Thus to represent the kinetic energy we need

$$\nabla_i^2 \Phi_N(\dots, \mathbf{r}_i, \dots) \to \frac{2d}{qa^2} \sum_{\mathbf{s}} \left\{ \Phi_N(\dots, \mathbf{r}_i + \mathbf{\delta}, \dots) - \Phi_N(\dots, \mathbf{r}_i, \dots) \right\}$$
(4.1.5)

where d is the dimensionality,  $\delta$  runs through the q nearest-neighbour lattice vectors of a site, and the lattice spacing is  $a = |\delta|$ .§

<sup>†</sup> The specification of this model and its implications were first set out clearly by Yang and Lee (1952 b) although the appreciation of its existence, and equivalence to the Ising model (see below), can be traced back much further via hole theories of liquids and Bragg and Williams' studies of binary alloys. It is worth noting that instead of imagining the particles confined to lattice sites one may suppose that they move continuously in a space divided into 'cells', but that their interactions are determined solely by which particular cells are occupied.

 $\ddagger$  It should be noted that  $N_{\mathscr{L}}$  must not here be confused with N, the number of *particles* in some configuration of the 'gas' on  $\mathscr{L}$ .

§ Evidently this finite-difference approximation is good only when  $\Phi$  does not vary too rapidly on the scale *a*. It will lead to artificial results at sufficiently high kinetic energies and hence at very high temperatures. At high temperatures, however, one has less need for a quantummechanical model. 650

To develop the theory and take account of the statistics it is most convenient (but not essential) to employ a second-quantized formulation. Thus for Bose statistics we introduce a set (one for each site) of commuting creation and destruction operators

$$\mathbf{a_r}^{\dagger} = v_0^{1/2} \boldsymbol{\psi}^{\dagger}(\mathbf{r}), \quad \mathbf{a_r} = v_0^{1/2} \boldsymbol{\psi}(\mathbf{r})$$
(4.1.6)

and a corresponding density or number operator

$$\mathbf{n}_{\mathbf{r}} = \mathbf{a}_{\mathbf{r}}^{\dagger} \mathbf{a}_{\mathbf{r}} = v_0 \, \boldsymbol{\rho}(\mathbf{r}). \tag{4.1.7}$$

The exclusion of double occupancy now allows one to specify the *anti*commutation relation

$$\mathbf{a_r}^{\dagger} \mathbf{a_r} + \mathbf{a_r} \mathbf{a_r}^{\dagger} = 1 \tag{4.1.8}$$

in place of the normal Bose commutation rule. (Operators for different sites commute.) This in turn ensures that the eigenvalues of  $\mathbf{n_r}$  are only 0 or 1 so that in a diagonal representation we have  $\mathbf{n_r} \equiv t_r$ .

The grand canonical partition function is then given by

$$\Xi(T, z) = \operatorname{Tr} \{ \exp\left(-\beta \mathscr{H}_{z}\right) \}$$
(4.1.9)

where the total second-quantized Hamiltonian may be written

$$\mathscr{H}_{z} = -\bar{\overline{\mu}}\sum_{\mathbf{r}}\mathbf{n}_{\mathbf{r}} + \sum_{(\mathbf{r},\mathbf{r}')}\phi(\mathbf{r}-\mathbf{r}')\mathbf{n}_{\mathbf{r}}\mathbf{n}_{\mathbf{r}'} - \frac{\hbar^{2}d}{mqa^{2}}\sum_{\mathbf{r}}\sum_{\delta}\mathbf{a}_{\mathbf{r}}^{\dagger}\mathbf{a}_{\mathbf{r}+\delta}$$
(4.1.10)

with the modified chemical potential

$$\bar{\bar{\mu}} = \mu - \frac{\hbar^2 d}{ma^2}.$$
(4.1.11)

Evidently, the last term in (4.1.10) derives from the kinetic energy and does not commute with the first two terms. As before one may include external fields ('diagonal fields') by setting  $\mu \rightarrow \mu(\mathbf{r})$ .

For theoretical purposes (see Bogoliubov 1960, Hohenberg and Martin 1965) it is also useful to add to  $\mathscr{H}_z$  non-classical 'off-diagonal fields' of the form

$$h = -v_0^{1/2} \sum_{\mathbf{r}} \left( \nu_{\mathbf{r}}^* \mathbf{a}_{\mathbf{r}} + \nu_{\mathbf{r}} \mathbf{a}_{\mathbf{r}}^\dagger \right)$$
(4.1.12)

even though these cannot apparently be realized physically. Indeed these fields turn out to be just the appropriate external fields needed to detect the off-diagonal superfluid order discussed in §2.8. Thus in the case of a uniform off-diagonal field one finds

$$\frac{\partial}{\partial \nu^*} \frac{k_{\rm B} T}{N_{\mathscr{L}} v_0} \ln \left\{ \Xi(T, z, \nu^*, \nu) \right\} = v_0^{-1/2} \langle \mathbf{a}_0 \rangle = \langle \mathbf{\psi} \rangle. \tag{4.1.13}$$

One can then define the superfluid order parameter  $|\psi|$  in the alternative fashion

$$|\psi(T,z)| = \lim_{\nu,\nu^* \to 0} |\langle \Psi(T,z,\nu^*,\nu) \rangle| \qquad (4.1.14)$$

in close analogy with the antiferromagnetic and ferromagnetic cases (equations (2.6.4), (2.4.1)). In any finite quantal system this off-diagonal expectation value must, of course, vanish identically when  $\nu^* = \nu = 0$  (just as a finite ferromagnet can have no true spontaneous magnetization). Following the ideas of Penrose and Onsager (1956), however, we expect that a non-zero value of the limit (4.1.14) for an infinite system will correctly characterize superfluid order.
# 4.2. Ising-Heisenberg model and equivalences

We have already referred to the theoretical simplification gained by assuming that the spins in a magnetic system are localized on lattice sites. This will be realistic for insulating magnetic materials but for metallic ferromagnets, like iron and nickel, the magnetic carriers are, at least to some extent, free. At present, however, significant mathematical progress on the critical behaviour of nonlocalized magnetic models is lacking. In magnetic systems with critical temperatures exceeding, say, 20 ° $\kappa$  the direct electromagnetic dipolar interactions are relatively small terms in the magnetic Hamiltonian and may probably be neglected in first approximation.<sup>†</sup> When this is so the Ising-Heisenberg Hamiltonian

$$\mathscr{H} = -2\sum_{\mathbf{r},\mathbf{r}'} \{ J_{\perp}(\mathbf{r} - \mathbf{r}') S_{\mathbf{r}}^{z} S_{\mathbf{r}'}^{z} + J_{\perp}(\mathbf{r} - \mathbf{r}') (S_{\mathbf{r}}^{x} S_{\mathbf{r}'}^{x} + S_{\mathbf{r}}^{y} S_{\mathbf{r}'}^{y}) \} - g\beta_{\mathrm{B}} \sum_{\mathbf{r}} \mathbf{S}_{\mathbf{r}} \cdot \mathbf{H}_{\mathbf{r}}$$

$$(4.2.1)$$

should be a reasonable representation of reality. ( $\mathscr{H}_{\mathbf{r}}$  is the external field on the site  $\mathbf{r}$ , while g is the gyromagnetic ratio and  $\beta_{\rm B}$  the Bohr magneton.)

Note that ferromagnetic coupling corresponds to positive J while negative J means an antiferromagnetic coupling. The pure isotropic Heisenberg Hamiltonian corresponds to exchange interactions satisfying  $J_{\perp}(\mathbf{r}) = J_{\perp}(\mathbf{r}) = J(\mathbf{r})$ . Most real materials have some magnetic anisotropy which (in simple uniaxial cases) would usually correspond to  $|J_{\perp}| > |J_{\perp}|$  so that in zero field the spins order 'parallel' to the z axis. The extreme anisotropic limit  $J_{\perp}(\mathbf{r}) = 0$  corresponds to the Ising model. For parallel fields  $\mathbf{H} = (0, 0, H_z)$  all operators in  $\mathcal{H}$  then commute and the system effectively obeys classical mechanics. Another classical case, the infinite spin limit, is obtained by writing

$$\mathbf{s}_{\mathbf{r}} = \frac{\mathbf{S}_{\mathbf{r}}}{S}, \quad J_{\parallel}(r) = \frac{\mathscr{J}_{\parallel}(r)}{S^2}, \quad J_{\perp}(\mathbf{r}) = \frac{\mathscr{J}_{\perp}(\mathbf{r})}{S^2}$$
(4.2.2)

and letting  $S \rightarrow \infty$ . The operators  $\mathbf{s_r}$  then commute and indeed reduce just to classical unit vectors. (Trace operations become integrations over the solid angles.)

We shall now establish the mathematical equivalences between lattice gas models and Ising-Heisenberg magnets with spin  $\frac{1}{2}$ . For simplicity consider firstly the classical lattice gas and an Ising magnet in a uniform parallel field. For the latter it is convenient to introduce the scalar variables<sup>‡</sup>

$$s_{\mathbf{r}} = 2\mathbf{S}_i^z = \pm 1 \tag{4.2.3}$$

(since  $S = \frac{1}{2}$ ). If we write

$$m = \frac{1}{2}g\beta_{\rm B} \tag{4.2.4}$$

for the magnetic moment per spin, the partition function for a lattice  $\mathscr L$  becomes

$$Z(T,H;\mathscr{L}) = \sum_{s_{\mathbf{r}}=\pm 1} \exp\left\{\sum_{(\mathbf{r},\mathbf{r}')} \frac{1}{2}\beta J_{\parallel}(\mathbf{r}-\mathbf{r}') s_{\mathbf{r}} s_{\mathbf{r}'} + \beta m H_z \sum_{\mathbf{r}} s_{\mathbf{r}}\right\}.$$
(4.2.5)

Now the relation

$$t_{\mathbf{r}} = \frac{1}{2}(1 - s_{\mathbf{r}}) \tag{4.2.6}$$

<sup>†</sup> Owing to their long range, it is not certain that residual dipolar interactions might not still play a role close to  $T_c$  as has been suggested by Kadanoff *et al.* (1967).

<sup>‡</sup> In the literature of the  $S = \frac{1}{2}$  Ising model these have been denoted  $\sigma_{\mathbf{r}}^{z}$ ,  $\sigma_{\mathbf{r}}$ ,  $\mu_{\mathbf{r}}$ , etc., and  $\frac{1}{2}J_{\pm}$  is usually denoted J.

associates (by common convention) an 'up' spin on site  $\mathbf{r}$  with a *vacant* site of the lattice gas (§2.2) and a 'down' or 'overturned' spin with an *occupied* site. Substitution of (4.2.6) in the expression (4.1.3) for the lattice gas grand canonical partition function and comparison with (4.2.5) lead at once to the following identifications between the two models:

$$\phi(\mathbf{r}) \equiv -2J_{\parallel}(\mathbf{r}) \tag{4.2.7}$$

$$\mu - \mu_{\sigma} \equiv -2mH_z \tag{4.2.8}$$

where

$$\mu_{\sigma} = \frac{1}{2}\hat{\phi}(0) + k_{\rm B} T \ln\left(\frac{\Lambda^d}{v_0}\right) \tag{4.2.9}$$

with

$$\hat{\phi}(0) = \sum_{\mathbf{r}\neq 0} \phi(\mathbf{r}) \equiv -2 \sum_{\mathbf{r}} J_{\parallel}(\mathbf{r}).$$
(4.2.10)

From the definitions of the thermodynamic potentials we then have

$$pv_0 \equiv -F - mH_z - \frac{1}{8}\hat{\phi}(0) = m \int_{H_z}^{\infty} \{1 - \mathcal{M}(H')\} dH'$$
(4.2.11)

where F is the magnetic free energy per spin and  $\mathcal{M}(T,H) = M/M_{\text{max}}$  is the reduced magnetization per spin. Finally by the usual thermodynamic formulae or by taking expectation values in (4.2.6) we have

$$\frac{\rho}{\rho_{\max}} = \frac{1}{2} \left( 1 - \frac{M}{M_{\max}} \right) \quad \left( M_{\max} = m, \ \rho_{\max} = \frac{1}{v_0} \right). \tag{4.2.12}$$

Further equivalences for specific heats, compressibilities, correlation functions, etc. are displayed in table 1.

These equivalences provide a precise expression for the magnet/fluid analogies. Equation (4.2.12) is the expected correspondence between magnetization and density changes. On the other hand, one might have expected the magnetic field to correspond directly to the pressure rather than to the chemical potential as is indicated by (4.2.8). This distinction, however, is unimportant close to the critical point as explained by equation (2.1.6). We may now check in particular that *all the critical exponents have precisely the same values for Ising ferromagnet and classical lattice gas.* In as far as these two models are realistic our conclusion shows why the close correspondence of exponent values observed experimentally should have been expected. (Indeed this was, historically, the main course of events.)

A few other features of the correspondence should be pointed out. For a simple Ising ferromagnet with  $J(\mathbf{r}) \ge 0$  (all  $\mathbf{r}$ ) the only transition occurs in zero field (Yang and Lee 1952 b) and the phase diagram is as in figure 4. The phase diagram for the corresponding lattice gas of attracting particles which have a 'hard-core' interaction diameter of only one site follows from (4.2.11). (There is, of course, no crystalline phase.) From (4.2.12) we then see that the law of rectilinear diameter (2.1.4) holds identically with slope a = 0 and

$$\rho_{\rm c} = \frac{1}{2} v_0^{-1} = \frac{1}{2} \rho_{\rm max}. \tag{4.2.13}$$

For real gases these results are artificial since  $\rho_c/\rho_{max} \simeq \frac{1}{3}$  and  $a \neq 0$ . They would, furthermore, *not* be reproduced by lattice gases with more realistic (but less tractable) repulsive interactions extending over one or more lattice spacings. Similarly

from (4.2.11) one finds  $\alpha^* = \alpha'$  (see equation (3.3.13)) which might be typical but (4.2.9) implies that  $d^2\mu_{\alpha}/dT^2$  can have no anomaly which is probably also artificial (Yang and Yang 1964, Barieau 1966).

# Table 1. Further equivalences between a lattice gas and an Ising magnet (see also equations (4.2.6) to (4.2.12))

$\mathbf{L}$	atti	ce	gas
			<u></u>

Ising magnet

configurational entropy density

isothermal susceptibility

entropy per spin  $\rho v_0 S^{\text{config}} \equiv S$ (a)

isothermal compressibility

$$4v_0 \rho^2 K_T \equiv \chi_T / m^2 \tag{b}$$

configurational specific heats

$$\rho v_0 C_V^{\text{config}} \equiv C_M = C_H - \frac{T \alpha_H^2}{\chi_T} \tag{c}$$

where 
$$\alpha_H = \left(\frac{\partial M}{\partial T}\right)_H$$
 with  $\alpha_H \equiv 0$  for  $H = 0, T > T_c$  (d)

$$\rho v_0 C_p^{\text{config}} \equiv T W^2 \chi_T + C_H + 2 T W \alpha_H \tag{e}$$

where 
$$W = \frac{S}{m} \left( 1 - \frac{M}{m} \right)^{-1}$$
 (f)

thermal pressure coefficient

$$v_0 \gamma_V = v_0 \left(\frac{\partial p}{\partial T}\right)_V \equiv S + \frac{\{1 - (M/m)\} \alpha_H m}{\chi_T}$$
(g)

pair correlation functions

$$\rho v_0 G(\mathbf{r}) = \rho v_0 \{ g_2(\mathbf{r}) - 1 \} \equiv \frac{\langle s_0 \ s_{\mathbf{r}} \rangle - \langle s_0 \rangle^2}{\langle s_0^2 \rangle - \langle s_0 \rangle^2} = \Gamma(\mathbf{r})$$
(h)

at 
$$\rho_{\rm c} = \rho$$
,  $T > T_{\rm c}$  at  $H = 0$ ,  $T > T_{\rm c}$   
 $\frac{1}{2}G(\mathbf{r}) \equiv \langle s_{\mathbf{0}} s_{\mathbf{r}} \rangle = \Gamma(\mathbf{r})$  (i)

If in place of the association (4.2.6) of a 'down' spin with a particle and an 'up' spin with a 'hole' we interpret 'down' spins as one species of particle, say A, and 'up' spins as a second, B, species, we obtain a lattice model of a dense binary fluid or alloy. It is clear that by constructing the corresponding grand partition function we shall again be able to prove a mathematical equivalence to the Ising magnet. Apart from the equivalence

$$-2J_{\parallel}(\mathbf{r}) \equiv \phi_{\rm AB}(\mathbf{r}) - \frac{1}{2} \{\phi_{\rm AA}(\mathbf{r}) + \phi_{\rm BB}(\mathbf{r})\}$$
(4.2.14)

for the interaction potentials we shall not give any details. Suffice it to say that the expected analogies are again confirmed and corresponding critical exponents are found to be identical. In parallel with (4.2.13) the critical composition for only single-site repulsions is 50 : 50, i.e.  $x_{A,c} = x_{B,c} = \frac{1}{2}$ .

The simplest Ising model of an antiferromagnet is obtained by taking  $J_{u}(\mathbf{r}) = -|J_{u}|$  whenever  $\mathbf{r} = \mathbf{\delta}$  is a nearest-neighbour vector, but  $J_{u}(\mathbf{r}) = 0$  otherwise. If the lattice is of alternating structure so that it can be decomposed into two

interlacing sublattices, long-range antiferromagnetic order is possible and will appear below  $T_c$ . In zero field the mathematical problem for such an antiferromagnetic model is *precisely* equivalent to that for the corresponding ferromagnet  $(J_{\parallel} = |J_{\parallel}|)$  since in (4.2.5) one may change the sign of all the spin variables  $s_r$  on one sublattice without altering the partition function (as the spins are dummy variables). Consequently the antiferromagnetic specific heat in zero field will exhibit precisely the same behaviour, with exponents  $\alpha$  and  $\alpha'$ , as the ferromagnetic  $C_{H=0}$ . Furthermore, spontaneous *sublattice* magnetization  $M_0'(T)$  will be identical with the ferromagnetic  $M_0(T)$  while for the spin-pair correlations we have simply

$$\langle s_0 s_{\mathbf{r}} \rangle_{\text{anti}} = \exp\left(i\mathbf{k}_0 \cdot \mathbf{r}\right) \langle s_0 s_{\mathbf{r}} \rangle_{\text{ferro}}.$$
 (4.2.15)

The uniform ferromagnetic field H evidently becomes H', the alternating staggered field (2.6.2) for the antiferromagnet (and generally Fourier space is shifted by a translation  $\mathbf{k}_0$ ). This all confirms our previous antiferromagnetic to ferromagnetic analogies in a finite or zero staggered field and shows that, within the applicability of the Ising model, all the exponents for antiferromagnets should be *identical* with those for ferromagnets.

The simple Ising antiferromagnet corresponds to a lattice gas with firstneighbour repulsions which at low temperatures forms a regular 'crystal' over a range of pressures or chemical potentials (corresponding to the continuance of the antiferromagnetic transition into a finite field (figure 6)). Alternatively, if one again interprets 'up' and 'down' spins as different atomic species one has a not unrealistic model of an ordering metallic binary alloy (in which AB contacts are favoured). Again without going into details one can see how the mathematical equivalence will go through with all exponents corresponding precisely in value. One should note, however, that the Ising model in zero field again describes only the 50:50 or simple AB alloy. Different compositions correspond to non-zero magnetizations and fields which might be large enough to change the nature of the transition (see figure 6).†

# 4.3. Quantal fluid-magnet analogies

Having explored the connection between classical lattice gases and Ising (and hence extremely anisotropic) magnets let us investigate the magnetic analogy for *quantal* lattice gases. Consider as before the Bose system with the second-quantized Hamiltonian (4.1.10) expressed in terms of the modified creation and destruction operators  $\mathbf{a_r}^*$  and  $\mathbf{a_r}$ . In terms of the Pauli operators

$$\sigma^x = 2S^x, \quad \sigma^y = 2S^y, \quad \sigma^z = 2S^z \tag{4.3.1}$$

which satisfy the standard spin-commutation relations, we find that the identifications<sup>‡</sup>

$$\mathbf{a}_{\mathbf{r}} = \frac{1}{2} (\sigma_{\mathbf{r}}^{x} + i\sigma_{\mathbf{r}}^{y})$$
  
$$\mathbf{a}_{\mathbf{r}}^{\dagger} = \frac{1}{2} (\sigma_{\mathbf{r}}^{x} - i\sigma_{\mathbf{r}}^{y})$$
  
(4.3.2)

 $\dagger$  Experimentally typical A<sub>3</sub>B alloys appear to exhibit straightforward first-order transitions (see the general review by Guttman (1956)).

<sup>‡</sup> We associate  $\sigma^+$  with **a** and  $\sigma^-$  with **a**<sup>†</sup> rather than vice versa, in order to retain the convention that a 'down' spin denotes the presence of a particle.

yield precisely the required commutation relations (4.1.8) for the  $\mathbf{a_r}$  and  $\mathbf{a_r}^{\dagger}$ . Further, the density operator is given by

$$\mathbf{n}_{\mathbf{r}} = \mathbf{a}_{\mathbf{r}}^{\dagger} \mathbf{a}_{\mathbf{r}} = \frac{1}{2} (1 - \sigma^z) \tag{4.3.3}$$

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which is just the quantal form of the classical gas-magnet relation (4.2.6). Taking expectation values yields the same density-magnetization equivalence (4.2.12) as previously.

However, the Hamiltonian (4.1.10) with the off-diagonal fields (4.1.12) becomes

$$\mathcal{H}_{z} = \frac{1}{2} (\mu - \bar{\mu}_{\sigma}) \sum_{\mathbf{r}} \sigma_{\mathbf{r}}^{z} - \sum_{\mathbf{r}} (\nu_{\mathbf{r}}^{x} \sigma_{\mathbf{r}}^{x} + \nu_{\mathbf{r}}^{y} \sigma_{\mathbf{r}}^{y})$$
  
+ 
$$\frac{1}{4} \sum_{(\mathbf{r},\mathbf{r}')} \phi(\mathbf{r} - \mathbf{r}') \sigma_{\mathbf{r}}^{z} \sigma_{\mathbf{r}'}^{z} - \frac{\hbar^{2} d}{2mqa^{2}} \sum_{[\mathbf{r},\mathbf{r}']} (\sigma_{\mathbf{r}}^{x} \sigma_{\mathbf{r}'}^{x} + \sigma_{\mathbf{r}}^{y} \sigma_{\mathbf{r}'}^{y})$$
  
- 
$$\frac{1}{2} N_{\mathscr{L}} \{\mu - \bar{\mu}_{\sigma} + \frac{1}{4} \hat{\phi}(0)\}$$
(4.3.4)

where

$$\bar{\mu}_{\sigma} = \frac{1}{2}\hat{\phi}(0) + \frac{\hbar^2 d}{ma^2}$$
(4.3.5)

$$\nu_{\mathbf{r}} = \nu_{\mathbf{r}}^{x} + i\nu_{\mathbf{r}}^{y} \tag{4.3.6}$$

and where  $[\mathbf{r}, \mathbf{r}']$  denotes that the sum runs only over nearest-neighbour bonds  $\mathbf{r}' = \mathbf{r} + \mathbf{\delta}$ . Comparison with (4.2.1) now shows that the quantal lattice gas corresponds precisely to the general Heisenberg–Ising magnet.

The potential energy or 'diagonal interaction'  $\phi(\mathbf{r})$  is related to the parallel exchange coupling  $J_{\parallel}(\mathbf{r})$  by (4.2.7) just as for the classical case. Similarly the chemical potential (rather than the pressure) is again related to the parallel magnetic field by (4.2.8) but with  $\mu_{\sigma}$  replaced by  $\bar{\mu}_{\sigma}$ .

The *kinetic* energy, or 'off-diagonal interaction', however, becomes the *trans*verse magnetic coupling (between nearest neighbours only) with the equivalence

$$\frac{\hbar^2 d}{mqa^2} \equiv J_\perp = J_\perp(\mathbf{\delta}). \tag{4.3.7}$$

This appears naturally as a ferromagnetic, i.e. attractive, interaction. (On an alternating lattice, however, the partition function for  $\nu^x = \nu^y = 0$  is unchanged if  $J_{\perp}$ is taken with negative sign, as can be seen by making the canonical transformation  $\sigma^z \rightarrow \sigma^z, \sigma^x \rightarrow -\sigma^x, \sigma^y \rightarrow -\sigma^y$  on the sites of one sublattice.) Similarly the unrealizable off-diagonal fields  $\nu_r$  introduced in (4.1.12) become simply *transverse* magnetic fields since

$$\nu_{\mathbf{r}}^{x} \equiv mH_{x}(\mathbf{r})$$

$$\nu_{\mathbf{r}}^{y} \equiv mH_{y}(\mathbf{r}).$$
(4.3.8)

Our model can now display quite a richness of behaviour. If we confine attention only to nearest-neighbour interactions we may anticipate some of the possibilities as follows:

(i) Dominant parallel ferromagnetic coupling. For  $J_{\parallel} > 0$  the dimensionless parameter

$$\frac{J_{\perp}}{J_{\parallel}} = \frac{d}{2\pi^2 q} \frac{h^2}{m\phi(a) a^2}$$
(4.3.9)

is proportional to the square of de Boer's quantal parameter  $\Lambda^*$  (see (2.1.12)). When it is small we expect simple ferromagnetic (or in the fluid, condensation) behaviour with the phase diagrams of figure 4. The spontaneous magnetization will always be parallel to the z axis corresponding, as before, to a density difference  $\rho_L - \rho_G$ . However, the exponents  $\alpha$ ,  $\beta$ , etc., for both magnet and fluid might possibly be modified by quantal effects (Yang and Yang 1964, Fisher 1966 a).

(ii) Isotropic ferromagnet. The limiting case  $J_{\parallel} = J_{\perp} > 0$  of a completely isotropic Heisenberg ferromagnet corresponds to a very strongly quantal gas with, according to (4.3.9),  $\Lambda^* \simeq 6-9$ . (We identify the collision diameter as approximately equal to the nearest-neighbour lattice distance a.) Since the largest experimental value of the de Boer parameter is  $\Lambda^* \simeq 3.08$  (for <sup>3</sup>He), this model probably does not have direct application to any real fluids. The phase diagram, however, should be unchanged, the only new feature being that the spontaneous magnetization below  $T_c$  need not point only along the z axis but might also have components in the x and y directions. Before interpreting such a transverse spontaneous magnetization in terms of the quantal fluid we shall indicate for what other coupling parameter values it should arise.

(iii) Dominant transverse coupling. When  $J_{\perp} > J_{\parallel} > 0$  we have a ferromagnet in which, clearly, the spontaneous magnetization vector  $\mathbf{M}_0$  in zero parallel field  $(H_z = 0)$  will lie wholly in the xy plane. (This model has been particularly studied by Whitlock and Zilsel (1963) and Zilsel (1965).) Imposition of a parallel field  $H_z$  will now be rather analogous to the antiferromagnetic situation. Since  $\mathbf{H}$  is perpendicular to the spontaneous magnetization  $\mathbf{M}_0$  it will act similarly on all domains and hence will not destroy the transition immediately. For large  $H_z$ , however, the total magnetization vector will tend to swing around towards the z axis until the transverse components vanish and the paramagnetic phase is restored. The phase diagrams should probably, therefore, be as in figure 9 with a definite lambda line of continuous transition points.

(iv) Dominant parallel antiferromagnetic coupling. If  $-J_{\parallel} = |J_{\parallel}| > |J_{\perp}|$  we have magnetically a model for the common system of a uniaxial antiferromagnet.<sup>+</sup> Below  $T_c$  in zero or small parallel fields the situation is just as for the highly anisotropic (Ising-like) antiferromagnet with the phase diagram of figure 6. As  $H_z$ increases, however, the antiferromagnetic ordering with a sublattice magnetization parallel to the z axis becomes less favourable until, when  $mH_z$  is of order  $|J_{\parallel}| - |J_{\perp}|$ , it becomes thermodynamically preferable for the spins to re-order with a transverse spontaneous magnetization (or sublattice magnetization if  $J_{\perp} < 0$ ).<sup>‡</sup> Consequently in a sufficiently large finite field a new phase appears and we effectively recapture

<sup>&</sup>lt;sup>†</sup> As explained above for the quantal gas on a 'loose-packed' or alternating lattice we may suppose that  $J_{\perp}$  is either negative or positive as convenient. Conceptually it is simpler to suppose  $J_{\perp} > 0$  so that the transverse interactions are always ferromagnetic. For real *magnetic* systems, however,  $J_{\perp}$  is normally negative.

<sup>&</sup>lt;sup>‡</sup> The plausibility of this 'spin-flop' transition, predicted many years ago by Néel, can be seen simply by considering the energetics of two classical spins (representing the two sublattices) coupled by  $\mathscr{H} = J_{\parallel} S_1^z S_2^z + J_{\perp}(S_1^x S_2^x + S_1^y S_2^y)$ . This simple picture, and its generalization to finite temperatures (Gorter and van Peski-Tinbergen 1956), suggests that the transition should be first order whereas the final high-field transition to the paramagnetic state should still be continuous (actually 'second order'). Neither of these conclusions should be regarded as really established theoretically or experimentally.

the behaviour of case (iii). Thus the overall phase diagram should have the form shown in figure 10 (a).

To interpret the quantal-gas analogue we note that the 'diagonal' interactions are all repulsive  $(\phi > 0)$ . Let us consider firstly the regular antiferromagnetically ordered phase where the spins point predominantly parallel or antiparallel to the z axis. As in the pure Ising case this must correspond to a 'crystal' with long-range 'diagonal' or density ordering. In the 'spin-flop' phase, however, there is no



Figure 9. Schematic phase diagram (a) of a ferromagnet with dominant transverse coupling  $(J_{\perp} > J_{\parallel} > 0)$  in a parallel field  $H_z$ , and (b) of the corresponding quantal lattice gas. The broken lines indicate where the transition might become first order.

diagonal or crystalline ordering so we must have a true fluid. If we define the transverse spontaneous magnetization by analogy with (2.4.1) and (2.6.4), by letting the transverse field  $\mathbf{H}_{\perp}$  approach zero with fixed direction, we conclude via the equivalence (4.3.2) that the expectation value  $\langle \mathbf{a}_{\mathbf{r}} \rangle \propto \langle \boldsymbol{\psi}(\mathbf{r}) \rangle$  is non-vanishing. By the discussion of §4.1 this is just the criterion for the existence of superfluid or off-diagonal order. Thus the spin-flopped state of an antiferromagnet corresponds to a superfluid. The phase diagram of the model as a quantal-particle system should thus be like figure 10 (b).

If we apply this model to helium 4, the only known atomic or molecular superfluid<sup>†</sup>, we see that the lambda line (figure 8) is analogous to a magnetic-transition line to an ordered (antiferromagnetic) state. Thus we confirm our expectation that the specific heat of helium at constant chemical potential, and hence  $C_n$ , should be

 $<sup>\</sup>dagger$  Our models are not applicable to 'electron-pair superfluids', i.e. superconductors, because they take no account of the dominant role played by the Fermi statistics of electrons as pointed out in § 2.9.

characterized by exponents  $\alpha$  and  $\alpha'$  similar to the magnetic case. The other exponents  $\beta$ ,  $\gamma$ ,  $\gamma'$ ,  $\delta$ ,  $\nu$ ,  $\nu'$  and  $\eta$  can evidently be defined in terms of the effects of the off-diagonal fields and the behaviour of the one-particle density matrix by analogy with the magnetic case, although they remain inaccessible to direct experiment.<sup>†</sup>



Figure 10. Schematic phase diagram for (a) a uniaxial antiferromagnet and (b) the analogous quantal lattice gas (only the low-pressure part of the phase diagram is shown).

It should be mentioned, however, that it is by no means certain that the values of the magnetic exponents on the transition to the spin-flopped state will be the same as in the H = 0 transition to the longitudinal antiferromagnetic state. However, the general physical similarity of the two magnetic states (x, y and z directions being fundamentally the same) does suggest that the values *might* not change. (At any rate, as already observed, the experimental lambda anomaly in helium seems very like that in antiferromagnets in zero field.)

# 5. Phenomenological and mean field theories

In this section we shall review briefly the 'classical'<sup>‡</sup> theories of critical phenomena (van der Waals' theory, Weiss' molecular-field theory, Landau's theory, etc.) and discuss their validity. The invariable classical predictions for the critical exponents are listed in the appropriate column of the fold-out table. They follow most readily from the phenomenological approach which we outline first. Here the

‡ We use 'classical' in its dictionary meaning, namely, 'often referred to, standard'.

<sup>&</sup>lt;sup>†</sup> A magnetic analogy for the superfluid density  $\rho_{s}(T)$ , the critical-point exponent  $\zeta$  of which is observable (§ 2.8), may also be found. Its behaviour, however, is not obviously related to the other magnetic properties.

crucial (and incorrect) assumption is that the relevant thermodynamic potentials may be expanded in Taylor series *about the critical point*. This is the reason that all the predicted exponents are multiples of  $\frac{1}{2}$ . Alternatively, the classical predictions follow from a very large class of more specific but approximate theoretical treatments in which the crucial assumption is that the fluctuating forces acting on a single element of the system may be replaced by an *effectively constant* 'mean field' due to the rest of the system. It is the total or partial neglect of these local fluctuations or correlations (sometimes by way of a 'superposition' or 'decoupling' approximation) that yields the characteristic classical answers.

That the classical predictions are wrong experimentally for most systems is clear by comparison with the experimental evidence surveyed in §2 (see also Heller 1967). Most striking is the discrepancy between the prediction  $\beta = \frac{1}{2}$  and the observed values of  $\beta \simeq \frac{1}{3}$ . Nevertheless, we should still review these approaches because they are theoretically valid in certain limits and because they yield a simple coherent picture often useful in a first discussion of a critical point.

# 5.1. Phenomenological approach for thermodynamic functions

The phenomenological derivation of the equation of state of a fluid or ferromagnet near the critical point is fairly well known (see, for example, Fowler and Guggenheim 1939, Rowlinson 1959, Fisher 1964 b, 1965 a). The essential steps are:

(i) Choose as primary thermodynamic variables T and  $\rho$  or M, respectively, since these latter variables are 'known' to become discontinuous below  $T_c$  as a function of p or H, and consider the appropriate thermodynamic potential (free energy).

(ii) Expand this free energy in powers of  $\rho - \rho_c$  or M at fixed T with coefficients, say,  $a_n(T)$ . This procedure should be generally valid *above*  $T_c$  but is dubious *at* and *below*  $T_c$ .

(iii) Expand the coefficients  $a_n(T)$  in powers of  $T - T_c$  with the assumption that appropriate leading coefficients  $a_{nm}$  vanish to yield an infinite compressibility or susceptibility at  $T_c$ .<sup>†</sup> There is, of course, no justification for this step, especially below  $T_c$  where it leads to 'metastable' and 'unstable' states.

(iv) Appeal to a 'minimization of the free energy' or a corresponding Maxwell 'equal-area' construction to remove the 'metastable' and 'unstable'  $(K_T, \chi_T \leq 0)$ parts of the isotherms below  $T_c$  and so generate the required discontinuous phase transition. This last step is also open to objection since the rigorous convexity and stability results discussed in §3 show that unstable or even metastable isotherms can *never* be found in a rigorous equilibrium calculation. Thus the free-energy minimization and Maxwell procedures cannot really be justified in the form used.<sup>‡</sup>

It is a little less obvious how one should approach a phase transition when none of the thermodynamic variables themselves display discontinuities, as for instance in the case of an antiferromagnet or a superfluid. The crucial first step, following Landau (see, for example, Landau and Lifshitz 1958), is now the introduction of an

<sup>‡</sup> An interesting discussion of the Maxwell rule and its relation to analyticity assumptions has been given by Griffiths (1967).

<sup>†</sup> By assuming that more coefficients  $a_{nm}$  vanish than the minimum needed to 'create' a critical point, other exponent values are predicted by these are generally farther from reality.

'order parameter'. This is supposed to be a (potential) thermodynamic variable which has, however, the 'equilibrium value' zero above the transition but can take two (or sometimes more) equivalent but non-zero equilibrium values in the 'ordered state' below the transition.

Since the procedure is less familiar we illustrate the approach by discussing an antiferromagnet. Evidently we should take the staggered magnetization M' as the order parameter. (However, the *thermodynamic* properties could be discussed even if the true physical nature of the order parameter were unknown.) We may then consider the free energy F(T, H; M'). Now for step (ii) expand F in powers of M' to obtain

$$F(T,H; M') = f_0(T,H) + f_2(T,H) M'^2 + f_4(T,H) M'^4 + \dots$$
(5.1.1)

Odd powers will vanish by symmetry but the first power must be absent in any case by the assumption that

$$M_{\rm eq}'(T,H) \equiv 0 \quad \text{for} \quad T \ge T_{\rm c}(H) \tag{5.1.2}$$

since this equilibrium value is to be found by minimizing F(M'), that is by equating to zero the 'field' conjugate to the order parameter, namely

$$\frac{\partial F}{\partial M'} = H' = 2f_2(T, H) M' + 4f_4(T, H) M'^3 + \dots$$
(5.1.3)

This is, of course, just the staggered magnetic field. To ensure that F(M') has a single minimum  $f_2$  and  $f_4$  should be positive above  $T_c$ . A double minimum and hence a non-zero  $M_{eq}'$  will develop if  $f_2(T,H)$  changes sign which must thus happen at the transition temperature  $T = T_c(H)$ .

Hence at step (iii) on expanding  $f_2$  and  $f_4$  in powers of  $T - T_c(H)$  we find, to leading order,

$$f_2(T,H) = f_{2,1}(H) \{T - T_c(H)\} + \dots$$
(5.1.4)

$$f_4(T,H) = f_{4,0}(H) + \dots$$
(5.1.5)

Substitution in (5.1.3) at  $T = T_c$  already yields the classical 'law'  $\delta = 3$  for the critical isotherm (i.e.  $H' \propto M'^3$ ).

The final minimization of F(M') below  $T_{\rm c}$  then leads, via (5.1.3), to the equilibrium values

$$\{M_{\rm eq}'(T,H)\}^2 = \frac{1}{2} \frac{f_{2,1}}{f_{4,0}} \{T_{\rm c}(H) - T\} + \dots \quad (T \le T_{\rm c}).$$
(5.1.6)

This relation is evidently the classical  $\beta = \frac{1}{2}$  law (compare with (2.6.5)).

The inverse staggered susceptibility follows from

$$\{\chi^{\dagger}(T,H)\}^{-1} = \frac{\partial H'}{\partial M'} = 2f_2(H) + 12f_4(H)M'^2 + \dots$$
(5.1.7)

so that by (5.1.4) and (5.1.6)

~ ~~~

$$\begin{split} \chi^{\dagger} &\simeq \frac{1}{2} f_{2,1}^{-1} \{ T - T_{\rm c}(H) \}^{-1} \quad (T \ge T_{\rm c}) \\ &\simeq \frac{1}{4} f_{2,1}^{-1} \{ T_{\rm c}(H) - T \}^{-1} \quad (T \le T_{\rm c}) \end{split}$$
(5.1.8)

<sup>†</sup> One could equally consider the thermodynamic potential A(T, M; M') but since the field H is usually under direct experimental control our choice is more convenient.

which establish the classical laws  $\gamma = \gamma' = 1$  (compare with (2.6.6)). (It should be noted that the amplitude above  $T_c$  is twice that below.)

To find the specific heat we calculate the free energy by substituting (5.1.4) to (5.1.6) in (5.1.1), which gives

$$F(T,H) = f_0(T,H) \quad (T \ge T_c(H))$$
  
=  $f_0(T,H) - \frac{1}{4} \frac{f_{2,1}^2}{f_{4,0}^2} \{T_c(H) - T\}^2 + \dots \quad (T \le T_c(H)).$  (5.1.9)

A double differentiation with respect to T (assuming  $f_0(T, H)$  is non-singular) shows that  $C_H$  has a simple discontinuity at the critical point with  $C_H(T_c-) > C_H(T_c+)$ corresponding to  $\alpha = \alpha' = 0$ .

By differentiating (5.1.9) with respect to the field one may also calculate the normal magnetic susceptibility  $\chi_T = (\partial M/\partial H)_T$ . As T increases through  $T_c$  this is found to decrease discontinuously like  $C_H$ , but by an amount proportional to  $(\partial T_c/\partial H)^2$ . For small fields one may assume, in the general spirit, that

$$T_{\rm e}(H) = T_{\rm e}^{\ 0} - cH^2 + \dots \tag{5.1.10}$$

The zero-field (initial) susceptibility then merely has a cusp at  $T_c$ , so that the *derivative*  $(\partial \chi_T / \partial T)_{H=0}$  now mirrors the specific heat but with a discontinuity proportional to  $c = -(d^2 T_c / dH^2)$  (see the comment and footnote in §2.6).

The reader may draw the corresponding conclusions for other systems by using the analogies that have been developed.

# 5.2. Phenomenological approach for correlation functions

We illustrate the phenomenological theory of the correlation functions by sketching the original Ornstein–Zernike (1914, 1918, 1926) treatment of critical opalescence in a fluid. Let us recall the basic relation (2.3.5) for the reduced scattering intensity and rewrite it as

$$\hat{\chi}(\mathbf{k}) = 1 + \rho \hat{G}(\mathbf{k}) = \frac{1}{1 - \rho \hat{C}(\mathbf{k})}$$
(5.2.1)

where  $\hat{C}(\mathbf{k})$  is the Fourier transform of the so-called *direct correlation function*  $C(\mathbf{r})$ . The direct correlation function is defined only through (5.2.1) or through the equivalent convolution-integral equation obtained by cross multiplying and Fourier inverting (see, for example, Fisher 1964 b). At low and moderate densities the virial expansion shows that  $C(\mathbf{r})$  is roughly proportional to the Mayer factor

$$f(\mathbf{r}) = \exp\left\{-\frac{\phi(\mathbf{r})}{k_{\rm B}T}\right\} - 1$$
(5.2.2)

and hence is of short range (when the pair potential  $\phi(r)$  is short ranged). Indeed, from the expansion one can see generally that  $C(\mathbf{r})$  is always shorter ranged than  $G(\mathbf{r})$  (Fisher 1964 b).

One now argues that  $C(\mathbf{r})$  should *remain* of short range even at the transition point, although one cannot, any longer, really expect the virial series to converge since  $G(\mathbf{r})$  certainly becomes long ranged and  $K_T$  diverges. Nevertheless if, equivalently, one assumes that  $\hat{C}(\mathbf{k})$  may always be expanded in powers of  $k^2$  and that for small k one may neglect terms of order  $k^4$ , one may rewrite (5.2.1) as

$$\hat{\chi}(\mathbf{k}) \simeq \frac{r_1^{-2}}{\kappa_1^2 + k^2} \tag{5.2.3}$$

where (compare with (2.3.9))

$$r_1^2(T) = c\rho \int r^2 C(\mathbf{r}) d\mathbf{r}$$
 (5.2.4)

and

$$\kappa_1^2(T) = \{1 - \rho \hat{C}(0)\} r_1^{-2}.$$
(5.2.5)

The conclusion (5.1.3) is to be compared with the general result (2.2.2) which should be valid *away* from the transition.

Letting k approach zero and using the fluctuation relation (2.3.7) now indicates that

$$\hat{\chi}(0) \sim \frac{1}{\{\kappa_1(T)\}^2} \sim K_T$$
 (5.2.6)

so that from the exponent definitions (2.2.5), (2.3.10) to (2.3.12) and (2.1.3) one derives the classical relation

$$2\nu = \gamma \tag{5.2.7}$$

and, similarly,  $\gamma' = 2\nu'$  below  $T_c$ . The classical predictions  $\gamma = \gamma' = 1$  then yield  $\nu = \nu' = \frac{1}{2}$ .

From (5.2.6)  $\kappa_1$  vanishes at the critical point so that

$$\hat{\chi}_{\rm c}(\mathbf{k}) \simeq \frac{1}{r_1^2 k^2} \quad (k \to 0)$$
 (5.2.8)

which by the definition (2.2.6) implies  $\eta = 0$ . This result has uncomfortable implications in two dimensions since inversion of (5.2.8) indicates that  $G_{\rm c}(\mathbf{r})$  should vary as  $\ln r$  for large r which is clearly unacceptable (Stillinger and Frisch 1961). This difficulty does not arise for d = 3, where by (2.3.8)  $\eta = 0$  implies  $G_{\rm c}(r) \sim 1/r$ , but none the less it suggests that the conclusion should not be trusted.

Many alternative versions of these arguments have been presented (see Fisher 1964 b). Frequently it is assumed that a local free energy may be constructed which involves terms proportional to the square of the local density gradient (or, generally, of the local order-parameter gradient) (see Fisher 1964 b, Kadanoff *et al.* 1967). This assumption is equivalent to making a Fourier expansion in powers of  $k^2$  and should be satisfactory *away* from the transition. Classically, however, it is supposed to remain true up to and *at* the transition. An interesting and quite different approach based on truncating the hyper-netted integral equation for the correlation functions has been proposed by Green (1960). This avoids the difficulty  $\eta = 0$  for d = 2, but nevertheless leads to results that are not generally correct (Stillinger and Frisch 1961, Fisher 1964 b).

The experimental evidence concerning the non-validity of the Ornstein– Zernike approach is not yet overwhelming, especially if one only retains  $\eta = 0$  and the relation (5.2.7) but allows the possibility  $\gamma, \gamma' \neq 1$ . However, the exact theoretical results for the two-dimensional Ising model and precise numerical estimates for the three-dimensional model (see §§ 6.2 and 8.1) definitely establish that the classical conclusions are generally untenable. Specifically one finds that  $r_1(T)$ , as defined by (5.2.4), diverges at the critical point so that  $C(\mathbf{r})$  also becomes of 'long range' (even though  $\int C(\mathbf{r}) d\mathbf{r}$  necessarily remains finite).

Finally we point out a rather common fallacious argument based on the mean field and phenomenological expressions for the correlation functions which lead to the conclusion that the specific heats should diverge with exponents  $\alpha = \alpha' = \frac{1}{2}$  (see Fisher 1966 b). One merely observes that the internal energy may, in principle, be calculated by multiplying  $G(\mathbf{r})$  (or  $\Gamma(\mathbf{r})$ , etc.) by the appropriate pair interaction potential and integrating. The specific heat should then follow by differentiating with respect to T. The error is that only values of  $G(\mathbf{r})$  for small r contribute to the energy integral (the potentials being short ranged) whereas, at best, the phenomenological expressions are expected to be valid only for *large r*. This obvious point is easily overlooked, however, if the calculations are performed entirely in Fourier space.

# 5.3. Mean field theory

The idea of a mean field (or a 'molecular' field) is most familiar in the study of magnetism where it was first introduced by Pierre Weiss in 1907 (see, for example, Kittel 1956). For this reason we prefer to illustrate the approach by deriving van der Waals' equation of state for a fluid. (For a systematic study of mean field theory in a variety of applications see Brout (1965); for specifically magnetic applications see Smart (1966).)

Let us consider a classical system of particles interacting with a pair potential  $\phi(\mathbf{r})$  which may be decomposed into two parts: (i) a strongly repulsive part  $\phi_a(\mathbf{r}) > 0$ , characterized by a core radius *a*, and (ii) a relatively weak attractive part  $\phi_b(\mathbf{r}) \leq 0$ , of range *b*. By decomposing the total potential energy  $U_N = U_N^{(\alpha)} + U_N^{(b)}$  in a corresponding way, the configurational partition function may be written

$$Q(T,N) = \frac{\int \exp\left(-\beta U_N\right) d\mathbf{R}^N \int \exp\left(-\beta U_N^{(a)}\right) d\mathbf{R}^N}{\int \exp\left(-\beta U_N + \beta U_N^{(b)}\right) d\mathbf{R}^N}$$
(5.3.1)  
$$= \frac{Q_a(T,N)}{\langle \exp\left(\beta U_N^{(b)}\right) \rangle}$$
(5.3.2)

where  $Q_a(T, N)$  is the partition function for a comparison system of particles interacting only with the repulsive potential  $\phi_a(\mathbf{r})$ . (As usual the angular brackets denote the canonical average in the *original* system.) To evaluate  $\langle \exp(\beta U_N^{(b)}) \rangle$ approximately we argue that in most configurations  $U_N^{(b)}$  may be replaced by its mean value, thereby neglecting fluctuations in the total energy. This mean value can be written

$$\langle U_N^{(b)} \rangle = \frac{1}{2} N \int \phi_b(\mathbf{r}) \, \rho_0(\mathbf{r}) \, d\mathbf{r}$$
 (5.3.3)

where  $\rho_0(\mathbf{r}) = \rho g_2(\mathbf{r})$  (see (2.3.2)) represents the average of the fluctuating local density in the neighbourhood of a particle fixed at the origin. If the influence of this particle on its environment is neglected we have simply  $\rho_0(\mathbf{r}) = \rho$  and the potential at **0** is just the average value in the fluid. Using this 'mean field' approximation

yields, say,

$$\langle U_N^{(b)} \rangle \simeq \frac{1}{2} N \rho \int \phi_b(\mathbf{r}) \, d\mathbf{r} = -\frac{1}{2} N \rho \left| \hat{\phi} \right|.$$
 (5.3.4)

From (5.3.2) the free energy per particle is then given approximately by

$$F(T,\rho) = F_a(T,\rho) - \frac{1}{2} |\hat{\phi}| \rho$$
 (5.3.5)

where the subscript a again denotes the properties of the comparison system with only repulsive interactions. The corresponding equation of state is

$$p = p_a(T, \rho) - \frac{1}{2} |\hat{\phi}| \rho^2.$$
(5.3.6)

Of course the calculation of the properties of the comparison system is very difficult even if  $\phi_a(\mathbf{r})$  is assumed to be just an infinite hard-core potential. The general behaviour of  $p_a(T, \rho)$  at low and high densities can, however, be readily seen and is well represented by the expression<sup>†</sup>

$$p_a(T,\rho) \simeq \frac{k_{\rm B} T \rho}{1 - \rho/\rho_{\rm max}} \tag{5.3.7}$$

which is, in fact, exact for a one-dimensional system of hard rods. (One might remark that this part of the problem is trivial for a lattice gas with single-site hard cores, or for a magnetic system.)

With this approximation (5.3.6) becomes precisely the well-known van der Waals equation of state. Below a temperature

$$k_{\rm B}T_{\rm c} = \frac{4}{27}\rho_{\rm max}\left|\hat{\phi}\right| \tag{5.3.8}$$

the isotherms are found to become non-monotonic (and equivalently the free energy ceases to be convex in  $v = 1/\rho$ ). On applying Maxwell's equal-area prescription or minimizing the free energy just as in §5.1, a first-order transition is generated. Of course, as in the phenomenological treatment, the appearance of the 'metastable' and 'unstable' van der Waals 'loops' is really a sign that our approximations for the partition function have broken down. In the absence of other justifications, there are few grounds, especially in the critical region, for trusting the 'repair' afforded by Maxwell's construction.

Without further detailed calculation it is clear from the phenomenological treatment that (barring accidentally vanishing coefficients due to some special property of  $p_a(T, \rho)$ ) all the classical critical behaviour and exponent values will be reproduced by (5.3.6) combined with (5.3.7) or with any other similar approximate (or exact) expression.

## 5.4. Validity of classical theories

There is no way of gauging the validity of the phenomenological approach other than by comparison with exact calculations, since its assumption of a Taylor-series expansion at the critical point is of a purely mathematical rather than of a physical

<sup>&</sup>lt;sup>†</sup> The approximation (5.3.7) overlooks a possible 'melting' transition which, however, can probably only occur at densities well above those relevant in the critical region implied by (5.3.6). Conversely, allowance for this transition leads to a fairly satisfactory description of the triple point of a simple fluid (Longuet-Higgins and Widom 1964).

nature. Conversely, in the mean field approach it is quite clear that the main approximation is the neglect of the local fluctuations and correlations. Indeed, within mean field theory one may go on to estimate the fluctuations, for example by introducing external fields and computing, by the same methods, the incremental free energy associated with the induced density inhomogeneities (see, for example, Kadanoff *et al.* 1967). One then, of course, finds that the fluctuations are very large in the region of the predicted critical point. Thus mean field theory has a self-imposed limitation which implies that it should be accurate only *outside* some 'critical region'.

To estimate the size of this critical region we shall examine the fluctuations in the number of particles within a volume  $V_b$  of radius the interaction range b. It is plausible that if the relative fluctuation

$$\epsilon = \frac{\Delta N}{\langle N \rangle_b} \tag{5.4.1}$$

in the number of particles interacting with some chosen particle is small, the replacement of  $\rho_0(\mathbf{r})$  in (5.3.3) by its mean value  $\rho$  will be accurate. This immediately suggests that when the *range of interaction b* is *large* mean field theory should be more reliable.

With large b in mind we may, for purposes of estimation, use standard fluctuation theory (e.g. Landau and Lifshitz 1958, §111) to calculate  $\Delta N$ . This gives

$$\langle \epsilon^2 \rangle \simeq \frac{k_{\rm B} T K_T}{V_b} = \frac{\rho_{\rm max}}{\rho} \frac{K_T}{K_T^{\rm ideal}} \frac{1}{N_b}$$
(5.4.2)

where

$$N_b = V_b \rho_{\rm max} \tag{5.4.3}$$

is the maximum number of particles that can be accommodated within the interaction volume  $V_b$ . This may be estimated by considering the packing of spheres of radius *a* in a large sphere of radius *b*. One concludes

$$N_b \simeq \left(\frac{\lambda b}{a}\right)^d \tag{5.4.4}$$

where the parameter  $\lambda$  is of order unity (and uniformly bounded for all d; see Rogers (1964)). Now when  $\rho = \rho_c$  mean field theory yields

$$K_T \simeq \frac{K_T^{\text{ideal}} C}{1 - T_c/T} \tag{5.4.5}$$

where C is of order unity. Finally we note that  $\rho_{\rm c}/\rho_{\rm max}$  always has the value  $\frac{1}{3}$  for the continuum van der Waals equation and  $\frac{1}{2}$  for a lattice gas. (The former value is also typical of real fluids.) Combining these estimates indicates that the size of the non-classical critical region is<sup>†</sup>

$$\frac{|T - T_{\rm c}|}{T_{\rm c}} \simeq c \left(\frac{a}{\lambda b}\right)^d \tag{5.4.6}$$

where c is of order unity.

 $\dagger$  A criterion of this sort, although somewhat differently expressed, seems first to have been advanced by Brout (1960).

In the limit  $b/a \to \infty$ , in which the range of the attractive forces becomes infinite, this non-classical region apparently shrinks to zero suggesting that mean field theory becomes exact. We have to note, however, that in order to keep  $T_c$  (and the ground-state energy per particle) finite as  $b \to \infty$  the potential  $\phi_b(\mathbf{r})$  must be 'scaled', say in the form

$$\phi_b(\mathbf{r}) = \left(\frac{a}{b}\right)^d w \frac{r}{b} \tag{5.4.7}$$

so that  $\int_a^{\infty} \phi_b(\mathbf{r}) d\mathbf{r}$  remains constant. Evidently the potential then becomes 'infinitely weak' as well as 'infinitely long ranged'.

While such potentials are clearly unrealistic it is interesting to note that our surmise regarding the limiting validity of mean field theory can be proved rigorously. This was first done by Baker (1961 a, 1962) who considered a one-dimensional Ising spin system in zero field with  $w(x) = e^{-x}$ . Kac *et al.* (1963) analysed explicitly a one-dimensional classical-continuum gas of hard cores at general density but also with an exponential w(x). They showed that van der Waals' equation with Maxwell's rule becomes rigorously correct when the limit  $b \to \infty$  is taken after the thermodynamic limit. Lebowitz and Penrose (1966) discussed a general classical gas in d dimensions and proved under wide conditions on the (constant) potential  $\phi_a(\mathbf{r})$  that the equation of state becomes of the form (5.3.6) together with Maxwell's rule, when the same double limit is taken. (If  $b \to \infty$  before the thermodynamic limit all properties reduce to those of the comparison system a.) Finally Lieb (1966) has extended Lebowitz and Penrose's theorem to quantum-mechanical systems.

It is important to realize that these theorems do not imply that the critical exponents approach their classical values when  $b \rightarrow \infty$ . On the contrary one should rather expect that the exponents, being always defined by the behaviour within the critical, albeit shrinking, region, do not change at all when the range increases, all other parameters remaining fixed. Confirmation of this expectation is provided, to anticipate §8 (see table 11), by explicit numerical studies of the Ising model (Domb and Dalton 1966).

From (5.4.6) we see that the critical region should also shrink to zero if the range b remains finite (but greater than  $a/\lambda$ ) while the dimensionality d becomes infinite. Although the conclusion that the mean field predictions should also become correct as  $d \rightarrow \infty$  is supported by a number of other lines of argument (e.g. Brout 1960) it has not yet been proved rigorously. One convincing piece of evidence we may cite, however, is the formal expansion for the critical temperature of the nearest-neighbour Ising model on the hyper-cubic lattices (of co-ordination number q = 2d) found by Fisher and Gaunt (1964), namely

$$\frac{T_{\rm c}(d)}{T_{\rm c}^{\rm mean \ field}} = \frac{k_{\rm B}T_{\rm c}(d)}{dJ_{\scriptscriptstyle \parallel}} = 1 - (2d)^{-1} - \frac{1}{3}(2d)^{-2} - \frac{4}{3}(2d)^{-3} - 21\frac{34}{45}(2d)^{-4} - 133\frac{14}{15}(2d)^{-5} - \dots$$
(5.4.8)

The expansion apparently has an asymptotic character and if truncated at the smallest term yields quite accurate values of  $T_{\rm e}(d)$  even for d = 2 and 3 (see §§ 6 and 7).

In the case of increasing d it seems very likely that the critical exponents do all approach their classical values. Thus, by methods to be discussed in §7, Fisher and

Gaunt concluded from their own and previous numerical work on the Ising model that<sup>†</sup>

 $\gamma(d) \simeq 1.75 \ (d=2), \quad 1.25 \ (d=3), \quad 1.094 \ (d=4), \quad 1.038 \ (d=5) \quad (5.4.9)$ and

$$\alpha(d) = 0 \quad \text{for} \quad d \ge 4 \tag{5.4.10}$$

(although for the singular part of the specific heat (see §1.4) they estimated  $\alpha_s(4) \simeq -0.17$ ,  $\alpha_s(5) \simeq -0.4$ ).

Despite the insight afforded by the discovery of the validity of the classical theories when d or b approaches infinity it remains true that Nature provides us only with systems of fixed low dimensionality interacting with forces of finite strength and (for the most part) finite range. We thus turn to the more detailed and accurate study of the model systems described in §4.

## 6. Analytic theory of the Ising model

In this section we review the analytic theory of the Ising model in as far as it is relevant to critical-point behaviour. This theory is restricted almost entirely to two-dimensional systems but reveals unequivocally the theoretical shortcomings of the phenomenological and approximate classical approaches. The exact results also point to the type of behaviour to be expected for three-dimensional and other more realistic models and serve as stringent testing grounds for the methods based on exact series expansions which will be described in the following section.

We shall not here discuss the detailed mathematical techniques used to 'solve' the two-dimensional Ising model; in the first place these are still rather elaborate but, secondly, they cast little, if any, light on the origins of the particular types of critical behaviour eventually revealed. For details of the many different mathematical techniques and devices used the reader should consult the reviews by Newell and Montroll (1953), Domb (1960), Dykhne and Rumer (1962), Montroll (1964), and the books by Green and Hurst (1964) and Mattis (1965) as well as the following original papers (and others to be cited below): Kramers and Wannier (1941), Onsager (1944), Kaufman (1949) and Yang (1952) for the algebraic/matrix method; Kac and Ward (1952), Potts and Ward (1955), Sherman (1960) and Burgoyne (1963) for the combinatorial/determinantal approach; Hurst and Green (1960), Green (1962), Kasteleyn (1963), Montroll *et al.* (1963) and Fisher (1966 c) for the Pfaffian/dimer methods; and Schultz *et al.* (1964) and Kadanoff (1966 a) for the fermion-operator approaches.

#### 6.1. Exact thermodynamic results

Unless specified otherwise we shall in this section always have in mind the  $S = \frac{1}{2}$  Ising model with only *nearest-neighbour interactions*.

As is well known the one-dimensional Ising model is easily soluble by a matrix method (Ising 1925, see, for example, Domb 1960) for all H and T. It exhibits no phase transitions except that the point H = T = 0 is non-analytic and may be

<sup>†</sup> It seems not unlikely in view of certain theoretical arguments that  $\gamma(6)$ , and even  $\gamma(5)$ , should already take the values unity. The small excesses  $\gamma - 1$  estimated by Fisher and Gaunt may be beyond the available accuracy for  $d \ge 5$ .

interpreted as a type of critical point (with  $T_c = 0$ ) since, for example, the range of correlation becomes infinite there.

Conversely, the two-dimensional ferromagnetic Ising model exhibits a phase transition in zero field (and *only* in zero field (Yang and Lee 1952 a, b)). The transition point for the square lattice was first located by Kramers and Wannier (1941) who found, in terms of the naturally arising variable<sup>†</sup>

$$v = \tanh\left(\frac{\frac{1}{2}J_{\parallel}}{k_{\rm B}T}\right) = \tanh\left(\frac{J}{k_{\rm B}T}\right)$$
 (6.1.1)

that

$$v_{\rm c} = \sqrt{2 - 1}.\tag{6.1.2}$$

They used a symmetry property of the partition function with respect to high and low temperatures. Onsager showed this reflected the *planarity*<sup>‡</sup> of the square lattice so that the argument cannot be generalized to any three-dimensional lattice (see Wannier 1945).

The first really crucial step was Onsager's (1944) exact calculation of the partition function of the plane square lattice in zero field with two interaction parameters:  $J_x$  for horizontal and  $J_y$  for vertical bonds. From the explicit expression

$$-\frac{F(T)}{k_{\rm B}T} = \frac{1}{2} \int_{-\pi}^{\pi} \frac{d\theta_1}{2\pi} \int_{-\pi}^{\pi} \frac{d\theta_2}{2\pi} \ln\left(\cosh 2K_x \cosh 2K_y - \sinh 2K_x \cos \theta_1 - \sinh 2K_y \cos \theta_2\right)$$
(6.1.3)

for the limiting free energy per spin, where

$$K_x = \frac{J_x}{k_{\rm B}T}, \quad K_y = \frac{J_y}{k_{\rm B}T}$$
 (6.1.4)

it is easily seen that there is a singularity at a critical temperature determined by

$$\sinh\left(\frac{2J_x}{k_{\rm B}T_{\rm c}}\right)\sinh\left(\frac{2J_y}{k_{\rm B}T_{\rm c}}\right) = 1 \tag{6.1.5}$$

which is equivalent to (6.1.2) when  $J_x = J_y = J = \frac{1}{2}J_{\parallel}$ . At this point the argument of the logarithm in (6.1.3) vanishes quadratically with T, whence it follows that, as  $T \rightarrow T_c \pm$ ,

$$F(T) = F_{\rm c} + a(T - T_{\rm c}) + b(T - T_{\rm c})^2 \ln |T - T_{\rm c}| + \dots$$
(6.1.6)

where a and b are constants (depending on  $J_x/J_y$ ). The appearance of the logarithmic factor in the second-order term proves that, contrary to the classical treatments, the zero-field free energy has no Taylor-series expansion about  $T = T_c$ . This conclusion is quite inescapable and it would be unreasonable to expect more complex and realistic models to be simpler in this respect.

† It should be noted that for consistency with the Ising-model literature we write  $\frac{1}{2}J_{\pm} = J$  here and below.

A planar lattice may be drawn in the plane with no crossing bonds (or 'lines'). The analytical significance of planarity is particularly evident in the 'dimer' solution of the Ising model; see Kasteleyn (1963) and Fisher (1966 c.)

Differentiation of (6.1.6) shows that the internal energy varies as

$$U(T) = U_{\rm c} + Ak_{\rm B}(T_{\rm c} - T) \ln \left| 1 - \frac{T}{T_{\rm c}} \right| + \dots \quad (T \to T_{\rm c})$$
(6.1.7)

and so has a vertical tangent at  $T = T_c$ . It also follows that the specific heat exhibits a symmetric logarithmically infinite singularity of the form

$$\frac{C_H(T)}{k_{\rm B}} = A \left| \ln \left| 1 - \frac{T}{T_{\rm c}} \right| - A_1 + O\{ (T - T_{\rm c}) \ln \left| T - T_{\rm c} \right| \}$$
(6.1.8)

so that

 $\alpha = \alpha' = 0 (\log) \quad (\text{Ising } d = 2).$  (6.1.9)

This is in marked contrast to the classical prediction of a finite, discontinuous and, hence, asymmetric anomaly (see figure 11 which indicates as well the erroneous



Figure 11. Exact specific heat of the plane square Ising model (full curve) compared with Bethe's approximation (dotted curve) and the Kramers–Wannier and Kikuchi approximation (broken curve). (After Domb 1960.)

critical temperatures predicted by two moderately sophisticated but approximate theories). The exact result also contrasts with the *asymmetric*, although near-logarithmic, experimental data.

From (6.1.5) one finds that  $k_{\rm B}T_{\rm c}/J_y \rightarrow 0$  when  $J_x/J_y \rightarrow 0$ , although even for the highly anisotropic case  $J_x/J_y = 1/100$  the critical temperature drops only to about half the value for  $J_x = J_y$ . The results (6.1.6) to (6.1.9) remain quite unchanged for all non-zero  $J_x$  and  $J_y$ . However, the 'critical region' in which the higher-order terms are relatively small, shrinks as  $T_{\rm c}$  decreases  $(\Delta T/T_{\rm c} \simeq 1/\{\ln (J_y/J_x)\})$  and, in particular, the specific-heat amplitude A drops fairly rapidly.

Nevertheless, the important theoretical point is that the *nature* of the singularity is *independent* of  $J_x/J_y$  provided that the lattice remains truly two dimensional (i.e. neither  $J_x$  not  $J_y$  vanishes). Precisely the same independence is found when the exact solutions for other lattices are examined. These have been obtained for the following planar lattices (q denotes the co-ordination number): triangular, q = 6(Houtappel 1950, Temperley 1950, Wannier 1950); honeycomb, q = 3 (Houtappel 1950); kagomé, q = 4 (Syozi 1951, Kano and Naya 1954, Naya 1954); various more general lattices (Utiyama 1951, Syozi 1955, Green and Hurst 1964, Vaks *et al.* 1966), including cases where a fraction of the spins are Ising spins with  $S > \frac{1}{2}$  or even more general systems (Fisher 1959). (Kasteleyn (1963) has shown how *any* regular or irregular planar Ising lattice may be 'solved'.)

The critical temperatures and amplitudes for the different lattices vary somewhat (typically by a few per cent) even when expressed in reduced form, as can be seen from table 2 where numerical values are listed for a number of parameters of the standard Ising lattices.<sup>†</sup> (Note in particular that the square and kagomé lattices have *different* critical temperatures although their co-ordination numbers are the same.) The logarithmic nature of the specific heat anomaly, however, is totally insensitive to the lattice structure (provided it remains two dimensional).<sup>‡</sup>

It should be noted that in table 2 the lattice-gas critical ratio satisfies

$$\frac{p_{\rm o}}{\rho_{\rm c} k_{\rm B} T_{\rm c}} = \frac{S_{\rm c}}{k_{\rm B}} - \frac{1}{2} q K_{\rm c} \, 1 - \frac{U_{\rm c}}{U_{\rm 0}}, \quad U_{\rm 0} = -\frac{1}{2} q J. \tag{6.1.10}$$

The antiferromagnetic entropy in the limit  $T \rightarrow 0$  is denoted by  $S_{anti}(0)$ .

Historically the next significant thermodynamic result was the expression

$$M_0(T) = \{1 - (\sinh 2K_x \sinh 2K_y)^{-2}\}^{1/8}$$
(6.1.11)

for the spontaneous magnetization of the plane square lattice (Onsager 1949, Yang 1952, Chang 1952, Montroll *et al.* 1963). From this we immediately have

$$\beta = \frac{1}{8}$$
 (Ising  $d = 2$ ) (6.1.12)

in sharp disagreement with the classical value  $\frac{1}{2}$  (and, as for the specific heats, with experimental observations on three-dimensional systems).

With this result and that for the specific heat we may apply the rigorous inequalities (3.2.1) and (3.3.1) to reach the conclusion

$$\gamma' \ge 1\frac{3}{4}$$
 (Ising  $d = 2$ ) (6.1.13)

and

$$\delta \ge 15$$
 (Ising  $d = 2$ ). (6.1.14)

Theoretical arguments given below show that the equality holds in (6.1.13) and numerical studies described later suggest strongly that (6.1.14) is also 'best possible'. In any event the large deviations from the classical predictions cannot be doubted.

The exact expression for  $M_0$  has been extended to most of the other planar lattices mentioned, in all cases yielding§

$$M_0(T) \simeq B \left( 1 - \frac{T}{T_c} \right)^{\beta}, \quad \beta = \frac{1}{8}.$$
 (6.1.15)

<sup>†</sup> The data for the three-dimensional lattices in this and the following tables are obtained from the series-expansion methods as will be explained in the next section.

 $\ddagger$  This statement does not, as yet, rigorously include lattices with further-neighbour interactions (and hence crossing bonds). Numerical evidence to be reviewed later (§ 8.1), however, suggests that the singularity should again be unchanged, provided the interactions remain of finite range.

§ See Potts (1952), Naya (1954), Fisher (1959), Syozi and Nakano (1955), Syozi and Naya (1960), Green (1962), Stephenson (1964) and Vaks *et al.* (1966). Only the penultimate two references contain full derivations of the result for the triangular lattice from which most of the other results follow by ingenious but straightforward transformations.

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Critical
Table 2.

Lattice	honeycomb	kagomé	square	triangular	diamond	simple cubic	body-centred cubic	face-centred cubic
d	3	4	4	6	4	9	8	12
<b>Critical</b> point								
$T_{c}[a]$	0.5062173	0.5358297	0.5672963	0.6068256	0.67601	0.75172	0.79385	0.8162
$\zeta_{c} = H_{E_{c}} T_{c}$	0.6584788	0-4665661	0.4406868	0.2746531	0.36982	0.22171	0.15746	0.10210
$t_c = t_{anh} K_c$	0.5773503	0.4354206	0.4142136	0.2679492	0.35383	0.21815	0.15617	0.10175
1910	1-7320508	2.296630	2-4142136	3.7320508	2.8262	4-5840	6.4032	9.828
$(-2K_{c})$	0.2679492	0.3933198	0.4142136	0.5773503	0.47729	0.64183	0.72985	0.8153
$-(T_{\rm c}/v_{\rm c})(dv/dT)_{\rm c}$	0.7603459	0-8683772	0-8813735	0.9514269	0-91433	0-96797	0-98366	0-99308
Inergy and specific heat (	see equations ((	5.1.7), (6.1.8),	((0.1.10))					
7.111.	0.7698003	0-7440169	0.7071068	0-666666	0.432	0.3284	0.270	0.245
$U_{L} /k_{\rm b} T_{\rm c} $	0.760346	0.694266	0-623225	0.549306	0.320	0.2184	0.170	0.150
4+	0.478106	0.480062	0.494538	0.499070	0.21	0.221	0.213	0.210
4-	0.478106	0-480062	0-494538	0.499070	0.59	0.51	0.46	0.41
$4^{-}/A^{+}$	1	Ţ	1		2.8	2.3	2.15	1.95
Intropy and pressure (see	equations (6.1.	.10))						
$p_c   p_c  k_{ m R}  T_c$	0.07468	0.08330	0.096644	0.11126	0.1876	0.226	0.252	0.258
Sc/ku	0.26471	0.28052	0.306470	0.33028	0.511	0.560	0-586	0.591
$S_m - S_n / k_B$	0.42844	0.41263	0.386677	0.36287	0.182	0.133	0.107	0.102
$S_{anti}(0)/k_B$	0	0-50183	0	0-32306	0	0	0	0
Magnetization and ferron	nagnetic suscepti	<i>bility</i> (see equa	ntions (6.1.15)	and (8.1.7))				
0	1.264904	1.2	1.222410	1.203270	1.661	1.5703	1.4911	1.4880
+	1.0466	1.0176	0.96272	0.9244		1.0604	0.9929	0.975
L C	0.0281	0.0273	0.0262	0.0248	0.191	0.193	0.193	0.193
$C^{+}/C^{-}$	37-3	37-3	36.8	37.3		5.49	5.14	5.05

values should be mainly confined to the last decimal digit. A dash indicates an inapplicable category while a blank space means the value has not yet been calculated. It should be noted that  $J = \frac{1}{2}J_i$ . It should be noted that in this table and tables 3 and 4 exact values are usually given to five or more places. The errors in the estimated

# The theory of equilibrium critical phenomena

Values for the amplitude B again vary slightly from lattice to lattice as can be seen in table 2.

Onsager (1944) also calculated the interfacial free energy (or 'surface tension') of the square lattice for an interface parallel to the lattice axes. His result has recently been extended to a diagonal interface by techniques that also yield the boundary (or wall) free energy (Ferdinand and Fisher 1967). The interesting critical behaviour of these quantities is beyond the scope of this article although reference should be made to the related conjectures of Widom (1965 a, see also § 9).

# Table 3. Critical parameters of the Ising model: perpendicular and antiferromagnetic susceptibilities

Lattice <sup>+</sup>	h.	sq.	t.	s.c.	b.c.c.
q	3	4	6	6	8
Perpendicular suscepti	<i>bilities</i> (see equat	ion (6.1.16))			
$(qJ/m^2)\chi_{\perp { m c}} \ X_{\perp}$	1·154701 0·4840	1·136951 0·4701715	1.120253		
$T_{ m max}/T_{ m c}$	1.104	1.08872	1.077		
$(qJ/m^2)\chi_{\perp m max}$	1.2126	1.183144	1.15976		
Antiferromagnetic susc	eptibilities (see e	quation (7.2.18))			
$\xi_{\rm c} = (k_{\rm B}T_{\rm c}/m^2) \chi_{\rm c}$	0.1214	0.1570		0.3397	0.3692
$(qJ/m^2)\chi_{\rm c}$	0.2398	0.2768		0.4519	0.4651
$X^+$	$\leq 0.33$	$\lesssim 0.32$		0.11	0.11
$X^-$	$\sim 0.25$	$\sim 0.23$	_	0.30	0.31
$T_{ m max}/T_{ m c}$	1.6877	1.5371		1.0981	1.0653

† h., honeycomb; sq., square; t., triangular; s.c., simple cubic; b.c.c., body-centred cubic.

0.42957

0.41628

The only other bulk thermodynamic property so far calculated generally for planar lattices is the *perpendicular* or transverse susceptibility  $\chi_{\perp}(T)$  in zero field (Fisher 1963 a, Stephenson 1964). Close to  $T_c$  this behaves like the energy, i.e. as

$$\chi_{\perp}(T) = \chi_{\perp e} + \frac{X_{\perp} m^2}{qJ} \left( 1 - \frac{T}{T_e} \right) \ln \left| 1 - \frac{T}{T_e} \right| + \dots$$
(6.1.16)

0.46444

0.47310

where  $\chi_{\perp c}$  and  $X_{\perp}$  are tabulated in table 3. Above  $T_c$  a plot of  $\chi_{\perp}$  passes through a rounded maximum with the parameters listed in table 3. (Classical theory predicts only a sharp finite peak at  $T = T_c$ .)

No exact expressions for the partition function of any two-dimensional lattices in a *finite* magnetic field have been found except for a rather special class of *anti*ferromagnetic 'superexchange' Ising models (Fisher 1960). In these models the magnetic spins 'decorate' the bonds of a normal Ising lattice and are coupled together antiferromagnetically via 'non-magnetic' spins on the lattice nodes which are supposed not to interact with the field. The free energy can be calculated explicitly for all H and T (in terms of the free energy of the underlying planar lattice in zero field) and one finds a phase diagram like figure 6 except that the transition line  $H_t(T)$  remains continuous (i.e. lambda like) right down to T = 0. The specific heat in a field still has the form (6.1.8) and so does the parallel susceptibility  $\chi(H, T)$ . In zero field, however, the antiferromagnetic parallel susceptibility

 $(qJ/m^2)\chi_{\rm max}$ 

behaves like  $\chi_{\perp}$  in the critical region (although it falls to zero rather than to  $\chi_{\perp}(0) = m^2/qJ$  as  $T \rightarrow 0$ ). Theoretical arguments and numerical studies (see later) indicate that this behaviour is most probably also correct for the antiferromagnetic susceptibilities of the standard Ising lattices.

#### 6.2. Exact results for the correlations

The true range of correlation  $\kappa$  of the Ising model can be expressed in terms of the ratio of the eigenvalues of the largest and second-largest modulus of the appropriate transition matrix.<sup>†</sup> From Onsager's (1944) calculation we thus find for the propagation of correlation along the x axis above  $T_c$ 

$$\kappa_x a = \ln \coth\left(\frac{J_x}{k_{\rm B}T}\right) - 2\left(\frac{J_y}{k_{\rm B}T}\right) \quad (T \ge T_{\rm c}). \tag{6.2.1}$$

## Table 4. Critical parameters of the Ising model: correlations<sup>‡</sup>

Lattice§	sq.	t.	s.c.	b.c.c.	f.c.c.
q	4	6	6	8	12
$F^{+}{\simeq}F_1^{+}$	1.762747	1.902854	2.0888	2.2435	2.3024
$f_1^+ \simeq f^+$	0.688	0.74	0.12	0.18	0.23
D	0.703380	0.66865	0.320	0.26	0.25
$\Gamma_{ m c}({f \delta})/D$	1.00530	0.99703	1.026	1.03	0.98
$\hat{D}$	1.07499	1.18100	3.87	4.1	4.3
$(r_1/a)_{\rm e}$	0.57959	0.54962	0.46448	0.44761	0.44027
$(a/r_1)e^{2-\eta}$	2.5974	2.8503	4.4418	4.7733	4.9292
С	0.350	0.311	0.491	0.467	0.457
$\boldsymbol{\phi}_{\mathrm{e}}$	0.02940	0.02940	0.084	0.073	0.065
$(\psi_{\rm c} - 1) \times 10^3$	0.108	0.108	0.20	0.15	0.12

‡ For definitions see equations (6.2.2), (6.2.5)-(6.2.7) and (8.1.14) to (8.1.18)

§ sq., square; t., triangular; s.c., simple cubic; b.c.c., body-centred cubic; f.c.c., face-centred cubic.

From Kaufman's (1949) complete diagonalization of the transition matrix one obtains below  $T_c$  precisely minus twice the expression (6.2.1). Near  $T_c$  we hence find

$$\kappa_x a = F^+ \left(\frac{T}{T_c} - 1\right)^{\nu} \left\{ 1 - \frac{f^+ (T - T_c)}{T_c} + \dots \right\}$$
(6.2.2)

for  $T \ge T_c$ , and a similar expression for  $T \le T_c$ , where

$$\nu = \nu' = 1$$
 (Ising  $d = 2$ ) (6.2.3)

and  $F^{+} = \frac{1}{2}F^{-}$  and  $f^{+}$  are tabulated in table 4. An explicit result is also available for the diagonal-lattice direction (and for the triangular lattice, see Fisher and Burford (1967) and Kadanoff (1966 a)). The behaviour near  $T_c$  is just like (6.2.2) with, moreover, the same amplitude. Indeed it is almost certain that  $\kappa$  becomes quite independent of direction as  $T_c$  is approached (Onsager 1944, Kadanoff 1966 a). The exact values (6.2.3) again disagree with the classical expectation  $\nu = \nu' = \frac{1}{2}$ .

<sup>&</sup>lt;sup>†</sup> This follows from the matrix expressions for the correlation functions (Ashkin and Lamb 1943, Kaufman and Onsager 1949, Domb 1960) but for an explicit derivation see Fisher and Burford (1967).

Kaufman and Onsager (1949) have shown how to calculate the spin-correlation function  $\Gamma(\mathbf{r}, T) = \langle s_0 s_{\mathbf{r}} \rangle$  of the square lattice explicitly in terms of determinants of order r/a (see also Potts and Ward 1955, Montroll *et al.* 1963). Near  $T_c$  the behaviour of  $\Gamma(\mathbf{r}, T)$  for all  $\mathbf{r}$  is just like that of the energy (6.1.7). It should indeed be noted that, quite generally,

$$\Gamma(\mathbf{\delta}, T) = \Gamma(a, 0, T) = \langle s_{\mathbf{0}} s_{\mathbf{\delta}} \rangle = \frac{U(T)}{U(0)}.$$
(6.2.4)

However, the critical values of  $\Gamma(\mathbf{r})$  and the amplitudes of the singular term depend on  $\mathbf{r}$ . (Fisher and Burford (1967) list some other explicit numerical values.) Precisely similar results have been obtained for the correlation functions of the triangular, honeycomb and other lattices (Stephenson 1964, Kano 1966, Vaks *et al.* 1966).

For the square lattice *at* the critical point Onsager (see Kaufman and Onsager 1949, footnote 7, Stephenson 1964) obtained an explicit product formula for the diagonal correlations at arbitrary distance. Analysis of his expression yields

$$\Gamma_{\rm c}(\mathbf{r}) \simeq D\left(\frac{r}{a}\right)^{-1/4} \left\{ 1 - O\left(\frac{a^2}{r^2}\right) \right\} \quad (r \to \infty) \tag{6.2.5}$$

where D is given numerically in table 4 (Fisher 1959, Fisher and Burford 1967). Wu (1966) has found a precisely similar result for the critical decay along an axis; in particular the amplitude D is unchanged, indicating complete cylindrical symmetry. Wu's analysis extends immediately, using Stephenson's (1964) work, to give a similar result for the triangular-lattice correlations along an axis (see also Vaks *et al.* 1966).

Fourier transformation of (6.2.5) yields

$$\hat{\Gamma}_{c}(\mathbf{k}) \simeq \hat{\chi}_{c}(\mathbf{k}) \simeq \frac{\hat{D}}{(ka)^{2-\eta}} \quad (k \to 0)$$
(6.2.6)

where, evidently,

$$\eta = \frac{1}{4}$$
 (Ising  $d = 2$ ) (6.2.7)

in contrast to the classical value  $\eta = 0$  (see (2.2.4), (2.5.2), (5.2.8)). Values of  $\hat{D}$  are given in table 4.

Wu (1966) and Kadanoff (1966 a)<sup>†</sup> have independently examined the decay of correlation *away* from the critical point. For *fixed* T above  $T_c$  they find

$$\Gamma(\mathbf{r}, T) \simeq \frac{(B^+ a^{1/2}) \exp(-\kappa r)}{r^{1/2}} \quad (r \to \infty, T > T_c)$$
(6.2.8)

where the power of r is in agreement with the classical Ornstein-Zernike prediction (2.3.13) for d = 2. This is not surprising since we are now *away* from the critical point and the forces of interaction are of short range. For fixed T below  $T_c$  the result is somewhat different, namely

$$\Gamma(\mathbf{r}, T) \simeq \frac{(B^- a^2) \exp\left(-\kappa r\right)}{r^2} \quad (r \to \infty, T < T_{\rm o}) \tag{6.2.9}$$

<sup>†</sup> Attention should also be drawn to work by Ryazanov (1966), although some of his results seem to be incorrect. Cheng and Wu (1967) have discussed angular dependence of the decay in some detail. McCoy and Wu (1967) have calculated the decay of correlation for an Ising model in the *imaginary* magnetic field  $H = i\pi k_{\rm B}T/2m$ .

where  $\kappa$ , of course, takes the appropriate value for  $T < T_c$ . The appearance of the inverse square of r is not in accordance with classical ideas even though we are again away from the critical point. Indeed this result seems to mean that, for reasons not yet understood, the decay of correlations is affected in a profound way by the existence of long-range order or, equivalently, by the potential or actual coexistence of oppositely magnetized domains.

Stephenson (1966) has similarly investigated the net four-spin correlation function

$$\Gamma_{(4)}(\boldsymbol{\delta}, \mathbf{r}, \mathbf{r} + \boldsymbol{\delta}) = \langle s_{\mathbf{0}} s_{\mathbf{\delta}} s_{\mathbf{r}} s_{\mathbf{r}+\boldsymbol{\delta}} \rangle - \langle s_{\mathbf{0}} s_{\mathbf{\delta}} \rangle \langle s_{\mathbf{r}} s_{\mathbf{r}+\boldsymbol{\delta}} \rangle$$
(6.2.10)

for large **r**, with the results

$$\Gamma_{(4)}(\boldsymbol{\delta}, \mathbf{r}, \mathbf{r} + \boldsymbol{\delta}) \simeq \frac{B_{(4)} a^2 \exp\left(-2\kappa r\right)}{r^2} \quad (r \to \infty, T > T_{\rm o}) \tag{6.2.11}$$

$$\simeq \frac{B_{(4)} a^2 \exp(-\kappa r)}{r^2} \quad (r \to \infty, T < T_c)$$
 (6.2.12)

while at the critical point

$$\Gamma_{(4)c}(\boldsymbol{\delta}, \mathbf{r}, \mathbf{r} + \boldsymbol{\delta}) \simeq \frac{D_{(4)} a^2}{r^2} \quad (r \to \infty, T = T_c)$$
(6.2.13)

where  $D_{(4)} = (2/\pi) B_{(4)}$ . Kadanoff *et al.* (1967) have reported similar calculations by Hecht (1967) has made similar calculations but also finds

$$\Gamma_{(3)}(\boldsymbol{\delta}, \mathbf{r}) = \langle s_0 \, s_{\boldsymbol{\delta}} \, s_{\boldsymbol{r}} \rangle - \langle s_0 \, s_{\boldsymbol{\delta}} \rangle \langle s_{\boldsymbol{r}} \rangle$$
$$\simeq \frac{B_{(3)} \, a^2 \exp\left(-\kappa r\right)}{r^2} \quad (r \to \infty, \, T < T_c). \tag{6.2.14}$$

Above  $T_{\rm e}$  this correlation function must vanish identically in zero field.

# 6.3. Scaling of correlations and relation for $\gamma$ , $\nu$ and $\eta$

Finally the exact correlation calculations have revealed that  $1/\kappa$  is essentially the only important correlation length near  $T_c$ . Specifically Kadanoff (1966 a, b) has justified<sup>†</sup> the result

$$\Gamma(\mathbf{r}, T) \simeq \left(\frac{r}{a}\right)^{-1/4} D^{\pm}(\kappa r)$$
(6.3.1)

for  $T \to T_c \pm , r \to \infty$  but  $\kappa r$  arbitrary, finite, which represents a 'scaling property' of the correlations near  $T_c$ . From (6.2.8) and (6.2.9) we see that

$$D^+(x) \sim \frac{e^{-x}}{x^{1/4}}$$
 and  $D^-(x) \sim \frac{e^{-x}}{x^{7/4}}$  (6.3.2)

as x becomes large. A form such as (6.3.1) was originally surmised by Fisher (1959, 1964 b) and leads, as we shall now show, to an important relation between  $\gamma$ ,  $\nu$  and  $\eta$  and between  $\gamma'$ ,  $\nu'$  and  $\eta$ .

To give the argument in general form applicable to any system exhibiting a critical point (Fisher 1964 b) let us suppose, in accordance with the definitions of  $\eta$ ,

<sup>†</sup> The details of the calculation are, unfortunately, not yet quite as complete as for the other results described. Kadanoff *et al.* (1967) report similar scaling formulae obtained by Hecht (1967) for  $\Gamma_4(\delta, \mathbf{r}, \mathbf{r} + \delta)$  and  $\Gamma_{(3)}(\delta, \mathbf{r})$  corresponding to (6.2.10) to (6.2.14).

that the appropriate pair correlation function satisfies

$$\Gamma(\mathbf{r}, T) \simeq \left(\frac{r}{a}\right)^{-(d-2+\eta)} D^+(\kappa r)$$
(6.3.3)

for  $T \to T_c +$ ,  $r \to \infty$ ,  $\kappa r$  arbitrary, where  $D^+(x \to 0) = D \neq 0$  and  $D^+(x)$  decays sufficiently fast for large x.<sup>†</sup> From the fluctuation relation (2.5.6) (or its appropriate analogue) we have

$$\frac{\chi_T}{\chi_T^{\text{ideal}}} \simeq 1 + \sum_{r \neq 0} \left(\frac{a}{r}\right)^{d-2+\eta} D^+(\kappa r).$$
(6.3.4)

As  $T \to T_c$  and  $\kappa \to 0$  the divergence of  $\chi_T$  comes entirely from large values of r so that the lower limit on the sum may be replaced by some fixed  $R \gg a$ . In the same limit the summand varies increasingly slowly with r and may thus be converted with vanishing relative error to an integral on  $x = \kappa r$  over the interval  $x_0 = \kappa R$  to  $\infty$  which becomes 0 to  $\infty$ . If  $S_d X^{d-1}$  is the surface of a d sphere of radius X we thus obtain

$$\frac{\chi_T}{\chi_T^{\text{ideal}}} \simeq \left(\frac{a^d}{v_0}\right) S_d \left\{ \int_0^\infty D^+(x) \, x^{1-\eta} \, dx \right\} \left(\frac{1}{\kappa a}\right)^{2-\eta}. \tag{6.3.5}$$

The integral is merely a constant so on substituting for the temperature dependence of  $\kappa$  from (2.3.11) or (6.2.2) we have

$$\chi_T \sim (\kappa a)^{-(2-\eta)} \sim \left(\frac{T}{T_c} - 1\right)^{-\nu(2-\eta)} \quad (T \to T_c + ).$$
 (6.3.6)

We conclude immediately that

$$(2-\eta)\nu = \gamma. \tag{6.3.7}$$

The same arguments below  $T_{\rm c}$  clearly yield

$$(2-\eta)\nu' = \gamma'. \tag{6.3.8}$$

These replace the classical relations (5.2.7) of generalized Ornstein–Zernike theory to which they reduce when  $\eta = 0$ .

Using the values (6.2.3) and (6.2.7) for the planar Ising models establishes

$$\gamma = \gamma' = \frac{7}{4} \quad (\text{Ising } d = 2) \tag{6.3.9}$$

which should be compared with (6.1.12).

In the same way it is easy to prove from (6.3.1) that the effective inverse correlation range  $\kappa_1(T)$  defined through the second moment of  $\Gamma(\mathbf{r})$  (equation (2.5.13)) is exactly proportional to  $\kappa(T)$  near  $T_c$  so that  $\nu_1 \equiv \nu$  and  $\nu_1' \equiv \nu'$  as anticipated in §2.3.‡ Similarly the scaling expressions corresponding to (6.2.11) to (6.2.13) (Kadanoff *et al.* 1967) lead via the appropriate fluctuation relation, which expresses the zero-field specific heat as a sum over  $\Gamma_{(4)}$ , to the correct logarithmic divergence (6.1.8). (The difference from the fallacious argument sketched at the end of §5.2 should be noted.)

† Actually we only assume the *finiteness* of  $\chi_T$  for  $T > T_c$  (see (6.3.5)) but may actually expect an exponential decay of D(x).

<sup>‡</sup> We must now assume also that  $D^{\pm}(x)$  vanishes at infinity sufficiently fast to ensure the existence of the second moment.

In summary the exact theory for the two-dimensional Ising model gives the values of  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ,  $\gamma'$ ,  $\nu = \nu_1$ ,  $\nu' = \nu_1'$  and  $\eta$ , and a strong inequality for  $\delta$ . The appropriate values are listed in the fold-out table at the end of the article. In all cases the classical critical-point predictions are found to be incorrect. To obtain any sensible comparison with experiment, however, one must turn to three-dimensional models for which the only really rigorous result is the *existence* of a transition (see Griffiths 1964 b, 1967).

## 7. Use of exact series expansions

In default of exact solutions less rigorous methods must be used to obtain information. 'Single-shot' approximation methods, however suggestive and seemingly accurate, are intrinsically unsatisfactory since they imply no systematic way of estimating the nature or magnitude of the errors. Techniques of successive approximation, on the other hand, enable reliable conclusions to be drawn by extrapolation provided the convergence is (i) regular and (ii) reasonably rapid. One can test for these properties by trying the methods on analogous exactly soluble problems. Of the many approximate methods developed for the Ising and Heisenberg models relatively few lead to systematic successive-approximation schemes and, of those that do, most appear to converge slowly or irregularly and, in particular, non-uniformly in the critical region. By far the most successful schemes of calculation have been based on exact power-series expansions for the free energy. This approach was pioneered by Domb (1949) and has been developed and extended by Domb, Sykes, Fisher and collaborators and by Baker, Rushbrooke and others. It has led to remarkably precise estimates of the critical exponents and amplitudes for both two- and three-dimensional Ising models (see the data already displayed in tables 2 to 4) and has also been applied successfully to the Heisenberg and other model systems. At the same time it has led, by comparison with closely related mathematical problems, to some insight into the underlying combinatoric origins of critical-point behaviour.

By confining attention to these methods we do not mean to dismiss out of hand all other approximation methods. A number of these give a useful degree of physical insight and some of them may well lead to more powerful theoretical developments. At present, however, none seems competitive with the seriesexpansion techniques for discussing the critical behaviour of the simple Ising and Heisenberg models (and indeed many go little further than the straightforward mean field and phenomenological approaches).

The layout of this section is as follows. In the first part we describe briefly the series expansions available and their character. The analysis of the series by the ratio method is described in the second part, while Padé approximants and their applications are discussed in the third part. The numerical results so far obtained for the Ising and Heisenberg models are surveyed in §8.

# 7.1. Derivation of expansions

Given a bounded Hamiltonian such as the general spin Ising-Heisenberg Hamiltonian, a formal high-temperature expansion in powers of 1/T may always be

constructed by expanding the Boltzmann factor  $\exp(-\mathscr{H}/k_{\rm B}T)$  and taking the trace term by term. It is to be anticipated that for sufficiently short-range interactions one will be able to prove rigorously that the resulting series expansion for the free energy,

$$F(T) = \sum_{n=0}^{\infty} f_n (k_{\rm B} T)^{-n}$$
(7.1.1)

converges absolutely for sufficiently high T. Although this has not been accomplished yet, such convergence has been proved for the not dissimilar case of the fugacity and density (or virial) expansions.<sup>†</sup>

We shall not review the extensive mathematical techniques that have been developed to derive such expansions correctly and to high order (as proves essential).<sup>‡</sup> We shall, however, point out some of their significant features. Firstly, because of the assumed pairwise interactions the expansion coefficients can be represented diagrammatically in terms of linear graphs  $\mathscr{G}_v^n$  of n lines and  $v \ (\leq 2n)$  vertices. Specifically the *n*th coefficient in the expansion (7.1.1) of the free energy on a lattice  $\mathscr{L}_N$  of N vertices has the form

$$f_n = \sum_v w(\mathscr{G}_v^n) \, \pi(\mathscr{G}_v^n; \, \mathscr{L}_N) \tag{7.1.2}$$

where the graph weight factor w depends only on the graph  $\mathscr{G}_v^n$  and the general properties of the Hamiltonian (spin, exchange parameters, etc.), while  $\pi(\mathscr{G}_v^n; \mathscr{L}_N)$  is an occurrence factor or 'lattice constant' (Domb and Sykes 1957 a, Domb 1960, Fisher 1965 a, b, c, Sykes et al. 1966) determined by the number of ways of embedding  $\mathscr{G}_v^n$  in the lattice  $\mathscr{L}_N$  according to appropriate rules.

For the general Ising-Heisenberg model one must, in a direct approach, consider graphs with multiple (or repeated) lines, and the calculation of the weights is difficult. For the nearest-neighbour  $S = \frac{1}{2}$  Ising model, however, one can avoid multiple lines by expanding in terms of the variable  $v = \tanh(J/k_{\rm B}T)$  since this 'linearizes' the basic bond Boltzmann factor via the identity

$$\exp\left(Ks_{\mathbf{r}}s_{\mathbf{r}+\boldsymbol{\delta}}\right) \equiv \cosh K\left(1 + vs_{\mathbf{r}}s_{\mathbf{r}+\boldsymbol{\delta}}\right). \tag{7.1.3}$$

The corresponding weights are then just unity for every allowed graph, and one is left only with the *combinatorial problem* of determining the lattice constants.

To illustrate this explicitly we quote the basic expansion for the  $S = \frac{1}{2}$  Ising correlation function  $\Gamma(\mathbf{r})$  in zero field. One finds

$$\Gamma(\mathbf{r}, T) = \sum_{n=1}^{\infty} v^n q_n(\mathbf{r}) \quad (\mathbf{r} \neq 0)$$
(7.1.4)

† Groeneveld (1962), Penrose (1963), Ruelle (1963 b, 1964 a, b), Lebowitz and Penrose (1964), Ginibre (1965).

‡ For a review of the methods used in constructing series expansions see Domb (1960), and, more briefly, Fisher (1965 a) and Domb (1965 b). For some more detailed accounts and recent developments see Sykes (1961), Sykes *et al.* (1965), Sykes *et al.* (1966), Rushbrooke and Wood (1958, 1963), Rushbrooke (1964), Domb and Wood (1964), Baker *et al.* (1964) and Strieb *et al.* (1963). Simplifications for the  $S = \infty$  Heisenberg model are discussed by Stanley and Kaplan (1966 a, b), Wood and Rushbrooke (1966), Joyce and Bowers (1966) and Joyce (1967).

where  $q_n(\mathbf{r}) = q_n(\mathbf{r}; 0)$  is the coefficient of  $N^0$  in

 $q_n(\mathbf{r}; N) =$  number of distinct graphs of *n* lines in a lattice  $\mathscr{L}_N$  $(N > n^d)$  with periodic boundary conditions, in which (i) no more than one line lies on each lattice bond, (ii) an odd number of lines (1, 3, 5, ...) meet at the sites **0** and **r** and (iii) an even number of lines meet at all other lattice sites. (7.1.5)

As illustrated in figure 12 the required graphical configurations consist of a *self-avoiding chain* of l lines from the origin to site  $\mathbf{r}$ , together with one or more 'separated polygons' of n-l lines (which may cross or touch at vertices, although no common lines are allowed).



Figure 12. Typical graphical configuration of a chain and 'polygons' contributing (in high order) to the expansion of  $\Gamma(\mathbf{r}, T)$  in powers of v.

Note by (2.5.6) the susceptibility has an expansion

$$\frac{\chi_T}{\chi_T^{\text{ideal}}} = 1 + \sum_{n=1}^{\infty} a_n v^n, \quad a_n = \sum_{\mathbf{r}} q_n(\mathbf{r})$$
(7.1.6)

in terms of the *total* number of self-avoiding chains and polygons. The known coefficients  $a_n$  for the square and simple cubic lattices are listed in table 5. By (6.2.4) the coefficients of the energy expansion are proportional to  $q_n(\delta)$  and so correspond, on insertion of the 'missing' line from **0** to  $\delta$ , only to closed walks or polygons.

Numerically the coefficient  $q_n(\mathbf{r})$  is dominated by  $C_n(\mathbf{r})$ , the number of *n*-line self-avoiding chains or 'walks'. This can be checked in table 5 where the total number of self-avoiding walks

$$c_n = \sum_{\mathbf{r}} C_n(\mathbf{r}) \tag{7.1.7}$$

is also listed for comparison with  $a_n$ . The numbers  $c_n$  and the distributions  $C_n(\mathbf{r})$  arise in other statistical problems and are particularly relevant to the theory of 'excluded volume' in polymers (see, for example, Flory 1953). As a consequence their properties have been studied extensively by direct enumeration (e.g. Fisher and Sykes 1959, Fisher and Hiley 1961, Martin 1962, Domb *et al.* 1965), by Monte Carlo techniques (extending to n = 800) (e.g. Wall *et al.* 1954, 1955, 1957, Wall and Erpenbeck 1959) and by rigorous analysis (e.g. Hammersley 1957, 1961, Kesten

1963, 1964). One knows, for instance, that the sum (or generating function)

$$\mathscr{C}(\mathbf{r}; w) = \sum_{n=1}^{\infty} w^n C_n(\mathbf{r})$$
(7.1.8)

which is analogous to  $\Gamma(\mathbf{r}, T)$ , converges absolutely up to a 'critical' value  $w = w_c = \lim |c_n|^{-1/n}$ , for which quite close rigorous bounds are available (Fisher and Sykes 1959). Furthermore,

$$C(w) = 1 + \sum_{\mathbf{r}} \mathscr{C}(\mathbf{r}, w) = 1 + \sum_{n=1}^{\infty} c_n w^n$$
(7.1.9)

which corresponds to the susceptibility, diverges at least as sharply as a simple pole but not unboundedly faster when  $w \rightarrow w_e$  (Kesten 1963).

# Table 5. Expansion coefficients $a_n$ for the Ising-model susceptibility $(S = \frac{1}{2})$ and the corresponding number $c_n$ of self-avoiding walks

	Square	e lattice	Simple cubic lattice		
n	$a_n$	$c_n$	$a_n$	$c_n$	
1	4	4	6	6	
2	12	12	30	30	
3	36	36	150	150	
4	100	100	726	726	
5	276	284	3510	3534	
6	740	780	16710	16926	
7	1972	2172	79494	81390	
8	5172	5916	375174	387966	
9	13492	16268	1769686	1853886	
10	34876	44100	8306862	8809878	
11	89764	120292	38975286	41934150	
12	229628	324932		198842742	
13	585508	881500		943974510	
14	1486308	2374444		4468911678	
15	3763460	6416596		21175146054	
16	9497380	17245332		100117875366	

Results taken from Sykes and Fisher (1962) and Sykes (1961, 1963).

The Ising model evidently differs from this excluded-volume problem only by the presence of the separated polygons. The consequent close analogies between the underlying combinatorics gives one some insight into the 'causes' of the critical behaviour and, for example, its dependence on dimensionality, the excluded volume being relatively much smaller for higher d. Equally the self-avoiding walk data provide a further testing ground for extrapolation methods.

In addition to the high-temperature expansions of the free energy one may also derive *high-field* expansions in powers of the variable

$$y = \exp\left(\frac{-2mH_z}{k_{\rm B}T}\right) \tag{7.1.10}$$

which enters on 'overturning' a spin from the fully aligned state. These expansions

have the character of Mayer activity expansions (indeed by (4.2.8) the variable y is proportional to the activity z of the corresponding lattice gas). Thus convergence is assured for sufficiently small y by extension of the continuum proofs of Ruelle (1963 b), Penrose (1963) and Ginibre (1965).

For the Ising model the corresponding coefficients  $B_l(T)$  are simply polynomials of degree  $q^l$  in the variable

$$x = \exp\left(\frac{-2J}{k_{\rm B}T}\right).\tag{7.1.11}$$

For  $S = \frac{1}{2}$  they have been calculated by Sykes *et al.* (1965) up to l = 13 for the honeycomb, square and diamond lattices, and up to l = 11, 9, 8 and 6 for the simple cubic, body-centred cubic, triangular and face-centred cubic lattices respectively. For ferromagnetic (but not *anti*ferromagnetic) interactions one may set y = 1 (i.e.  $H_z = 0$ ) and rearrange to obtain a zero-field *low-temperature* expansion in powers of x. Convergence may justifiably be assumed for sufficiently small T although it has not yet been proved (except, of course, for the free energy and spontaneous magnetization of the planar Ising models). As an example of these series the spontaneous magnetization of the face-centred cubic lattice is given by

$$\begin{split} M_0(T) &= 1 - 2x^{12} - 24x^{22} + 26x^{24} + 0 + 0 - 48x^{30} - 252x^{32} + 720x^{34} - 438x^{36} \\ &\quad - 192x^{38} - 984x^{40} - 1008x^{42} + 12\ 924x^{44} - 19\ 536x^{46} + 3062x^{48} - 8280x^{50} \\ &\quad + 26\ 694x^{52} + 153\ 536x^{54} - 507\ 948x^{56} + 406\ 056x^{58} - 79\ 532x^{60} \\ &\quad + 729\ 912x^{62} + 631\ 608x^{64} - 9\ 279\ 376x^{66} + \dots \end{split}$$

For the Heisenberg model, on the other hand, the  $B_l(T)$  have a complicated functional form and they have not been evaluated explicitly for any  $l \ge 3$  (Dyson 1956, Katsura 1965, Wortis 1965). Furthermore, in the isotropic case one cannot obtain the low-temperature zero-field behaviour (spin-wave expansion) by a simple rearrangement. Indeed it is likely that the spin-wave expansion is only asymptotic and contains no information on the critical-point behaviour (Dyson 1956).

# 7.2. Ratio method

The radius of convergence  $r_0$  of a power series

$$F(z) = \sum_{n=0}^{\infty} a_n z^n$$
 (7.2.1)

is determined by the singularity (non-analytic point)  $z_0$  of F(z) which lies nearest to the origin in the complex z plane; specifically

$$r_0 = |z_0| = \lim_{n \to \infty} |a_n|^{-1/n}.$$
(7.2.2)

(There may, of course, be a number of singularities of equal modulus.) Generally the 'physical domain' of z will be the positive real axis and we may then divide series expansions into two classes:

(i) The dominant or strongest singularity on the circle of convergence lies on the positive real axis at  $z = z_c = r_0$ ; this will, in general, be identified as the critical point.

(ii) The point  $z = r_0$  on the real positive axis is non-singular or is dominated by other singularities on the circle of convergence. (The dominant singularity  $z_0 = r_0 \exp(i\theta_0)$  has the most negative exponent  $\lambda_s$  in the sense of (1.4.7) with  $x \to 0 +$  corresponding to  $r = |z| \to r_0 -$  with  $\arg(z) = \theta_0$ .)

If the coefficients  $a_n$  are all positive, as they seem to be for the high-temperature susceptibility expansions (see table 5), the function must belong to class (i). For this class of function the asymptotic behaviour of the coefficients  $a_n$  as  $n \to \infty$ determines directly the nature (and position) of the critical-point singularity. For class (ii) functions, which we shall consider later, the leading asymptotic behaviour describes only non-physical singularities. This seems to be the situation for (7.1.2), the expansion of  $M_0(T)$  for the face-centred cubic lattice, and for most other lowtemperature expansions in three dimensions.

To demonstrate the connection between the asymptotic behaviour of the coefficients and the singularity at  $z_c$  suppose<sup>†</sup>

$$a_n \simeq A \binom{g+n}{n} \mu^n \simeq \frac{A n^g \mu^n}{\Gamma(g+1)} \quad (n \to \infty)$$
(7.2.3)

where  $\Gamma(x)$  is the gamma function. This, at first sight arbitrary, assumption is actually surprisingly general since by Appell's comparison theorem (see Dienes 1957) we can conclude for g > -1 and real z that

$$F(z) = A(1 - \mu z)^{-(g+1)} \{1 + o(1 - \mu z)\}$$
  

$$z \to z_{c} - = \left(\frac{1}{\mu}\right) - .$$
(7.2.4)

as

In other words, the parameter g determines directly the exponent of divergence at the singularity  $z_e = 1/\mu$ .

The converse problem of determining the complete asymptotic form of  $a_n$  given the singularities of F(z) is, in full generality, rather subtle (see Dienes 1957, chap. XIV). However, one can see that more distant singularities  $z_j$  contribute to the expression for  $a_n$  factors like  $1 + O\{(z_c/z_j)^n\}$  which become negligible exponentially fast. However, other (weaker) singularities on the circle of convergence lead to more slowly decaying oscillating factors typically of the form  $1 + Bn^{-h} \exp(\pm in\theta)$ with h > 0. Conversely (7.2.4) remains valid for the singular part of F(z) even when  $g \leq -1$ . (For g = -1, -2, -3, ... a factor  $\ln(1 - \mu z)$  arises.)

Given the practical problem of estimating the critical point  $z_e = 1/\mu$  and its exponent, say,  $\gamma = 1 + g$ , it is natural, as first stressed by Domb and Sykes (1957 b), to consider the ratios

$$\mu_n = \frac{a_n}{a_{n-1}}.$$
(7.2.5)

From (7.2.3) we expect

$$\mu_n = \mu \left\{ 1 + \frac{g}{n} + O\left(\frac{1}{n^2}\right) \right\} \quad (n \to \infty)$$
(7.2.6)

so that the ratios should vary *linearly* with 1/n. Figure 13 shows a plot of  $\mu_n$  against 1/n for the susceptibility expansions of the triangular and face-centred

† The notation  $a_n \simeq p_n$  means  $\lim_{n \to \infty} (a_n/p_n) = 1$ .

cubic Ising lattices. Even for small n the behaviour is quite linear and, assuming this continues to large n, one may estimate the limiting ratio  $\mu$ , and hence the 'critical point', by linear extrapolation to 1/n = 0. This is conveniently effected by calculating the sequences of estimates<sup>†</sup>

$$\mu_n' = \frac{1}{2} \{ (n+\epsilon) \,\mu_n - (n+\epsilon-2) \,\mu_{n-2} \} \tag{7.2.7}$$

where choice of different values of the (small) 'shift'  $\epsilon$  gives a range of sequences and allows for the effects of the higher order,  $1/n^2$ , in terms in (7.2.6).



Figure 13. Successive ratios of the coefficients  $a_n$  of the susceptibility expansions of the triangular (A) and face-centred cubic (B) lattices.

From the twelve expansion coefficients available for the triangular lattice we find the sequences

$$\mu_n'(\epsilon = 0) = 3.753, 3.741, 3.740, 3.7395, 3.7381, 3.7369, \dots$$
$$\mu_n'(\epsilon = \frac{1}{2}) = 3.716, 3.714, 3.719, 3.7228, 3.7245, 3.7257, \dots$$

From these one would probably estimate, say,  $\mu = 1/v_c = 3.731 \pm 0.002$ , where the uncertainty indicates the *apparent* consistency of the procedure. (Note the last few mean values of the two sequences.) This result may be checked against the exact

<sup>†</sup> Alternate ratios, rather than successive ratios, are used since they often lead to somewhat smoother sequences. In particular they are needed for 'loose-packed' lattices of alternating structure because of a regular oscillation of the ratios (see figure 14). value  $1/v_c = 2 + \sqrt{3} = 3.7320...$  (e.g. Houtappel 1950). Evidently the estimate is correct to within 3 parts in  $10^4$  and, furthermore, the anticipated error is of the correct magnitude.

The same procedure may be tried on the self-avoiding walks  $c_n$  as shown in figure 14 for the square lattice (table 5). Apart from the regular alternation (characteristic of 'loose-packed' lattices and indicative of another, 'antiferro-magnetic' singularity of C(z) on the circle of convergence) the variation of  $\mu_n$  is



Figure 14. Ratios  $\mu_n = c_n/c_{n-1}$  for walks on the square lattice illustrating similarity to behaviour of susceptibility coefficients: A, with only reversals and squares disallowed (analogous to some classical approximations); B, with no self-intersections (standard self-avoiding walks); C, with no self-intersections or nearest-neighbour contacts. (From Fisher and Hiley 1961.)

again quite linear. Estimation of the limiting ratio from eighteen terms leads to  $\mu = \lim |c_n|^{1/n} \simeq 2.6390$  (Hiley and Sykes 1961). This in turn can be checked against Monte Carlo studies by Wall and Erpenbeck (1959) who sampled walks with up to  $n \simeq 800$  steps and found  $\mu = 2.6395 \pm 0.0015$ . The differences are again only a couple of parts in 10<sup>4</sup> which suggests that the observed linearity holds at least up to *n* of the order of a thousand.

With this validation of the procedure (similar results are found for all planar Ising lattices) one feels confident in applying the method to the three-dimensional lattices where, if anything, convergence to limiting asymptotic behaviour seems faster. Thus from the analysis of the simple cubic susceptibility series presented in table 6 one concludes (see also the refined methods described below)

$$1/v_{\rm e} = 4.5840 \pm 0.0015. \tag{7.2.8}$$

Corresponding estimates of the critical temperature for this and other lattices are listed in table 2.

# Table 6. Estimation of the critical temperature of the simple cubic Ising model from the susceptibility series<sup>†</sup>

n	$\mu_n' (\epsilon = 0)$	$\frac{1}{2}(\mu_n' + \mu_{n-1}')$	$\mu_n^* (g' = 0.250)$	$\frac{1}{2}(\mu_n^* + \mu_{n-1}^*)$
6	4.6021	4.5944	4.5703	4.5874
7	4.5637	4.5829	4.5932	4.5817
8	4.5961	4.5799	4.5765	4.5849
9	4.5759	4.5860	4.5895	4.5830
10	4.5918	4.5838	4.5795	4.5845
11	4.5793	4.5855	4.5877	4.5836
estimate		$\mu = 1/v_{ m c} =$	$4.5840 \pm 0.0015$	

† See equations (7.2.7) and (7.2.12).

Given the exact value of  $\mu$  or a good estimate of  $\mu'$  one may estimate the slope of the 1/n plot, and hence the critical exponent, from the sequences

$$g_n = \gamma_n - 1 = (n + \epsilon) \left(\frac{\mu_n}{\mu'} - 1\right)$$
(7.2.9)

where, as before, the selection of a few values of  $\epsilon$  reveals the trends more reliably.

# Table 7. Estimation of the exponent $\gamma$ for the square and simple cubic lattices<sup>†</sup>

Square				Simple cubic		
n	$\gamma_n \left(\epsilon = \frac{1}{2}\right)$	$\overline{\gamma}_n$	n	$\gamma_n (\epsilon = 0)$	$ar{\gamma}_n$	
9	1.7652	1.7496	5	1.2735	1.2484	
10	1.7425	1.7539	6	1.2313	1.2524	
11	1.7602	1.7514	7	1.2646	1.2480	
12	1.7452	1.7527	8	1.2365	1.2506	
13	1.7583	1.7517	9	1.2611	1.2488	
14	1.7464	1.7523	10	1.2399	1.2505	
15	1.7568	1.7516	11	1.2590	1.2495	
16	1.7475	1.7521				

† See equations (7.2.9) and (7.2.10).

Table 7 lists the corresponding estimates of  $\gamma$  for the square lattice using  $\epsilon = \frac{1}{2}$  and also the successive means

$$\bar{\gamma}_n = 1 + \frac{1}{2}(g_n + g_{n-1}) \tag{7.2.10}$$

which converge even more rapidly. From this evidence one would estimate, say,  $\gamma = 1.751 \pm 0.003$  which corresponds closely with the exact result  $\gamma = \frac{7}{4}$  found in §6.3.

In table 7 the same method is also applied to the simple cubic lattice using the estimate (7.2.8). The means  $\bar{\gamma}_n$  suggest strongly that  $\gamma = 1.250 \pm 0.001$ , but allowance for the uncertainties in the critical point increases the error limits here to about  $\pm 0.005$ . The behaviour of the estimates for the body-centred cubic, face-centred cubic and diamond lattices is equally regular and numerically closely

similar (Domb and Sykes 1957 b, 1961, Essam and Sykes 1963). One is tempted to conjecture that the *exact* value for the three-dimensional Ising model is simply

$$\gamma = 1\frac{1}{4}$$
 (Ising  $d = 3$ ). (7.2.11)

Even if this result is not exact it appears to be accurate to within  $\frac{1}{2}$ % and certainly provides an excellent representation of the form of the susceptibility coefficients.

An estimate g' of the slope can, even if approximate, be used to construct a useful alternative sequence of critical-point estimates, namely

$$\mu_n^* = \frac{n\mu_n}{n+g'} \simeq \mu \left\{ 1 + O\left(\frac{1}{n^2}\right) \right\}$$
(7.2.12)

which is often rather regular (Domb and Sykes 1961). Similarly one may estimate the amplitude A of the singularity (assuming this exists, i.e. that there is no confluent weaker, but *diverging*, singularity such as a factor  $\ln(1-\mu z)$ ) from

$$A_n = \frac{a_n \mathbf{\Gamma}(1+g)}{n^g \mu^n} \quad \text{or} \quad A_n^* = a_n / {\binom{g+n}{n}} \mu^n.$$
 (7.2.13)

Finally, in terms of the first N 'known' coefficients, one may evaluate the expansion approximately by writing

$$F(z) = \sum_{n=0}^{N} a_n z^n + R_N(z)$$
 (7.2.14)

with

$$R_{N}(z) \simeq \frac{A}{(1-\mu z)^{1+g}} - A \sum_{n=0}^{N} {\binom{g+n}{n}} (\mu z)^{n}.$$
(7.2.15)

Of course one should only expect this expression for F(z) to be accurate when z is on or near the positive real axis and  $|z| \leq z_c = 1/\mu$ .

In certain cases, however, when g > -1, it has proved possible to 'divide out' the dominant singularity of F(z) by writing

$$G(z) = \sum_{n=0}^{\infty} b_n z^n = F(z) (1 - \mu z)^{1+g}$$
(7.2.16)

or

$$H(z) = \sum_{n=0}^{\infty} h_n z^n = \ln\left(\sum_{n=0}^{\infty} a_n z^n\right) - (1+g) \sum_{n=1}^{\infty} \frac{(\mu z)^n}{n}$$
(7.2.17)

and to analyse afresh the resulting coefficients  $b_n$  or  $h_n$ . Thus Sykes and Fisher (1962) found for the susceptibility expansions of the honeycomb, square, simple cubic and body-centred cubic Ising lattices that the coefficients  $h_n$  alternated regularly in sign, indicating that the dominant singularity was now on the *negative* v axis at the *antiferromagnetic* critical point  $v_c = -|v_c|$ . On analysing the asymptotic forms they concluded that

$$\chi_{\text{anti}}(T) \simeq \frac{m^2}{k_{\text{B}}T} \left\{ \xi_{\text{c}} + X^{\pm} \left( 1 - \frac{v}{v_{\text{c}}} \right) \left| \ln \left| 1 - \frac{v}{v_{\text{c}}} \right| \right\} + \dots \right\}$$
(7.2.18)

as  $|v| \rightarrow |v_c| \mp$ . The parameters  $\xi_c$ ,  $X^+$  and  $X^-$  are given in table 3. This behaviour is the same as that found rigorously in two dimensions for the superexchange model and for  $\chi_{\perp}$  (see §6.2). It has also been confirmed by an independent theoretical argument based on the fluctuation relation and the exact behaviour of the correlation
functions (Fisher 1959, 1962). In three dimensions, however, it is possible that the true singularity is somewhat sharper than  $(1-x)\ln(1-x)$  although this will have little effect numerically.

We defer further discussion of the applications of the ratio method until we have described the Padé approximant technique which is also applicable to expansions of class (ii) where the critical singularity does not dominate. Some general remarks on the ratio method should, however, be made here.

Firstly, it is clear that the use of sufficiently large values of n renders the ratio method quite insensitive to transformations of the series coefficients such as induced by  $F(z) \rightarrow kz^{j}F(z) + l(z)$ , where k is a constant, j is a small positive or negative integer and l(z) is a low-order polynomial. However, other singularities of F(z)very close to z<sub>o</sub> or *confluent* non-algebraic diverging singularities, such as logarithmic factors, may slow convergence or lead to misleadingly high initial estimates of the exponent. Thus one should not automatically expect the very smooth behaviour found for the susceptibility series. In particular, weak singularities like logarithmic divergencies  $(g \simeq -1)$ , which characterize specific heat and similar 'polygon-only' series, generally yield more slowly convergent and less regular sequences of estimates, since the coefficients are numerically smaller and the residual singularities are relatively stronger. Nevertheless, once the graphical configurations contributing to the coefficients are sufficiently numerous to 'sample' the lattice structure fairly extensively (which for lattices with simple structure usually means n > 10-15) most class (i) expansions have been found to settle down and the ratio method then yields increasingly reliable information on the critical singularity.

## 7.3. Padé approximants

The ratio method is clearly useless for a series of class (ii) like (7.1.2) in which both the magnitudes and signs of the coefficients are quite irregular. Baker (1961 b), however, showed that Padé approximants could be successfully applied to *analytically continue* such expansions beyond the circle of convergence, determined by complex or negative non-physical singularities, and up to the physical (criticalpoint) singularity on the real axis. An interesting, but less successful, precursor of the Padé approximant technique is Park's (1956) method (see Essam and Fisher 1963). One may also mention at this point the recently proposed scheme of Alexanian and Wortman (1966) which may prove useful in some circumstances.

An [L, M] Padé approximant<sup>†</sup> is a ratio of two polynomials of degree L and M,

$$[L, M] = \frac{P_L(z)}{Q_M(z)} = \frac{p_0 + p_1 z + \dots + p_L z^L}{1 + q_1 z + \dots + q_M z^M}$$
(7.3.1)

in which the L+M+1 coefficients  $p_0, p_1, ..., p_L, q_1, ..., q_M$  are chosen so that the coefficients of  $a_n(L, M)$  in the expansion of [L, M] in powers of z agree with the coefficients  $a_0, a_1, a_2, ...$  of F(z) up to order L+M=N, i.e. so that

$$F(z) = [L, M] + O(z^{N+1}) \quad (L+M=N).$$
(7.3.2)

To calculate the  $p_i$  and  $q_j$  explicitly from the  $a_n$  one simply equates coefficients of

<sup> $\dagger$ </sup> Most authors write [M, L] where M is the degree of the denominator and L of the numerator but we prefer to adhere to normal alphabetical conventions.

 $z^m$  in (7.3.2), solves the resulting set of M linear equations<sup>†</sup> for  $q_1$  to  $q_M$  and substitutes into the explicit linear relation for  $p_0$  to  $p_L$ . It may be mentioned that Padé approximants are equivalent to a certain class of continued fractions from which one finds an alternative iterative method for computing the approximants [M+l, M], l = 1, 2, 3, ... (Wall 1948).

Whereas the domain and nature of convergence of power series are well understood rigorous knowledge of the convergence of Padé approximants to the function F(z) is not complete. Normally the domain of convergence is much larger than the circle of convergence of the corresponding power series. In particular if F(z) has m poles within its circle of meromorphy<sup>‡</sup> the approximants [L, M] with  $M \ge m$  converge uniformly inside the circle, as  $L \to \infty$  except near the poles. More generally it seems to be true that at least a sub-sequence of the diagonal [M, M], or near-diagonal [M+l, M] approximants converge to the function F(z) everywhere in the complex plane as  $M \to \infty$ , except at the singularities of F(z) and on certain cuts needed to make F(z) single valued§ (see Baker *et al.* 1961, Chisholm 1966, and the review by Baker 1965). These cuts are generated by the approximants and their location cannot always be predicted.

To illustrate the power of the diagonal approximants we note that their convergence is invariant under the Euler transformation

$$z = \frac{bw}{1 + cw} \tag{7.3.3}$$

which is often used to hasten power-series convergence. Furthermore, when F(z) is given by a series of Stieltjes (Wall 1948), i.e. can be written formally as

$$F(z) = \sum_{n=0}^{\infty} a_n z^n = \int_0^{\infty} \frac{d\phi(u)}{1+uz}$$
(7.3.4)

where  $\phi(u)$  is monotonic non-decreasing, the [M, M] and [M-1, M] approximants form upper and lower bounds to F(z) for real positive z. Increasing M improves the bounds, which thus converge monotonically. Baker (1964, 1965) has shown how a function, whose real part has a known lower bound in some region of the complex plane and whose imaginary part satisfies a certain condition, can always be converted into a series of Stieltjes. Unfortunately this type of information is seldom available and it may be dangerous to assume it without good evidence.

As a practical matter convergence of Padé approximants is extremely rapid inside the circle of meromorphy but slow near branch cuts, especially when the discontinuity across the cut is not small. (The Padé approximants simulate the discontinuity by a linear sequence of alternating poles and zeros.) Furthermore, the convergence is frequently somewhat irregular, and increasing the order of the approximants may lead to the improvement of the approximation near some distant singularity at the cost of some loss of accuracy closer to the origin (unlike a

<sup>†</sup> If the determinant vanishes an approximant of the order sought does not exist. In practice the determinant is often rather small and precautions may be needed to solve the resulting 'ill-conditioned' equations with sufficient accuracy.

 $\ddagger$  The circle of meromorphy is the largest circle containing only poles, or multiple poles, of F(z).

§ Convergence is, of course, to be expected only inside any natural boundaries of F(z).

power series). Similarly 'tears', i.e. spurious poles with small but non-zero residues, may suddenly appear in approximants of high order in a region near the origin where F(z) is regular and 'nearby' approximants are convergent and well behaved. The reason for this and similar phenomena is not yet understood. Despite these drawbacks the Padé approximants are of great utility as we shall now illustrate.

# Table 8. Estimation of critical points and susceptibility exponents from the poles and residues of the [M, M] Padé approximants to the high-temperature susceptibility series

Square	e		Simple cubic		
$(v_{\rm c})_{\rm est}$	$\gamma_{\mathrm{est}}$	M	$(v_{\rm c})_{\rm est}$	$\gamma_{\mathrm{est}}$	
0.4093	1.626	2	0.2151	1.205	
0.4164	1.797	3	0.2189	1.281	
0.4121	1.682	4	0.21815	1.2505	
0.41412	1.746	5	0.21818	1.2518	
0.4142106	1.7496				
0.4142135	1.7500	ratio estimates	0.21815	1.250	
	Squart $(v_c)_{est}$ 0.4093 0.4164 0.4121 0.41412 0.4142106 0.4142135	Square $(v_c)_{est}$ $\gamma_{est}$ $0.4093$ $1.626$ $0.4164$ $1.797$ $0.4121$ $1.682$ $0.41412$ $1.746$ $0.4142106$ $1.7496$ $0.4142135$ $1.7500$	Square $(v_c)_{est}$ $\gamma_{est}$ $M$ $0.4093$ $1.626$ $2$ $0.4164$ $1.797$ $3$ $0.4121$ $1.682$ $4$ $0.41412$ $1.746$ $5$ $0.4142106$ $1.7496$ $7atio$ $0.4142135$ $1.7500$ $ratio$ estimates	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

After Baker (1961 b).

With a critical point in mind, let us firstly suppose, essentially as before, that the function F has an algebraic branch point at  $z = z_c$  with

$$F(z) = (z_{\rm e} - z)^{-\gamma} z_{\rm e}^{\gamma} G(z)$$
(7.3.5)

where G(z) is regular at  $z = z_c$ . Then the logarithmic derivative

$$D(z) = \sum_{n=0}^{\infty} d_n z^n = \frac{d}{dz} \ln F(z)$$
$$= \frac{(-\gamma)}{z - z_c} + \frac{d}{dz} \ln G(z)$$
(7.3.6)

has only a simple pole at  $z = z_c$  so that the Padé approximants for D(z) should converge much more rapidly than for F(z). Convergence will still be good if G(z) has some confluent residual singularity at  $z = z_c$  provided  $\gamma$  is not too small in relation to the exponent of the residual singularity. For a logarithmic or near-logarithmic singularity, however, this device breaks down since the residual singularity is normally of comparable (even if only moderate) strength. In favourable cases, however, we may estimate  $z_c$  by calculating the appropriate poles of the approximants to D(z). Furthermore, the corresponding residues will provide estimates for the exponent  $\gamma$ .

Table 8 illustrates the application of this procedure to the high-temperature susceptibility series of the square and simple cubic Ising lattices. Using fifteen terms the close agreement of the last few estimates with the exact critical point of the square lattice is quite amazing. The estimates of  $\gamma$  are also excellent. In three dimensions, with only eleven terms, convergence appears to be equally rapid. Agreement with the ratio estimates is well within the expected errors and the

conclusion  $\gamma = 1\frac{1}{4}$  is confirmed closely. Results for the body-centred cubic and face-centred cubic lattices are quite comparable.

Given an exact value or good estimate of  $z_c$  a better method of estimating the exponent should be to *evaluate* at  $z = z_c$  Padé approximants to the series for<sup>†</sup>

$$\gamma^{*}(z) = (z - z_{\rm c}) \frac{d}{dz} \ln F(z) = \gamma + o(z - z_{\rm c}) \quad (z \to z_{\rm c} - ).$$
(7.3.7)

Again this method should work well if any residual confluent singularities are weak, but the behaviour of  $\gamma^*(z)$  for  $z < z_c$  can still yield useful information even when the residual singularities are not negligible.

For the square lattice the last four estimates obtained using this procedure are  $\gamma \simeq 1.728$ , 1.7516, 1.7499, 1.7498, while for the honeycomb, where twenty-four terms are available, the last four estimates are  $\gamma \simeq 1.7503$ , 1.75019, 1.75019, 1.75009. In three dimensions one finds for the simple cubic lattice, using (7.2.8) for  $v_{\rm e}$ ,

 $\gamma \simeq 1.22, 1.30, 1.2502, 1.2507, 1.2505$  (simple cubic)

with similar numerical results for the body-centred cubic and face-centred cubic lattices even though the series for  $\chi_T$  are shorter.

Given accurate estimates of  $z_e$  and  $\gamma$  one can evaluate the function itself most accurately by dividing out the singularity and calculating direct approximants to G(z) in (7.3.5). (One may also form approximants to  $\{F(z)\}^{1/\gamma}$  which should converge fairly rapidly near  $z_e$ .)

Turning now to series of class (ii) let us, following Baker (1961 b), apply the method to the Ising-model spontaneous-magnetization expansions. Firstly, one should note that in estimating the critical point  $z_c$  from the vanishing of  $M_0(T)$  via (7.3.6) one obtains the same critical temperature to better than 1 part in 10<sup>3</sup>, as found from the high-temperature susceptibility expansions. This is important evidence of the uniqueness (and correctness) of the Ising-model critical points for d = 3 and of the fact that  $M_0(T)$  does vanish continuously as in two dimensions. Accepting this, and using the high-temperature estimates of the critical point, one obtains the sequence of estimates for the exponent  $\beta$  displayed in table 9. Despite the slightly erratic convergence, probably indicative of a confluent but weaker singularity, one may conclude with confidence<sup>‡</sup>

$$0.305 \le \beta \le 0.315$$
 (Ising  $d = 3$ ). (7.3.8)

It is fairly natural to conjecture (Essam and Fisher 1963) that

$$\beta = \frac{5}{16} = 0.31250 \quad (\text{Ising } d = 3). \tag{7.3.9}$$

Again, even if not exact, this value is probably correct to within +1% or -2%.

<sup>†</sup> It should be noted that this function and its analogues can also be employed with advantage in the ratio method (Essam and Sykes 1963), in other theoretical contexts (Domb and Hiley 1962) and especially in the analysis of experimental data (see Kouvel and Fisher (1964) and figure 17 below).

‡ Originally Baker (1961 b) found  $\beta \simeq 0.30$  but Essam and Fisher (1963) re-examined the problem using longer series with the conclusion  $0.303 \le \beta \le 0.318$ . A few further terms have since been derived and are included in table 9 (see Gaunt 1966, Ph.D. Thesis, University of London, Baker and Gaunt 1967). The range (7.3.8) is also supported by the diamond-lattice series which are of class (i) so that ratio techniques may be used (Essam and Sykes 1963).

After all the effort expended in obtaining the result (7.3.8) it is gratifying to discover that it lies so close to the experimental values  $\beta \simeq 0.33$  for fluids and magnets, discussed in §2. It seems certain, however, that the small deviation from these experimental values,  $\Delta\beta \simeq 0.02$ , is significant. Conversely Als-Nielsen and Dietrich's (1967) estimate,  $\beta = 0.305 \pm 0.010$  for beta-brass (see §2.7), is surprisingly close to the Ising value, as is their result  $\gamma = 1.25 \pm 0.02$ . Evidently the Ising model can provide an excellent description of the ordering of a binary metallic alloy even though it is not completely accurate for a fluid or ferromagnet.

# Table 9. Estimation of the spontaneous magnetization exponent $\beta$ by evaluation of Padé approximants to $\beta^*(T)$ at the critical point

	Simple cu	bic	Boc	ly-centred	l cubic	Fac	e-centred	cubic
M	$\beta_{e}$	st	M	$\beta_{e}$	$_{\rm st}$ <sup>+</sup>	M	$eta_{ ext{e}}$	st
4	0.304	0.301	6	0.303	0.285	9	0.307	0.307
5	0.304	0.303	7	0.308	0.305	10	0.309	0.308
6	0.278	0.302	8	0.302	0.310	11	0.306	0.308
7	0.314	0.307	9	0.316	0.340	12	0.306	0.306
8	0.314	0.301	10	0.316	0.316	13	0.306	0.306
9		0.310	11	0.315	0.324	14	0.373	0.305
			12	0.313	0.313	15	0.309	0.306
			13	0.314	0.314	16		0.315

Results from Essam and Fisher (1963) and Gaunt (1966, Ph.D. Thesis, University of London).

† The two columns refer to diagonal and next-to-diagonal sequences.

## 8. Survey of numerical results

In this section we review briefly the results so far found for the Ising and Heisenberg models by application of the ratio and Padé approximant techniques. The resulting critical exponent values are collected in the fold-out table at the end of the article while the various other critical-point amplitudes, etc., are presented in tables 2 to 4 and further tables in this section. As explained in §7 the uncertainty limits quoted below are in no sense rigorous bounds; they represent, however, the maximum ranges consistent with the observed regularity of the extrapolations.

## 8.1. Ising model

We consider in turn various features of the model. Except where discussed below the spin  $\frac{1}{2}$  model is implied.

8.1.1. Specific heats. As mentioned above, the specific-heat series lead to rather irregular and slowly converging critical-point estimates. (On loose-packed lattices the high T series are also very short since odd-order terms vanish.) The first study by Domb and Sykes (1957 c) yielded only

$$0 \le \alpha < 0.25$$
 (Ising  $d = 3$ ). (8.1.1)

Although the face-centred cubic lattice, in particular, suggested  $\alpha \simeq 0.2$ , the series could be fitted consistently with logarithmic singularities and this has been assumed

in calculating the critical energies and amplitudes in table 2 (Sykes and Fisher 1962, see also Baker 1963, Fisher 1964 c). The estimates will change only in the last one or two decimal places; however, if  $-\ln|1 - (T/T_c)|$  is replaced by

$$l_{\alpha}\left(\frac{T}{T_{\rm c}}\right) = \alpha^{-1}\left\{\left(1 - \frac{T}{T_{\rm c}}\right)^{-\alpha} - 1\right\}$$
(8.1.2)

with small  $\alpha > 0$  (see (1.18)). Recently Sykes *et al.* (1967) have extended the series for the face-centred cubic lattice and from this one can conclude

 $\alpha = 0.125 \pm 0.015 \simeq \frac{1}{8} \quad \text{(Ising face-centred cubic)} \tag{8.1.3}$ 

which is no doubt applicable to the other three-dimensional lattices also.

Below  $T_c$  a logarithmic or even milder singularity again appeared plausible (Sykes and Fisher 1962, Baker 1963, Essam and Sykes 1963, Fisher 1964 c, Gaunt and Essam 1965) but a careful investigation by Baker and Gaunt (1967) in the light of the rigorous inequalities (§ 3) indicates

$$\alpha' = 0.066^{+0.160}_{-0.040} \simeq \frac{1}{16} \quad (\text{Ising } d = 3). \tag{8.1.4}$$

Numerically the d = 3 specific heat curves display just the asymmetry characteristic of real systems as is evident from the comparison with the argon data (Bagatskii *et al.* 1962) shown in figure 15. Indeed, above  $T_c$  the *quantitative* agreement for appropriate normalization is rather close. Below  $T_c$ , however, the almost constant difference of about 1.0  $k_B$  indicates a significant defect of the simple lattice gas model, perhaps associated with the trivial 'one-site' hard cores. It should also be noted from figure 15 that the asymptotic behaviour above  $T_c$  (and to a lesser extent below  $T_c$ ) only dominates rather close to  $T_c$  (say,  $\Delta T/T_c < 3 \times 10^{-3}$ ). The values of critical energies and entropies for d = 3 also accord fairly closely with appropriate experiments; see especially the review by Domb and Miedema (1964).

8.1.2. *Magnetization*. We have discussed the study of the magnetization series in §7.2 and pointed out the close quantitative agreement with experimental data on beta-brass. For completeness here we restate only the result

$$\beta \simeq 0.312^{+0.003}_{-0.006} \simeq \frac{5}{16}.$$
(8.1.5)

Amplitudes were estimated by Essam and Fisher (1963) and Baker and Gaunt (1967) (see table 2).

8.1.3. *Ferromagnetic susceptibilities*. From the combined evidence of the ratio and Padé approximant studies already reviewed one may conclude that

$$\gamma = 1.250 \pm 0.003 \quad (\text{Ising } d = 3) \tag{8.1.6}$$

which, as pointed out, agrees closely with the observations on beta-brass. The amplitudes  $C^+$  in

$$\chi_T(T) \simeq \frac{(m^2/k_{\rm B}T) C^+}{\{1 - (T_{\rm c}/T)\}^{\gamma}}$$
(8.1.7)

can be estimated very precisely (Sykes and Fisher 1962, Baker 1961 a, b) and are given in table 2. The estimates of Fisher and Gaunt (1964) of the critical points and values of  $\gamma$  (and  $\alpha_s$ ) for hypercubical lattices of dimensions 4, 5, ... have already been mentioned in §5.4 (see equations (5.4.9) and (5.4.10)).

The low-temperature susceptibilities were first studied by Essam and Fisher (1963) who found the behaviour of the Padé approximants to  $\gamma'$  rather erratic for d = 3 and so could only conclude that  $1 \cdot 23 \leq \gamma' \leq 1 \cdot 32$ . The advent of longer series has hardly changed this situation but bearing in mind the rigorous inequalities (§ 3) and the evidence for  $\alpha'$ ,  $\beta$  and  $\delta$  (see below) one can now conclude (Baker and Gaunt 1967)



$$\gamma' = 1.310^{+0.030}_{-0.050} \simeq 1^{\frac{5}{1.6}}_{1.6}.$$
(8.1.8)

Figure 15. Logarithmic plot of the reduced configurational specific heat of argon (circles and curve A) compared with Ising-model predictions: B, above T<sub>c</sub> assuming α = 0 (log) (full curve, face-centred cubic); C, above T<sub>c</sub> assuming α = 0·20 (face-centred cubic); D, below T<sub>c</sub> for the face-centred cubic lattice assuming α' 20; E, below T<sub>c</sub> for the simple cubic lattice (Fisher 1964 a, b, c). Note that the latest estimates indicate α 20·125 and α' 20·066.

In fact it seems quite likely, although more evidence is still desirable, that the symmetry  $\gamma' = \gamma$  found in two dimensions does *not* apply in three dimensions. This turns out to be an important conclusion.

The low-temperature amplitudes  $C^-$  listed in table 2 were calculated on the assumption  $\gamma' \simeq 1.25$  but they change little by using (8.8) (see Baker and Gaunt 1967). The ratio  $C^+/C^- \simeq 5$  for d = 3 contrasts with the classical value of 2 and the

Ising d = 2 value of about 37, but seems to correspond better with experiment (e.g. Als-Nielsen and Dietrich 1967).

8.1.4. Antiferromagnetic susceptibilities. These have been studied carefully for H = 0 by Sykes and Fisher (1962) using ratio methods and by Marshall and Gammel (unpublished) using Padé approximants. The conclusions were summarized in §7.2, especially equation (7.2.18). Numerical values are given in table 3. (The *transverse* susceptibilities of the three-dimensional lattices have not yet been studied.) The phase-transition line in the (H, T) plane has been estimated for antiferromagnetic square, simple cubic and body-centred cubic lattices by Bienenstock (1966) and Bienenstock and Lewis (1967).

8.1.5. Critical isotherm. The critical isotherm has been examined by Gaunt *et al.* (1964) using the 'activity' series in powers of y (equation (7.1.8)) and ratio and approximant techniques. For the planar lattices they concluded that

$$\delta = 15.00 \pm 0.08 \simeq 15 \quad (\text{Ising } d = 2) \tag{8.1.9}$$

which, in view of the rigorous inequality (6.1.14), strongly indicates that  $\delta = 15$  is exact. In three dimensions they found

$$\delta = 5 \cdot 20 \pm 0.15 \quad (\text{Ising } d = 3). \tag{8.1.10}$$

The integer value 5, which might be reconciled with some generalized phenomenological or Taylor-series approach, seems definitely excluded. (However, in a recent re-analysis using a somewhat different, and so far less fully tested, approach Gaunt (1967) has suggested that  $\delta = 5$  might be correct.) As seen in §2 the value  $\delta \simeq 5.2$ is some 20% to 30% higher than indicated experimentally by present data on fluids and ferromagnets although these data do not extend as close to the critical point as may be necessary. As yet the corresponding amplitudes for  $H(T_c)$  against M are not available.

8.1.6. Correlations and scattering. For  $T \ge T_c$  the scattering and correlations have been considered in detail by Fisher and Burford (1967) (see also Fisher 1964 b, 1966 b). Firstly, they showed for d = 2 and 3 that the series for the effective range parameter  $\kappa_1$  and for the true correlation range  $\kappa$  were closely related and hence that the critical behaviour of  $\kappa$  and  $\kappa_1$  is the same, i.e.  $\nu_1 = \nu$ . Further, the corresponding amplitudes  $F^+$  and  $F_1^+$  (see (6.2.2)) are almost indistinguishable numerically. From the series for  $(\kappa_1 a)^2$  and  $\kappa a$  they checked their procedures by rederiving the rigorous result  $\nu = 1$  (d = 2) and then estimated

$$\nu = 0.6430 \pm 0.0025 \simeq \frac{9}{14} \quad (\text{Ising } d = 3) \tag{8.1.11}$$

for the simple cubic, body-centred cubic and face-centred cubic lattices. This result is again close to the value  $\nu = 0.647 \pm 0.022$  observed by Als-Nielsen and Dietrich (1967) for beta-brass.

The behaviour of the higher correlation moments indicated, as known for d = 2, that  $\kappa^{-1}$  is essentially the only correlation length; thus using the relation  $(2 - \eta)\nu = \gamma$  (§ 6.3) and (8.1.6) they concluded that

$$\eta = 0.056 \pm 0.008 \simeq \frac{1}{18} \quad (\text{Ising } d = 3). \tag{8.1.12}$$

This was confirmed, although with lower accuracy, by direct estimates of the critical

correlations  $\Gamma_c(\mathbf{r})$  for the simple cubic lattice. (The corresponding amplitudes, defined as in (6.2.5), are listed in table 4.)

They found that the overall behaviour of the scattering intensity above  $T_c$  was very well approximated by

$$\hat{\chi}(\mathbf{k},T) \simeq \left(\frac{a}{r_1}\right)^{2-\eta} \frac{\{(\kappa_1 a)^2 + \phi^2 a^2 K^2(\mathbf{k})\}^{1/2}}{(\kappa_1 a)^2 + \psi a^2 K^2(\mathbf{k})}$$
(8.1.13)

with

$$\eta = \frac{1}{4} \quad (d = 2) \tag{8.1.14}$$

$$\eta = \frac{1}{18} \quad (d = 3) \tag{8.1.15}$$

where the slowly varying length  $r_1(T)$  satisfies

$$\frac{r_1}{a} = \left(\frac{r_1}{a}\right)_{\rm e} \left\{ 1 - c \left(\frac{T}{T_{\rm e}} - 1\right) + \ldots \right\} \quad (T \to T_{\rm e} + ).$$

$$(8.1.16)$$

The variable

$$a^{2} K^{2}(\mathbf{k}) = 2d \left\{ 1 - q^{-1} \sum_{\mathbf{r}=\mathbf{\delta}} \exp\left(i\mathbf{k} \cdot \mathbf{r}\right) \right\} \simeq (ka)^{2}$$
(8.1.17)

allows for the influence of lattice structure at larger values of ka. Finally

$$\psi = 1 + \frac{1}{2}\eta\phi^2(T) \tag{8.1.18}$$

where  $\phi(T)$  is a slowly varying function, vanishing rapidly at high temperatures and with magnitude, at  $T = T_c$ , 0.03 for d = 2 and 0.06 to 0.09 for d = 3 (see table 4 for precise values of  $\phi$ ,  $\psi$ ,  $(r_1/a)_c$  and c). An Ornstein-Zernike plot  $\hat{\chi}^{-1}$  against  $(ka)^2$  for the simple cubic lattice is shown in figure 16 (compare with figure 3). The intersection of the isotherms for different T means that  $\hat{\chi}(\mathbf{k}, T)$  at fixed  $\mathbf{k} \neq 0$  exhibits a maximum at a temperature above  $T_c$  contrary to previous expectations. For small ka this maximum is quite close to  $T_c$  and may thus be difficult to detect experimentally. The recent neutron scattering experiments of Bally *et al.* (1967), however, do not display such a maximum.

Comparable calculations have not yet been performed below  $T_e$  but if we accept the estimates (8.1.2) and (8.1.8) and the relation  $(2-\eta)\nu' = \gamma'$  (§6.3) we may conclude

$$\nu' = 0.675^{+0.022}_{-0.029} \simeq \frac{27}{40} \neq \nu.$$
(8.1.19)

We repeat, however, that this has not been tested by direct calculation.

8.1.7. Higher field derivatives. Essam and Fisher (1963) suggested that it would be of theoretical interest to study the H = 0 critical behaviour of higher derivatives of the free energy with respect to field (or, in a fluid, with respect to pressure) although these quantities are not readily accessible to experiment. Below  $T_c$  we may define the sequence of 'gap' exponents  $\Delta_2', \Delta_3', \ldots$  as follows

$$\left(\frac{\partial^2 F}{\partial H^2}\right)_0 = \chi_T \sim (T_c - T)^{\beta - \Delta_2'}, \quad \Delta_2' = \beta + \gamma'$$
(8.1.20)

$$\begin{pmatrix} \frac{\partial^3 F}{\partial H^3} \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \end{pmatrix}_0 = F_0^{(3)} \sim (T_c - T)^{-\gamma' - \Delta_3'}$$

$$(8.1.21)$$

$$\left(\frac{\partial^k F}{\partial H^k}\right)_0 = F_0^{(k)}(T) \sim (T_c - T)^{-\Delta_k'} F_0^{(k-1)}(T).$$
(8.1.22)

Above  $T_e$  where only even derivatives are non-vanishing for H = 0 we can similarly define 'double gaps'  $2\Delta_4, 2\Delta_6, \dots$  by

$$\left(\frac{\partial^4 F}{\partial H^4}\right)_0 = \left(\frac{\partial^2 \chi_T}{\partial H^2}\right)_0 \sim (T - T_c)^{-\gamma - 2\Delta_4}$$
(8.1.23)

$$\left(\frac{\partial^{2k} F}{\partial H^{2k}}\right)_0 = F_0^{(2k)}(T) \sim (T - T_c)^{-2\Delta_{2k}} F_0^{2(k-1)}(T).$$
(8.1.24)



Figure 16. Inverse scattering intensity of the simple cubic lattice against  $(ka)^2$  for temperatures near critical. The numbers on the curves give the values of  $T/T_c$ . The crossing of the isotherms which implies that  $\hat{\chi}(\mathbf{k}, T)$  exhibits a maximum for  $T > T_c$  when  $k \neq 0$  should be noted. (From Fisher and Burford 1967.)

The theoretical significance of these exponents will be seen in the next section but we may remark here that according to classical theories

$$\Delta_{k}' = \Delta_{2j} = 1\frac{1}{2} \quad \text{all } j, \ k \text{ (classical theory)}. \tag{8.1.25}$$

For the square lattice Essam and Fisher found<sup>†</sup>

$$\Delta_{3}' = 1.87 \pm 0.05 \simeq 1\frac{7}{8} \quad (\text{square}) \tag{8.1.26}$$

but no other estimates have so far been made below  $T_c$ . Above  $T_c$  Domb and Hunter (1965 and private communication) have made more extensive calculations with the

<sup>†</sup> There is a misprint of  $\frac{3}{8}$  for  $\frac{5}{8}$  in their paper.

results

$$\Delta_4 \simeq \Delta_6 \simeq \Delta_8 \simeq 1.87 \pm 0.04 \simeq 1\frac{7}{8} \quad (\text{Ising } d = 2) \tag{8.1.27}$$

and

$$a_4 = a_6 = a_8 = 107 \pm 007 \pm 18$$
 (1311g  $a = 2$ ) (0.1.27)

$$\Delta_4 \simeq \Delta_6 \simeq \Delta_8 \simeq 1.56 \pm 0.03 \simeq 1\frac{9}{16} \quad (\text{Ising } d = 3). \tag{8.1.28}$$

(The quoted uncertainties are only preliminary.)

8.1.8. Higher spin. For general S only six or seven terms of the high temperature series are available at present (Domb and Sykes 1962) so that extrapolation is necessarily less certain. However, by comparing the behaviour of the susceptibility coefficients of the face-centred cubic lattice for general S with those for  $S = \frac{1}{2}$  Domb and Sykes (1962) concluded that  $\gamma$  did not change with S (to within, say,  $\pm 0.02$ ). However, the specific heat singularity seemed to grow sharper with increasing S and they suggested tentatively that  $\alpha \simeq 0.25$  (S = 1) and  $\alpha \simeq 0.33$  (S =  $\infty$ ). Appreciably longer series are needed to confirm these estimates, however, and it is quite likely that they are too high and that  $\alpha$  does not change. Nevertheless, fairly accurate estimates of critical temperatures, energies, etc., may be made and these are displayed in table 10.

# Table 10. Critical parameters of the face-centred cubic Ising lattice for general spin

	$S = \frac{1}{2}$	S = 1	S = 2	$S = \infty$
$k_{\rm B} T_{\rm c}/\frac{2}{3}q J_{\parallel} S(S+1)$	0.816	0.851	0.864	0.874
${S}_{ m c}/k_{ m B}$	0.591	0.983	1.486	$\infty$
$(S_{\infty}-S_{\rm c})/k_{\rm B}$	0.102	0.116	0.123	0.131
$\mid U_{ m c} \mid / k_{ m B} T_{ m c}$	0.120	0.160	0.167	0.175
$(\dot{U_{\mathrm{c}}}-\dot{U}_{\mathrm{0}})/k_{\mathrm{B}}T_{\mathrm{c}}$	0.463	0.721	0.990	1.541

From Domb and Miedema (1964).

8.1.9. Further-neighbour interactions. Domb and Dalton (1966, see also Dalton 1965, Ph.D. Thesis, University of London, 1966) have calculated high-temperature expansions for the 'equivalent-neighbour' model in which equal interactions with further-neighbour shells r = 2, 3, ... are introduced. From the leading six to eight terms they were able to conclude that  $\gamma$  does not change with increasing range of interaction although the 'critical region', in which a plot of  $1/\chi_T$  against T is appreciably curved, shrinks when r increases as anticipated in § 5.4. Since this conclusion is of theoretical importance a sample ratio analysis demonstrating the constancy of  $\gamma$  is displayed in table 11. In the limit of large total co-ordination number q, Domb and Dalton (1966) found for all three-dimensional lattices

$$\frac{T_{\rm c}}{T_{\rm c}(\infty)} - 1 \simeq \frac{4 \cdot 46}{q} \quad (d = 3) \tag{8.1.29}$$

where  $T_{\rm c}(\infty)$  denotes the classical mean field critical point, and

$$\frac{S_{\infty} - S_{\rm c}}{k_{\rm B}} \simeq \frac{1.77}{q}, \quad \frac{U_{\rm c}}{k_{\rm B}T_{\rm c}} \simeq \frac{2.23}{q} \quad (d = 3).$$
(8.1.30)

These are of the form suggested by the discussion of §5.4 and by various approximate theories, in particular by 'high-density' expansions (Brout 1959, 1960, 1965, Horwitz and Callen 1961, Stinchcombe *et al.* 1963), but the coefficients differ significantly. (In two dimensions the different asymptotic form  $A/q^{\epsilon}$  with  $0 < \epsilon < 1$  is anticipated.) For moderate values of q the formulae (8.1.29) and (8.1.30) are more accurate numerically if the coefficients are reduced by some 10% to 20%.

# Table 11. Analysis of the susceptibility expansion for the simple cubic lattice with equal first- and second-neighbour interactions demonstrating the unchanged value of $\gamma$

n	$\mu_n'$ $\epsilon = \frac{1}{2}$	$\mu_n'$ $\epsilon = 1$	$\epsilon = \frac{1}{2}$	$\epsilon = 1$
3	15.5294	15.1765	1.2433	1.2781
4	15.5399	15.3777	1.2440	1.2712
5	15.5177	15.4204	1.2443	1.2665
6	15.5145	15.4502	1.2446	1.2634
7	15.5150	15.4694	1.2450	1.2613
estimate	$\mu = k_{\rm B}T_{\rm c}$	/J	$\gamma = 1.24$	$7 \pm 0.012$
	$\simeq 15.51$	$0 \pm 0.015$	$\simeq 1\frac{1}{4}$	

Series coefficients from Domb and Dalton (1967). Notation as in equations (7.2.7) and (7.2.9).

8.1.10. Long-range interactions. The independence of  $\gamma$  of the range of interaction is not to be expected for inverse power potentials of the form  $1/r^{d+\sigma}$  with small  $\sigma$ . Joyce (1966, see also Domb *et al.* 1965) has tested this surmise by studying the susceptibility expansion to fifth order for an  $S = \frac{1}{2}$  Ising model in two dimensions with  $\sigma = 1$  (i.e.  $J(r) \sim 1/r^3$ ). He finds the exponent is reduced from the finite-range value  $1\frac{3}{4}$  to

$$\gamma = 1.13 \pm 0.01$$
 (Ising  $d = 2$ , long range  $\sigma = 1$ ). (8.1.31)

Such long-range (totally attractive) interactions are not, however, directly relevant to experiment and it seems likely (e.g. by analogy with the spherical model (Joyce 1966) that for  $\sigma > 2$  the thermodynamic exponents will already take their characteristic finite-range values. (The decay of correlation, however, will no longer be exponential in a model with, for example,  $1/r^6$  potentials.)

# 8.2. Heisenberg model

8.2.1. One and two dimensions. It should firstly be pointed out that Mermin and Wagner (1966) have recently proved rigorously that the two-dimensional (and one-dimensional) isotropic Heisenberg ferromagnet cannot display a spontaneous magnetization if the interactions are of finite range. Specifically, by exploiting a generalized Schwarz inequality due to Bogoliubov (1962) they prove that as  $H \rightarrow 0$ 

$$|M(H,T)| \leq BT^{-1/2} |\ln|H||^{-1/2} \quad (d=2)$$
 (8.2.1)

$$\leq BT^{-2/3} |H|^{1/3}$$
  $(d = 1)$  (8.2.2)

where B is a constant, so that M always vanishes with H. Their arguments apply for all S, including  $S = \infty$ , and likewise rule out a sublattice magnetization in the isotropic antiferromagnet or a *transverse* magnetization in the Ising-Heisenberg model with axial symmetry (i.e.  $J_x = J_y = J_{\perp}$ ). (Similarly the existence of offdiagonal long-range order in the sense (4.1.14) can be proved impossible for a Bose continuum or lattice system at non-zero temperature in one or two dimensions (Hohenberg 1967).)

Although these results have long been expected on heuristic grounds they must not be taken as excluding the existence of some special sort of phase transition in which, for example,  $\chi_T = \infty$  for H = 0 and  $T \leq T_c$  even though  $M_0 \equiv 0$ . The possibility of such a transition in the two-dimensional Heisenberg model has recently been raised by Stanley and Kaplan (1966 a, b, 1967) who point out that the leading six terms of the high-temperature susceptibility expansions are not inconsistent with the divergence of  $\chi_T$  at a finite, and indeed moderately high, temperature (see also Rushbrooke and Wood (1955, 1958), but for some contrary evidence Marshall *et al.* (1963)). We shall not discuss this interesting problem here, except to say that the use of short-series expansions to investigate the rather subtle *existence* question must be regarded with special caution since it would be reasonable to expect a non-uniformity of convergence in the isotropic limit in view of Mermin and Wagner's analysis. In the remainder of this section we consider only threedimensional systems.

8.2.2. Ferromagnets. For general spin only six terms of the high-temperature susceptibility expansions and five terms of the specific-heat expansions have been calculated (Rushbrooke and Wood 1958). The behaviour of the coefficients is much less regular than for the Ising model especially for low-spin values. However, moderately accurate estimates of critical temperatures, energies and entropies can be given (Rushbrooke and Wood 1958, Domb and Sykes 1957 c, 1962). These parameters are listed for the face-centred cubic lattice in table 12. When properly

# Table 12. Critical parameters for the Heisenberg-model face-centred cubic lattice for various spin values $(J_{\parallel} = J_{\perp})$

	$S = \frac{1}{2}$	S = 1	S = 2	$S = \infty$
$k_{\rm B}T_{\rm c}/\frac{2}{3}qJ_{\parallel}S(S+1)$	0.679	0.747	0.774	0.798
$S_{ m c}/k_{ m B}$	0.473	0.810	1.305	$\infty$
$(S_{\infty}-S_{\rm c})/k_{\rm B}$	0.220	0.289	0.304	0.322
$ U_{ m c} /k_{ m B}T_{ m c}$	0.439	0.449	0.459	0.474

From Domb (1965 c).

normalized they generally vary almost linearly with 1/S(S+1). The specific heat has a larger 'tail' above  $T_c$  than for the Ising model but the singularity seems weaker with

$$\alpha \simeq 0$$
 (Heisenberg  $d = 3$ ) (8.2.3)

and  $C_H$  might well be finite at  $T_c$ . However, longer series are needed to confirm this point.

For  $S = \infty$  the series are smoother and, as first pointed out by Domb and Sykes (1962), one can conclude

$$\gamma = 1.32 - 1.37 \simeq \frac{4}{3}$$
 (Heisenberg  $d = 3, S = \infty$ ) (8.2.4)

with reasonable confidence. This result has been confirmed by Marshall et al.

(1963) using Padé approximants and more accurate estimates may be expected from the longer series being calculated at present for  $S = \infty$  (Stanley and Kaplan 1966 a, b, Wood and Rushbrooke 1966, Joyce and Bowers 1966, Joyce 1967).<sup>†</sup>

The value (8.2.4) is significant, firstly because it is quite distinct from the Isingmodel result (see §9.1), and secondly because it is in much better accord with experiments on real ferromagnets (§2.4). This is illustrated in figure 17 which shows the variation of the effective exponent  $\gamma^*(T)$  (equation (7.3.7)) found by Kouvel and Fisher (1964) who analysed the classic experiments of Weiss and Forrer (1926).



Figure 17. Plot of the effective exponent  $\gamma^*(T)$  for nickel leading to the conclusion  $\gamma = 1.35 \pm 0.02$  (Kouvel and Fisher 1964). The broken lines are from the Padé approximants of Marshall *et al.* (1963) for the nearest-neighbour Heisenberg model.

With only six terms of the expansion of  $\chi_T$  available it seemed likely that the value  $\gamma \simeq \frac{4}{3}$  might apply for all spin values (although some indications of *higher* values could be seen and the terms for  $S = \frac{1}{2}$  were particularly irregular). Recently, however, new techniques have been used to derive up to ten terms for spin  $\frac{1}{2}$  (Domb and Wood 1964, 1965, Rushbrooke 1964, Wood 1965, Baker *et al.* 1966 a). On analysis by Padé or ratio methods these yield

$$\gamma = 1.43 \pm 0.04 \simeq \frac{10}{7}$$
 (Heisenberg  $d = 3, S = \frac{1}{2}$ ) (8.2.5)

which is significantly higher than for spin  $\infty$  (Baker *et al.* 1966 a).<sup>‡</sup> This interesting and unexpected result has so far received no theoretical interpretation. At present it is also not clear whether for intermediate spin values  $\gamma$  should take one or other of the extreme values 1.33 or 1.43, or should pass through a sequence of intermediate values.§ From the practical numerical viewpoint, however, it should be remembered that even S = 1 is 'over half-way' to  $S = \infty$  since, as mentioned, most parameters vary fairly linearly with 1/S(S+1). Thus values of  $\gamma > 1.33$  might only become apparent graphically in an 'inner critical region' close to  $T_c$ .

<sup>†</sup> These tend to support the higher range near 1.37.

<sup>‡</sup> In view of these results the estimate in table 12 for  $T_c$  with  $S = \frac{1}{2}$  should be reduced from 0.679 to 0.669, and the other estimates should also be altered although by smaller factors.

§ This last conclusion tends to follow naturally from short-series expansions (Stanley and Kaplan 1967) since each coefficient is just a polynomial in  $\{S(S+1)\}^{-1}$ .

8.2.3. Higher field derivatives. Baker et al. (1966 b) also studied the higher-field derivatives and for the exponents defined in (8.24) found

$$\Delta_4 = 1 \cdot 81 \pm 0 \cdot 04 \qquad \qquad \Delta_6 = 1 \cdot 83 \pm 0 \cdot 08 \\ \Delta_8 = 1 \cdot 80 \pm 0 \cdot 15 \qquad (\text{Heisenberg } d = 3, S = \frac{1}{2}).$$
 (8.2.6)

As for the Ising model, these suggest a constant value, but close to 1.81 rather than 1.56.

8.2.4. *Correlations*. Fisher and Burford (see Fisher 1966 b, Burford 1966, Ph.D. Thesis, University of London) have obtained expansions for the second correlation moment for general spin to sixth order. For infinite spin they estimate

$$\nu = 0.692 \pm 0.012$$
 (Heisenberg  $d = 3, S = \infty$ ) (8.2.7)

and hence, using  $\gamma \simeq \frac{4}{3}$ , they conclude

$$\eta = 0.075 \pm 0.035 \tag{8.2.8}$$

which seems to be significantly higher than for the Ising model. For lower spin the short series available do not permit very accurate extrapolation, but even allowing for the change of  $\gamma$  discovered for spin  $\frac{1}{2}$  it appears that the values of  $\eta$  do not change appreciably (although the estimates for  $\nu$  change in accordance with  $(2 - \eta)\nu = \gamma$ ).

8.2.5. Antiferromagnets. For  $S = \infty$  the antiferromagnetic critical temperature of an alternating lattice with nearest-neighbour interactions must be the same as for the corresponding ferromagnet  $(J_{\text{ferro}} = |J_{\text{anti}}|)$  just as for the general Ising model. For finite spin, however, this symmetry is lost and by studying the staggered susceptibility  $\chi_T^{\dagger}$  Rushbrooke and Wood (1963) showed, in fact, that

$$\frac{T_{\rm c}^{\,\rm anti}}{T_{\rm c}^{\,\rm ferro}} \simeq 1 + \frac{0.63}{qS(S+1)} > 1. \tag{8.2.9}$$

The value of  $\gamma$  seems not to have been estimated for the staggered susceptibilities although for  $S = \infty$  we must by symmetry still have  $\gamma \simeq \frac{4}{3}$ . General arguments referred to before (Fisher 1962) indicate that the antiferromagnetic susceptibility should have a mild singularity at  $T_c^{\text{anti}}$  with a peak, possibly infinite, in  $\partial \chi_{\parallel} / \partial T$ . Some inkling of this can be seen in the susceptibility series (Marshall *et al.* 1963, Domb *et al.* 1965, Baker *et al.* 1966 a) but although this weak singularity should *eventually*<sup>+</sup> dominate the convergence for  $S < \infty$  (since  $T_c^{\text{anti}}$  exceeds  $T_c^{\text{ferro}}$ ) it is heavily masked in the lower terms by the strong ferromagnetic divergence.

8.2.6. Further-neighbour interactions etc. High-temperature expansions for interactions extending to second- and third-neighbour shells have been obtained by Wojtowicz and Joseph (1964), Wojtowicz (1964), Dalton and Wood (1965), Pirnie and Wood (1965), Dalton (1965, Ph.D. Thesis, University of London, 1966), Domb and Dalton (1966), and lead to estimates of critical temperatures, energies and entropies, and expressions analogous to (8.1.29) and (8.1.30). Present series, however, seem to be too short to yield really useful information on the constancy (or

 $\dagger$  One may estimate that an alternation of the signs sets in after about 80 terms (Domb *et al.* 1965).

otherwise) of the critical exponents. Wojtowicz (1967) has also obtained series for Heisenberg *ferri*magnets in which the two sublattices have different spin values. Joseph (1965) has introduced biquadratic spin terms.

# 8.2.7. Intermediate Ising-Heisenberg model. In view of the difference

$$\gamma_{\rm Heis} - \gamma_{\rm Ising} \simeq 0.1 - 0.2$$

it is of great interest to determine how  $\gamma$  varies with  $J_{\perp}/J_{\parallel}$  for the intermediate anisotropic Ising-Heisenberg model. Perhaps the most natural conjecture is

$$\gamma \frac{J_{\perp}}{J_{\parallel}} = \gamma_{\text{Ising}} \quad \text{for} \quad 0 \leq \frac{J_{\perp}}{J_{\parallel}} < 1$$
$$= \gamma_{\text{Heis}} \quad \text{for} \quad \frac{J_{\perp}}{J_{\parallel}} = 1 \quad (8.2.10)$$

(see, for example, Fisher 1966 a). Some definite evidence for this has been advanced recently by Dalton and Wood (1967) who have obtained five terms of the  $S = \frac{1}{2}$  high-temperature expansions, but the problem merits further attention, particularly because of its significance for quantal lattice gases.

8.2.8. Temperatures below  $T_c$ . At present there is no reliable information on the values of the Heisenberg model exponents below  $T_c$  or on the critical-isotherm exponent  $\delta$ , although results may eventually be obtained from the high-field (activity) expansions. On the basis of various conjectured relations between the exponents discussed in the next section, however, one may speculate that  $0.3 < \beta < 0.4$  (see table 13 below) which is not implausible. It may also be mentioned that Callen and Callen (1965, 1966) have observed that an exponent  $\beta = \frac{1}{3}$  in the simple expression (6.15) fits the predictions of certain truncated cluster expansion (and Green function) theories quite well numerically in the region below  $0.9T_c$ . Of course the true exponent  $\beta$  is defined for T close to, and approaching,  $T_c$ . Nevertheless, these results might be quite suggestive if they were reproduced and extended towards  $T_c$  in higher-order truncations. Unfortunately this does not seem to happen.

# 9. Theory of exponents

In this section we outline and attempt to assess a number of recently developed theoretical ideas which aim at throwing light on the values of the critical singularities and, more particularly, on deriving relations between them.<sup>†</sup> Indeed the central question that might be posed is: how many *independent* critical exponents does a physical system have? The most optimistic answer, suggested by some of the approaches to be described, is 'only two'—essentially, one for the temperature variation and one for the field (or pressure, etc.) variation. In the light of present knowledge, however, none of the various theories is fully convincing but we may hope they point the way forward to a deeper understanding of the numerical results so far found experimentally and theoretically.

<sup>†</sup> This section follows fairly closely a recent lecture (Fisher 1967).

#### 9.1. Droplet or cluster model

In this section we describe a theory of the critical region based on the droplet (or 'physical-cluster') picture of condensation in a low-density gas. The underlying ideas go back to Frenkel (1939), Band (1939) and Bijl (1938, Doctoral Dissertation, University of Leiden) (see also Fierz 1951 and de Boer 1952) but only recently has it been pointed out that they can be extended to describe the critical point (Essam and Fisher 1963, Fisher 1965 a, c).<sup>†</sup> We shall present the arguments for the fluid case but for an anisotropic ferromagnet they may be translated easily into magnetic terms (see Fisher 1967).

The basic idea is that in a gas of particles interacting with repulsive cores and *short-range* attractive forces, the typical configuration at low densities and temperatures will consist of essentially isolated clusters of one, two, three or more particles. A sufficiently large cluster is just a small droplet of the liquid phase at the same temperature. These droplets will be in dynamic equilibrium and the relative proportions of differently sized droplets will change with temperature and pressure (or activity). Condensation in this picture corresponds to the growth of a macroscopic droplet of the liquid.

To formulate these ideas mathematically let us, in first approximation, neglect the excluded volume between droplets (but not between particles within a droplet). The grand partition function is then given approximately by

$$\ln \Xi(T, z, \Omega) = \sum_{l=1}^{\infty} q_l z^l \tag{9.1.1}$$

where  $q_l = q_l(T; \Omega)$  is the configurational partition function for a single cluster of l particles in the domain  $\Omega$  (see, for example, de Boer 1952). At low temperatures, where the gas is always at low density, this will be an excellent approximation. The principal results of the theory are not altered by taking account of the excluded volume to first order (or rigorously, in certain one-dimensional models (Fisher 1965 c), but to assess the effects of this approximation in general, especially near the critical point, seems very difficult.

Now the centre of mass of a cluster is free to move through the volume so that  $q_l$  is proportional to  $V(\Omega)$ . The energy of a cluster in some fixed configuration contains (i) a bulk term  $-lE_0$  where  $E_0$  is the binding energy per particle in the dense fluid (more generally we should take  $E_0$  as a *free* energy per particle), and (ii) a surface term +ws where s is the surface area (or perimeter for d = 2) of the cluster and w is a surface energy arising through loss of binding energy by particles near the surface.<sup>‡</sup>

Now we may expect that the most probable or mean surface  $\bar{s}$  of a cluster of size l will vary as

$$\bar{s}(l) \simeq a_0 l^{\sigma} \quad (l \to \infty) \tag{9.1.2}$$

with, necessarily for  $d \ge 2$ ,

$$0 < \sigma < 1. \tag{9.1.3}$$

Indeed at sufficiently low temperatures a typical cluster will be rather globular in

 $\dagger$  However, attention should also be drawn to the interesting early papers by Mayer and Streeter (1939) and Rice (1947).

 $\ddagger$  The definitions of  $E_0$ , w and s can be made quite precise by considering a hard-core plus attractive square-well pair potential, or a lattice gas with nearest-neighbour interactions only.

shape so that the surface should be characterized by an exponent

$$\sigma \simeq 1 - \frac{1}{d} = \frac{1}{2}$$
 for  $d = 2$   
=  $\frac{2}{3}$  for  $d = 3$ . (9.1.4)

We may now write approximately

$$q_l(\Omega, T) \simeq V(\Omega) g(\tilde{s}) \exp\left(l\beta E_0\right) \exp\left(-\beta w \tilde{s}\right)$$
(9.1.5)

where the combinatorial factor  $g(\bar{s})$  is proportional to the number (or, more correctly, volume in d(l-1)-dimensional configuration space) of configurations of l identical particles with fixed centre of mass and surface  $\bar{s}$ . For a simple lattice gas in two dimensions  $g(\bar{s})$  would be the number of polygons of perimeter  $\bar{s}$  (and area l). By a study of this and related combinatorial questions (see the excluded-volume problem discussed in §7.1), one can conclude that  $g(\bar{s})$  will have the form

$$g(\vec{s}) \simeq \frac{g_0 \lambda^{\vec{s}}}{\vec{s}^{\tau/\sigma}} \quad (\vec{s} \to \infty) \tag{9.1.6}$$

where  $g_0$  and  $\lambda$  are constants and the new exponent  $\tau$  satisfies  $\tau/\sigma \gtrsim 2$ . Although the value of  $\lambda$  can be understood readily, especially for lattice gases (note  $k_{\rm B} \ln \lambda = \varpi$  is the limiting entropy per unit of cluster surface), it is difficult to predict the exponent  $\tau$  (in contrast with our intuitive feelings about the surface exponent  $\sigma$ ). Its presence and positive value, however, follow fundamentally because the surface of a cluster is 'closed'.<sup>†</sup>

If we combine these results and introduce the variable

$$y = z \exp\left(\beta E_0\right) \tag{9.1.7}$$

to measure the activity, and the variable

$$x = \lambda^{a_0} \exp\left(-\beta w a_0\right) = \exp\left\{-\frac{a_0(w - \varpi T)}{k_{\rm B}T}\right\}$$
(9.1.8)

to measure the temperature, we finally find for the pressure of an infinite system

$$\frac{p}{k_{\rm B}T} \simeq g_0 \sum_{l=1}^{\infty} l^{-\tau} x^{l\sigma} y^l$$
(9.1.9)

provided the series converges.

It is easy to see that the series always converges for

$$y \leqslant y_{\sigma} = 1. \tag{9.1.10}$$

For a one-dimensional system ( $\sigma = \tau = 0$ ) the pressure diverges when  $y \rightarrow 1$  and there is no phase transition. When  $\sigma > 0$ , however, the pressure and all its derivatives with respect to T and z converge at  $y = y_{\sigma}$  provided T is below the 'critical temperature'

$$T_{\rm c} = \frac{w}{\varpi} \tag{9.1.11}$$

<sup>†</sup> Thus for example, on a lattice of co-ordination number q the number of open *l*-step random walks is  $q^i$  but the number of closed walks (returning to the origin) varies as  $Aq^i/l^{1/2d}$  when  $l \to \infty$ . For one-dimensional clusters, however, we have  $\sigma = 0$  and  $\tau = 0$ .

at which the 'microscopic' surface tension  $(w - \varpi T)$  in (9.1.8) vanishes. Thus  $y_{\sigma} = 1$  is identified as the condensation point.<sup>†</sup> Despite the existence of all the derivatives,  $y = y_{\sigma}$  is a mathematical singularity (of essential type) so that the system 'knows' it is due to become unstable and condense into a macroscopic cluster. We shall not, however, discuss this aspect of the problem further here despite its interest (see Katsura 1963, Andreev 1964, Fisher 1965 c, Langer 1967).

If one is prepared to trust the model qualitatively at higher temperatures (which are certainly outside the range of any obvious validity) one can also calculate the critical exponents. (One might, however, expect the exponents  $\sigma$  and  $\tau$  to be 'renormalized' by the droplet-droplet interactions.) Thus the variation with temperature of the *k*th activity derivative of the pressure at condensation is determined by the series

$$\left(z\frac{\partial}{\partial z}\right)^{k}\frac{p}{k_{\mathrm{B}}T}\Big|_{\sigma}\simeq g_{0}\sum_{l=1}^{\infty}l^{k-\tau}x^{l^{\sigma}}.$$
(9.1.12)

It is not difficult to see, for example by approximating the sum by an integral, that the singular part of this function when  $T \rightarrow T_c$   $(x \rightarrow x_c = 1)$  has an exponent  $-(k+1-\tau)/\sigma$ . From this we find<sup>‡</sup>

$$\alpha_{\rm s}' = 2 - \frac{\tau - 1}{\sigma} \quad (k = 0)$$
 (9.1.13)

$$\beta = \frac{\tau - 2}{\sigma} \qquad (k = 1) \tag{9.1.14}$$

$$\gamma' = \frac{3-\tau}{\sigma} \qquad (k=3) \tag{9.1.15}$$

and generally, for the 'gap' exponents defined in equations (8.1.19) to (8.1.21) we discover the *constant* value

$$\Delta_k' = \Delta' = \frac{1}{\sigma} \quad \text{all} \quad k \ge 1. \tag{9.1.16}$$

Similarly by setting  $x = x_c = 1$  in (9.1.9) we find that the critical isotherm is specified by

$$\delta = \frac{1}{\tau - 2}.\tag{9.1.17}$$

Evidently all the critical exponents are determined by just the *two* exponents  $\sigma$  and  $\tau$ . Thus between any three critical exponents there will be a relation. In particular one finds

$$\alpha_{\rm s}' + 2\beta + \gamma' = 2 \tag{9.1.18}$$

and

$$\alpha_{s}' + \beta(1+\delta) = 2.$$
 (9.1.19)

The close similarity of these two relations to the rigorous inequalities proved in

<sup>†</sup> For  $y > y_{\sigma}$  the series (9.1.9) diverges and the pressure becomes that for the liquid phase. To describe this phase properly one should also consider 'bubbles' and 'cracks' in the liquid but this has not yet been done. Consequently our results will not display the usual near symmetry between liquid and gas.

<sup>+</sup> We assume implicitly that  $\tau > 2$  so that  $\beta > 0$ . This is also needed to ensure  $\delta > 0$ ; see equation (9.1.17).

§3 should be noted but it should also be observed that  $\alpha_s'$ , for the singular part of the specific heat, appears in place of  $\alpha'$ . Elimination of  $\alpha_s'$  yields

$$\delta = 1 + \frac{\gamma'}{\beta} = \frac{\Delta'}{\beta}.$$
(9.1.20)

The first part of this relation was advanced originally by Widom (1964) on quite different heuristic grounds.

In assessing these relations let us note firstly that they are all satisfied by the classical critical-point exponents (see fold-out table). If they are tested for the planar Ising models they are also found to hold precisely. For the three-dimensional Ising lattices they are verified to well within the numerical uncertainties. (But it should be noted that  $\Delta_3'$ ,  $\Delta_4'$ , etc., have not yet been studied numerically for d = 3). How do the values of the gap  $\Delta' (= \beta + \gamma')$  compare with our expectations based on (9.1.16) and (9.1.4)? We have

$$\frac{1}{\Delta'} = \frac{8}{15} = 0.533... \quad (\text{Ising } d = 2)$$
  
$$\frac{1}{\Delta'} = 0.605 - 0.635 \simeq \frac{8}{13} \quad (\text{Ising } d = 3)$$
  
(9.1.21)

in surprisingly close correspondence with our guesses  $\frac{1}{2}$  and  $\frac{2}{3}$ . This suggests that our analysis, despite its obvious shortcomings, has grasped at least a significant part of the way dimensionality enters the problem.

However, on this simple picture we cannot completely understand the behaviour as  $d \to \infty$  since (9.1.4) suggests  $\Delta' (d = \infty) = 1$ , whereas, as argued in §5.4, one should obtain the classical value which is  $\Delta' = 1\frac{1}{2}$ . One might, on a purely *ad hoc* basis, introduce an exponent  $\mu_1'$  and alter the microscopic surface tension in (9.1.8) by taking

$$w - \varpi T \sim T_{\rm c} - T \Rightarrow W_{\rm surface} \sim (T_{\rm c} - T)^{\mu_1'}$$
(9.1.22)

on the condensation line (only). The effect is to replace  $\sigma$  by  $\sigma_1' = \sigma/\mu_1'$  so that one could retain  $\sigma = \frac{1}{2}$  and  $\frac{2}{3}$  in two and three dimensions and obtain agreement with (9.1.21) by taking  $\mu_1' = \frac{15}{16}$  (d = 2) and  $\mu_1' = 1.05 - 1.10$  (d = 3). Furthermore,  $\mu_1' = 1\frac{1}{2}$  would then yield the expected classical behaviour when  $d \to \infty$ . This may have some significance, since a classical van der Waals treatment of the macroscopic surface free energy yields an exponent  $\mu = 1\frac{1}{2}$  (see Widom 1965 a). For the plane Ising models, however, the exactly known macroscopic surface tension exponent  $\mu = 1$  (Onsager 1944) does not quite correspond with the microscopic exponent  $\mu_1'$  needed for agreement with  $\alpha'$ ,  $\beta$  and  $\gamma'$ .

By extending the analysis of (9.1.9) to  $T > T_c$  (all  $\rho$ ) one can also determine the high-temperature droplet-model exponents. These are firstly characterized by the *full symmetry* 

$$\alpha = \alpha', \quad \gamma = \gamma'$$
  

$$\Delta_{2j} = 1 + \frac{1}{2}(\gamma - \alpha_{s}) = \Delta = \Delta' \quad (\text{all } j).$$
(9.1.23)

While such symmetry is undoubtedly correct for the plane Ising models (and also holds for the classical theories), it does seem doubtful for the three-dimensional models since, in particular, the numerical evidence reviewed in §8 indicates

$$\gamma' - \gamma \simeq 0.06 > 0$$
 and  $\Delta' - \Delta \simeq 0.06 > 0$ .

It should be noted, however, that the predicted *constancy* of the gap exponents is observed to hold generally above  $T_{\rm e}$ .

One could again allow for an asymmetry by choosing a different exponent  $\mu_1$  for the (negative) microscopic surface free energy above  $T_c$  when  $\rho = \rho_c$ . Apart from its undesirable *ad hoc* nature this procedure also leads to difficulties on crossing the critical isotherm unless something more elaborate is assumed away from  $\rho = \rho_c$ .

Present experimental evidence is reasonably consistent with the relations (9.1.18) to (9.1.20) and their high-temperature analogue

$$\delta = \frac{2 - \alpha_{\rm s} + \gamma}{2 - \alpha_{\rm s} - \gamma} = \frac{\Delta}{\Delta - \gamma} \tag{9.1.24}$$

although, unfortunately, precise measurements of all the relevant exponents for a single physical system are still lacking and, in particular, the important question of symmetry, or lack of it, has not yet been resolved by observation.<sup>†</sup>

Although there is clearly much left to be understood concerning the droplet picture of the critical point let us, as a last problem, turn to ferromagnetism and try to understand from the droplet viewpoint the results (i) that the *isotropic* two-dimensional Heisenberg model does not exhibit a spontaneous magnetization and (ii) that the values of  $\gamma$  and  $\Delta$  for the three-dimensional Heisenberg model are larger than for the corresponding Ising model (§8).

A 'droplet' now becomes a 'microdomain' of overturned spins and its surface becomes the domain, or Bloch wall. The difference between the diffuse structure of the domain wall in an isotropic ferromagnet and the abrupt spin reversal characterizing the wall in a highly anisotropic ferromagnet is well known. In the isotropic case the mean direction of the spins in the wall turns almost continuously from 'up' to 'down'. Let us consider such a *d*-dimensional 'spherical' domain of radius *ma* containing  $l \sim m^d$  down spins surrounded by a wall of *n* layers which hence contains the order of

$$\mathcal{N} = (m+n)^d - m^d \tag{9.1.25}$$

spins. The change in mean angle between successive layers of the wall spins will be of magnitude  $\Delta \theta = \pi/n$ . As a reflection of the exchange coupling  $|S_1||S_2|\cos\theta_{1,2}$ between adjacent spins we may expect the incremental (free) energy associated with a pair of non-parallel spins to be proportional to  $\cos(\Delta \theta) - 1 \simeq \frac{1}{2} (\Delta \theta)^2$ . (More generally one could suppose the energy is proportional to  $(\Delta \theta)^{\epsilon}$ .) The total wall free energy should thus vary as

$$W_{l} \sim \mathcal{N}(\Delta \theta)^{2} \sim \frac{(m+n)^{d} - m^{d}}{n^{2}}$$
$$\sim \xi^{-2} \{ (1+\xi)^{d} - 1 \} l^{1-2/d} \quad \xi = \frac{n}{m}.$$
(9.1.26)

For d = 2 this expression is minimized by taking *n* indefinitely great so that, however large one makes *l* (and hence *m*), the total wall free energy need never exceed some constant value. This corresponds to an exponent  $\sigma = 0$  in (9.1.2) and

<sup>&</sup>lt;sup>†</sup> Except, perhaps, for the lambda point of <sup>4</sup>He where  $\alpha = \alpha' = 0$ , as discussed. However,  $\gamma$ ,  $\gamma'$ ,  $\Delta$  and  $\Delta'$  are unknown for helium and might not display symmetry.

leads via the previous calculation to a lack of stability of magnetization in zero field.<sup>†</sup> Conversely for d = 3 the energy is minimized by  $\xi = 3^{1/2}$  so that we expect  $W_l$  to vary as  $l^{1/3}$  in place of  $l^{2/3}$  as for the anisotropic case. This leads us to expect a correspondingly larger value of the gap exponent  $\Delta' \simeq 1/\sigma$  and, by the required symmetry, of  $\Delta$  also. Since  $\alpha$  is probably fairly close to zero for both Ising and Heisenberg models, when d = 3 we have  $\Delta \simeq 1 + \frac{1}{2}\gamma$  so that larger values of  $\gamma$  may also be expected to correspond to larger values of  $\Delta$ . However, the difference  $(1/\Delta)_{\text{Ising}} - (1/\Delta)_{\text{Heis}} \simeq 0.09$  is rather smaller than would follow directly from the expected changes in  $\sigma$  so, once again, the simple picture tells only part of the story. In real systems, nevertheless, it is plausible that larger values of  $\Delta$  and  $\Delta'$  will correspond to the more isotropic systems while systems with pronounced anisotropy should exhibit lower values.

Table 13.	Sets of exponents consistent with the various 'homogeneity'	and
	'scaling' relations (listed in order of decreasing $\gamma$ )	

Exponent	Exact Ising	'Heisenl	oerg like'	' Ising lil	ke'	Classical
	(d=2)	$(S=\frac{1}{2})$	$(S = \infty)$	(d = 3)	)	$(d = \infty)$
$\alpha_{s} = \alpha_{s}'$ $\beta$ $\gamma = \gamma'$ $\delta$ $\Delta = \Delta'$	0	$ \begin{array}{r} -0.19 \\ 0.38 \\ 1.43 \\ 4.8 \\ 1.81 \end{array} $	0 <del>13</del> 45 5 1 <del>3</del>	16 56 15 55 15 15 15 8	$\frac{\frac{1}{8}}{\frac{1}{16}}$ 1 $\frac{1}{4}$ 5 1 $\frac{9}{16}$	$\begin{array}{c} 0\\ \frac{1}{2}\\ 1\\ 3\\ 1\frac{1}{2} \end{array}$
$\sigma \  au$	$\frac{8}{15} = 0.53$ $2\frac{1}{15}$	$\begin{array}{c} 0.55\\ 2.21 \end{array}$	$\frac{\frac{3}{5}}{2\frac{1}{5}} = 0.60$	$\frac{\frac{8}{13}}{2\frac{5}{26}} \simeq 0.615$	$\frac{\frac{16}{25}}{2\frac{1}{5}} = 0.64$	2 1 3
$\gamma = \nu'$	1 1	0·73 0·04	0 <del>2</del> 3	$-\frac{1}{31} \simeq -0.032$ 0.6458	$0_{\frac{5}{8}}$	$(-\infty)$

To close this section we list in table 13 various sets of exponent values which are consistent with the relations so far derived from the simple droplet picture. (The relations for the exponents  $\eta$ ,  $\nu$  and  $\nu'$  also listed are discussed below in §§ 9.3 and 9.4.) The two columns headed 'Ising like' represent good fits to the numerical evidence for d = 3 below  $T_c$  and above  $T_c$ , respectively. The columns headed 'Heisenberg like', on the other hand, may be taken as plausible speculations based solely on the estimated values of  $\alpha$  and  $\gamma$  ( $S = \frac{1}{2}$ ), and  $\gamma$  and  $\Delta$  ( $S = \infty$ ). The values of  $\beta \simeq 0.38$  and 0.33 are very suggestive but recall that there is no evidence for them.

## 9.2. Homogeneity arguments

We have discussed a microscopic picture of the critical point which, perhaps, gives some insight into the magnitudes and inter-relations of the critical exponents. By contrast we may also follow a more phenomenological macroscopic approach which will at least show why the exponent relations (9.1.16) to (9.1.20) and (9.1.24) are 'most natural'.

<sup>†</sup> The essence of this argument is given in the book by Wannier (1959) (see also Herring and Kittel (1951, footnote 8 a)).

For simplicity we shall now consider a ferromagnet. Firstly, we recall that above  $T_{e}$  we can always expand the free energy as

$$A(M, T) = a_0(T) + a_2(T) M^2 + a_4(T) M^4 + \dots$$
(9.2.1)

According to the classical approach (§5.1) we may also expand the coefficients in powers of  $T - T_c$  near and at the critical point thus obtaining

$$\left(\frac{\partial A}{\partial M}\right)_{T} = H = 2a_{2,1}(T - T_{\rm c})M + 4a_{4,0}M^{3} + \dots$$
(9.2.2)

where  $a_{2,1}$  and  $a_{4,0}$  are constants. From this, of course, one finds the classical and generally false result  $\beta = \frac{1}{2}$ . To allow for a different value of  $\beta$  we may, following Widom's (1965 b) treatment of the fluid case, modify (9.2.2) near the critical point to read

$$H = bM\{(T - T_{c}) + c | M|^{1/\beta}\}$$
(9.2.3)

where b and c are constants of appropriate dimensions.

It should now be noticed that the factor in curly brackets in (9.2.3) is a homogeneous function (of degree unity) in the variables

$$t = T - T_{\rm c}$$
 and  $u = c |M|^{1/\beta}$ . (9.2.4)

Again following Widom, we postulate that this factor should be replaced by a general homogeneous function  $\Psi(t, u)$  of a degree which, as one easily sees by evaluating the initial susceptibility above  $T_c$ , should be chosen equal to  $\gamma$  rather than to unity. We thus conclude that the equation of state close to the critical point might reasonably have the general form

$$H = M\Psi\{(T - T_{\rm c}), c \,|\, M|^{1/\beta}\}$$
(9.2.5)

with

$$\Psi(\lambda t, \lambda u) = \lambda^{\gamma} \Psi(T, u). \tag{9.2.6}$$

Effectively this same conclusion has been reached by Domb and Hunter (1965) and Domb (1966) following a somewhat similar route. (They also suggested on heuristic grounds that  $\gamma'/\beta$  might always be an even integer but present evidence, reviewed in §8, indicates  $\gamma'/\beta \simeq \delta - 1 \simeq 4.2$  for the three-dimensional Ising model.)

Restrictions on  $\Psi(t, u)$  follow from general considerations: when  $H \neq 0$  or  $M > M_0$  the free energy varies quite smoothly even at  $T = T_c$ . This means one must have a valid Taylor-series expansion

$$\Psi(t,1) = \psi_0 + \psi_1 t + \psi_2 t^2 + \dots \tag{9.2.7}$$

for small t. Similarly the general validity of the expansion (9.2.1) above  $T_c$  implies the existence of the expansion

$$\Psi(1, u) = f_0 + f_1 u^{2\beta} + f_2 u^{4\beta} + \dots$$
(9.2.8)

for small u. Finally, the existence of an initial susceptibility (and higher derivatives) at zero field or  $M = M_0$  below  $T_c$  means that  $\Psi(t, u)$  has the corresponding derivatives on the line u = -t > 0. (For  $T < T_c$ , i.e. t < 0,  $\Psi(t, u)$  is not defined inside the 'coexistence' region |u| < |t|.)

With these results it is now straightforward to deduce the values of the critical exponents  $\gamma'$ ,  $\delta$ ,  $\Delta_4$ ,  $\Delta_6$ , ... and  $\Delta_2'$ ,  $\Delta_3'$ , .... By integrating H with respect to M from some fixed value  $M_1$  (where  $A(M_1, T)$  may be supposed quite regular for all T) to

min  $\{M_0, 0\}$  one can also obtain expressions for the *singular* part of the free energy and hence for the specific heat exponents  $\alpha_s$  and  $\alpha_s'$ . Clearly all these exponents will depend only on  $\beta$  and  $\gamma$ . Indeed, one finds precisely the relations already generated by the droplet picture, namely (9.1.16), (9.1.18) to (9.1.20) and (9.1.24) together with the symmetry (9.1.23). More specifically one finds that  $\alpha_s = \alpha_{s'} = 0$  corresponds to a logarithmic singularity plus, in general, a discontinuity but that in the 'classical case'  $\beta = \frac{1}{2}$ ,  $\gamma = 1$  the logarithmic term may vanish, but need not (Griffiths 1967), leaving only a discontinuity.

At first sight one might think that the symmetry of the exponents about  $T_c$  could be avoided by assuming a different degree of homogeneity above and below  $T_c$ . This allows one to have  $\gamma' \neq \gamma$  but then necessarily implies that the entropy S(T, H) in a non-zero field H has a discontinuity at  $T = T_c$  (Griffiths 1967).<sup>†</sup> This is clearly quite unacceptable.

As observed before, the known exponents for the two-dimensional Ising model are in complete agreement with these 'homogeneity relations', but the apparent lack of symmetry about  $T_c$  in three dimensions seems to mean that the equation of state (9.2.5) cannot be quite generally valid. Nevertheless, it is worth while to explore its consequences a little further.

Using the homogeneity of  $\Psi(t, u)$  we may rewrite (9.2.5) in the form

$$\frac{M}{\mathfrak{m}(T)} = Y_{+} \left( \frac{H}{\mathfrak{h}(T)} \right) \quad (T \ge T_{\mathrm{c}})$$
$$= Y_{-} \left( \frac{H}{\mathfrak{h}(T)} \right) \quad (T \le T_{\mathrm{c}}) \tag{9.2.9}$$

where the 'scaling functions' are

$$m(T) = m_0 |T - T_c|^{\beta}$$
(9.2.10)

and

$$\mathfrak{h}(T) = h_0 | T - T_c |^{\Delta} \quad \Delta = \gamma + \beta \tag{9.2.11}$$

in which  $\Delta$  is again the gap exponent and  $m_0$  and  $h_0$  are constants. The two functions  $Y_+(w)$  are defined in terms of  $\Psi$  through their inverses as

$$Y_{\pm}^{-1}(v) = \frac{m_0}{h_0} v \Psi\{\pm 1, c(m_0 v)^{1/\beta}\}.$$
(9.2.12)

(For simplicity we consider only non-negative M and H.) They are not completely independent functions since (9.2.7) implies that they have the common expansion

$$Y_{\pm}(w) = w^{\beta/\Delta} (1 \pm g_1 w^{-1/\Delta} + g_2 w^{-2/\Delta} \pm \dots)$$
(9.2.13)

for large w. Notice that by (9.1.20),  $\beta/\Delta = 1/\delta$ , so that this form represents the critical isotherm  $M \sim H^{1/\delta}$ . For small w the function  $Y_{-}(w)$  must have a Taylor series in odd powers of w while  $Y_{-}(w)$  is expected to have at least one or two derivatives (assuming  $\chi_0(T)$  exists below  $T_c$ ). Griffiths (1967) has shown how suitable explicit analytic expressions for the functions  $Y_{\pm}$  and  $\Psi$  can be constructed when  $\beta$  is a rational fraction.

† It is a similar difficulty that arises in the droplet picture when the *ad hoc* microscopic surface tension indices are introduced.

Evidently (9.2.9) is stronger than the exponent relations alone since it states a law of corresponding states for the whole critical neighbourhood, i.e. it means that different isotherms near  $T_c$  should map onto one another through the scalings (9.2.10) and (9.2.11). Recent studies of  $CrO_2$  and Ni by Kouvel and Rodbell (1967a, b) have shown that, to within the experimental precision, such scaling functions can, indeed, be found (at least above  $T_c$ ). This is demonstrated in figure 18. It is an important development since it opens the possibility of a fully systematic comparison of the critical behaviour of different physical systems.<sup>†</sup>

#### 9.3. Correlation exponent relations

So far we have considered exponent relations only for the thermodynamic functions but, as already seen in §6.3, the exponents for the decay of the correlation functions can also be interrelated. To recapitulate and extend slightly the previous discussion let us assume that there is only a *single* correlation length  $\kappa^{-1}$  which diverges at the critical point. If we adopt magnetic language we may then, as in §6.3, write the 'scaling relation'

$$\Gamma(\mathbf{r}; T, H) \simeq \frac{D(\kappa r)}{r^{d-2+\eta}} \quad (r \to \infty, \kappa \to 0)$$
(9.3.1)

where  $\kappa^{-1}(T, M)$  satisfies

$$\kappa(T, 0) \sim (T - T_{c})^{\nu} \quad (T \ge T_{c})$$
  

$$\kappa(T_{c}, M) \sim |M|^{\nu_{c}} \quad (T = T_{c})$$
  

$$\kappa(T, 0) \sim (T_{c} - T)^{\nu'} \quad (T \le T_{c}). \quad (9.3.2)$$

By the arguments already given in §6.3 this leads via the fluctuation relation to

$$(2-\eta)\nu = \gamma$$
 and  $(2-\eta)\nu' = \gamma'$  (9.3.3)

and also

$$(2 - \eta)\nu_{\rm c} = \delta - 1. \tag{9.3.4}$$

All these relations are in agreement with the classical predictions. The first two are exact for the Ising model in two dimensions (§6.3) and seem valid in three dimensions above  $T_{\rm e}$  (§8.1). The last relation (9.3.4) has not so far been tested.

The assumption of a single diverging correlation length seems very plausible in a general physical system provided the interactions themselves are fairly simple and do not, in particular, include contributions of drastically different type or range which might none the less co-operate at the transition. To illustrate how the existence of, say, *two* diverging correlation lengths might destroy (9.3.3), let us suppose in place of (9.3.1) that for  $T \ge T_c$ 

$$\Gamma(\mathbf{r}, T, 0) \simeq \frac{D_a(\kappa_a r)}{r^{d-2+\eta_a}} + \frac{D_b(\kappa_b r)}{r^{d-2+\eta_b}}$$
(9.3.5)

where  $D_a(x)$  and  $D_b(x)$  decay exponentially as  $x \to \infty$ . Our asymptotic definition of the true correlation range must then yield

$$\kappa = \min\{\kappa_a, \kappa_b\} \quad \text{and} \quad \nu = \max\{\nu_a, \nu_b\}. \tag{9.3.6}$$

 $\dagger$  Such a study of the existing data for fluids has recently been initiated by Green *et al.* (1967).



Figure 18. Logarithmic plots of scaled magnetization ( $\sigma \equiv M$ ) data just above the Curie point with  $\sigma' = \mathfrak{m}(T) = m_0(T-T_c)^{\beta^+}$  and  $H' = \mathfrak{h}(T) = h_0(T-T_c)^{\Delta}$  for (a)  $\operatorname{CrO}_2$  with  $\beta^+ = 0.34$  and  $\Delta = 1.97$ , and (b) nickel with  $\beta^+ = 0.41$  and  $\Delta = 1.71$ . Broken lines represent limiting behaviour at high and low relative magnetization imposed, respectively, by the measured critical isotherm and by the normalization procedure. It should be noted that  $\operatorname{CrO}_2$  satisfies a scaling law even though the values of  $\gamma$  ( $\simeq 1.6$ ) and  $\delta$  ( $\simeq 5.8$ ) are not typical for ferromagnets.

Similarly the 'true' susceptibility exponent will be

$$\gamma = \max\{\gamma_a, \gamma_b\} = \max\{(2 - \eta_a)\nu_a, (2 - \eta_b)\nu_b\}$$
(9.3.7)

where the analysis of §6.3 has again been used. Finally, the asymptotic criticalpoint decay is determined by

$$\eta = \min\{\eta_a, \eta_b\}. \tag{9.3.8}$$

One may now check that, for example,  $\eta_a = \frac{1}{8}$ ,  $\nu_a = \frac{3}{5}$  and  $\eta_b = \frac{1}{4}$ ,  $\nu_b = 1$  lead to  $\nu = 1$  and  $\gamma = 1\frac{3}{4}$  but  $\eta = \frac{1}{8}$ , which violates (9.3.3).

Might it be possible to express, say,  $\nu'$  and hence, accepting (9.3.3) and (9.3.5),  $\nu$ ,  $\nu$ , and  $\eta$  entirely in terms of the thermodynamic exponents? The following heuristic argument due to Widom (1965 a) suggests the answer may be yes. Let us consider a ferromagnet below  $T_c$  in a vanishingly small field and try to estimate the magnitude of the fluctuations of the magnetization density which occur in a region of linear dimension equal, or proportional to, the correlation length (and hence of volume, or area, about  $\kappa^{-d}$ ). According to general theory the fluctuations in a sufficiently large volume V are given by

$$\langle \Delta M^2 \rangle_V \simeq \frac{k_{\rm B} T \chi_T}{V}.$$
 (9.3.9)

Clearly the linear dimensions of V should be much greater than the range of interaction; the correlation length satisfies this criterion close to  $T_c$ . However, more generally one would expect that the dimensions of V should also be much greater than  $\kappa^{-1}$  (although this question does not seem to have been discussed carefully in the literature). If, none the less, we assume that the correlation length, or some multiple of it, does indeed specify a sufficiently large volume, the right-hand side of (9.3.9) will vary as  $(T_c - T)^{d\nu' - \gamma'}$ . On the other hand, it is natural to suppose that near  $T_c$  the spontaneous fluctuations in an 'up' domain in zero field will be such as to produce quite frequently a coherent but small 'down' domain of dimension proportional to  $\kappa^{-1}$ . Thus we suggest the identification

$$\langle \Delta M^2 \rangle_V \sim M_0^2(T) \sim (T_c - T)^{2\beta}.$$
 (9.3.10)

Combination of these two estimates yields the new relation

$$d\nu' = \gamma' + 2\beta \tag{9.3.11}$$

which, accepting the original relation (9.1.13), can also be written

$$d\nu' = 2 - \alpha_{\rm s}'. \tag{9.3.12}$$

Alternatively (9.3.11) can be rewritten as a relation for  $\eta$ , namely, using (9.3.3),

$$\eta = 2 - \frac{d\gamma'}{\gamma' + 2\beta} \tag{9.3.13}$$

or, accepting (9.1.20),

$$\eta = 2 - \frac{d(\delta - 1)}{\delta + 1} \tag{9.3.14}$$

which is suggestive since it involves only exponents defined for  $T = T_{c}$ .†

<sup>&</sup>lt;sup>†</sup> This last expression for  $\eta$ , but with the additional restriction  $\eta \ge 0$ , has been derived independently by Stell (1967) by neglecting the remainder in a certain functional Taylor-series expansion of the critical-point correlation function. This general approach was introduced by Lebowitz and Percus (1961, 1963) and Percus (1962) who studied the relation to Ornstein-Zernike theory (see the review by Fisher (1964 b)).

Happily these four relations again check precisely for the two-dimensional Ising model. But there are serious difficulties: for large d we should expect, as argued in §5.4, to recover the classical results, namely  $\gamma' = 1$ ,  $\beta = \frac{1}{2}$ ,  $\delta = 3$ , and  $\nu' = \frac{1}{2}$ ,  $\eta = 0$ . Clearly, however, this does not happen. On the contrary  $\eta$  becomes negative and large, which, as regards the critical scattering isotherm, is a rather disquieting prediction since it implies an indefinitely large enhancement for finite **k**. Maybe there is some special non-uniformity for large d that prevents us taking the limit so directly (as suggested by Kadanoff 1966 b) or maybe for some reason, as yet not explained, the heuristic argument applies only in sufficiently low dimensions.<sup>†</sup>

Perhaps more serious is the situation for the three-dimensional Ising model. As discussed,  $\beta = \frac{5}{16}$  is established with quite high precision and it seems certain that  $\gamma' \ge \frac{5}{4}$  and  $\delta \ge 5$  (§ 8.1). The formulae (9.3.13) and (9.3.14) then imply  $\eta \le 0$  (see table 13) which clearly contradicts the positive value (8.1.12) found by Fisher and Burford (1967) (§ 8.1). At present one might still hope that the numerical uncertainties will blunt this contradiction and that when direct estimates of  $\nu'$  are made they will confirm (9.3.11), but this looks somewhat doubtful.

Disregarding these difficulties for the moment, we may point out, following Kadanoff<sup>‡</sup>, an alternative, although perhaps less convincing, fluctuation argument yielding

$$d\nu' = 2 - \alpha'$$
 and  $d\nu = 2 - \alpha.$  (9.3.15)

It should be noted that these specific-heat exponents are *not* those for the singular part, so that (9.3.15) does not always imply (9.3.12). Again we consider a zero-field fluctuation near  $T_c$  in a volume of linear dimension  $\kappa^{-1}$  but now we ask for the temperature fluctuation  $\langle \Delta T^2 \rangle$ . By general theorys this will be inversely proportional to the product of the specific heat per spin and the volume, and hence

$$\langle \Delta T^2 \rangle \sim |T - T_c|^{\alpha + d\nu}$$
 or  $|T - T_c|^{\alpha' + d\nu'}$   $(T \ge T_c)$  (9.3.16)

where, as before, we have assumed that the volume chosen is sufficiently large to justify standard fluctuation theory. One now argues heuristically that the probable temperature fluctuations in such a volume should, most naturally, be of order  $T-T_{\rm c}$ . This immediately yields (9.3.15).

As below the critical point, the Ising model is consistent with (9.3.15) when d = 2, but causes difficulty for d = 3. Using the estimate (8.1.11) for  $\nu$  yields  $\alpha = 0.07 \pm 0.01$  which falls short of the best present estimate (8.1.3) by  $0.055 \pm 0.030$ . (It should be noted that the observed constancy of  $\Delta_{2j}$  (see (8.1.27)) and the previous homogeneity relations independently support the estimate  $\alpha \simeq \frac{1}{8} = 0.125$ .) Some values for  $\eta$  and  $\nu = \nu'$  consistent with the exponent relations are listed in table 13.

## 9.4. Complete scaling of the correlations

In the previous section we reviewed the relations (9.3.3) and (9.3.4) connecting the exponents  $\eta$ ,  $\nu$ ,  $\nu'$  and  $\nu_c$  to the thermodynamic exponents  $\gamma$ ,  $\gamma'$  and  $\delta$ . By somewhat less compelling arguments we also advanced the relations (9.3.11) to (9.3.15)

‡ Kadanoff (1966 b) attributes this thermal fluctuation argument to Pippard and to Ginsberg. We present it here in a slightly different, but more physical, way.

§ See, for example, Landau and Lifshitz (1958, p. 352).

<sup>&</sup>lt;sup>†</sup> See also the footnote to p. 713.

which depend explicitly on the dimensionality. Although on balance one cannot at present be convinced of the general validity of these latter formulae, it is interesting to see how they, and all the previous homogeneity relations, can be derived together in a unified way from effectively one single hypothesis.

We follow Kadanoff's arguments (Kadanoff 1966 b, Kadanoff *et al.* 1967) for a nearest-neighbour spin  $\frac{1}{2}$  Ising model. A related, but somewhat less direct, set of general arguments has been presented by Patashinskii and Pokrovskii (1966). Near the critical point the lattice can be divided into cells labelled  $\rho, \rho', \ldots$  of side *L* satisfying

$$a \ll L \ll \kappa^{-1} \tag{9.4.1}$$

*a* being the lattice spacing. Since  $\kappa \to 0$  at the critical point, it is certainly possible for sufficiently small

$$t = \frac{T - T_{\rm c}}{T_{\rm c}} \tag{9.4.2}$$

to find a wide, although *not* infinite, range of possible L values. (The ability to vary L arbitrarily will, however, be used below.) Now we argue that the properties of an isolated cell which does not interact with neighbouring cells will, since it is finite, not vary very rapidly for sufficiently small t. Furthermore, since  $L \ll \kappa^{-1}$  all the spins in one cell will be well correlated and so we postulate that on average they point mostly 'up' or mostly 'down'. This is a crucial assumption; it is appealing but has not been established more rigorously.

If  $s_r = \pm 1$  is the Ising spin variable for the site **r** our assumption enables us to write

$$\sum_{\mathbf{r}(\mathbf{p})} s_{\mathbf{r}} = \tilde{s}_{\mathbf{p}} \langle s \rangle_L L^d \tag{9.4.3}$$

where the sum runs over sites in the cell  $\rho$  and where  $\tilde{s}_{\rho} = \pm 1$  is a *new* spin variable associated with the whole cell. The mean spin magnitude  $\langle s \rangle_L$  is defined by

$$\langle s \rangle_L^2 = \sum_{\mathbf{r}(\rho)} \sum_{\mathbf{r}'(\rho)} \frac{\langle s_{\mathbf{r}} s_{\mathbf{r}'} \rangle}{L^{2d}}$$
(9.4.4)

and should not vary significantly with t near the critical point.

We are now in a position to map the original Ising problem with spins  $s_r$ , reduced temperature t and reduced field

$$h = \left(\frac{g\beta_{\rm B}}{k_{\rm B}T}\right)H\tag{9.4.5}$$

into a new Ising problem for the cells, with spin variables  $\tilde{s}_{\rho}$  and reduced temperature and field  $\tilde{t}$  and  $\tilde{h}$ . This entails, of course, the assumption that the complicated interactions through the cell interfaces in the original lattice can be represented by a bilinear cell-cell interaction term  $\tilde{s}_{\rho}\tilde{s}_{\rho'}$  with an interaction energy that is not too singular a function of t, h and L. Of course, this also is very hard to prove. (It should be mentioned that Buckingham (1966) has independently argued that a fluid system with short-range forces can be mapped into a nearest-neighbour Ising model.)

From (9.4.3) it is clear that

$$\tilde{h} = \tilde{h}(t, h, L) = h \langle s \rangle_L L^d$$
(9.4.6)

and

$$\langle s_{\mathbf{0}} s_{\mathbf{r}} \rangle \simeq \langle s \rangle_{L^{2}} \langle \tilde{s}_{\mathbf{O}} \tilde{s}_{\mathbf{\rho}} \rangle \tag{9.4.7}$$

where **0** is in cell **O** and **r** in cell  $\rho$ . In terms of the correlation function  $\Gamma(r, t, h)$  for the Ising model this can finally be rewritten as

$$\Gamma(r,t,h) \simeq \langle s \rangle_L^2 \Gamma\left(\frac{r}{L,\bar{t},\bar{h}}\right). \tag{9.4.8}$$

From this basic scaling relation all the previous formulae for the exponents can be derived by simply noting that the right-hand side must be independent of the choice of L.

Thus by letting t = h = 0 and using the definition of  $\eta$  we see that  $\hat{t}(0, 0, L) = 0$  and that

$$\langle s \rangle_L \simeq L^{-\psi} \quad \psi = \frac{1}{2}(d-2+\eta).$$
 (9.4.9)

Summing (or, effectively, integrating) on  $\mathbf{r}$  and using the fluctuation relation yields for the susceptibility

$$\chi_T(t,h) \simeq L^{2-\eta} \chi_T(\tilde{t},hL^{d-\psi}).$$
 (9.4.10)

When h = 0 we have (essentially by definition)  $\chi_T \sim t^{-\gamma}$  for t > 0. This implies

$$\tilde{t} \simeq L^{\phi} t \quad \phi = \frac{2 - \eta}{\gamma}.$$
 (9.4.11)

Since we expect the effective interaction constant between cells for *finite* fixed L to be a non-singular function of temperature, the exponent  $\phi$  should not depend on the sign of t. Using the definition of  $\gamma'$  below  $T_c$  we are thus led to expect the symmetry  $\gamma = \gamma'$ . Eventually, however, we would have to impose symmetry in any case for the reasons given previously in connection with the original homogeneity formula (9.31) (Griffiths 1967).

If we return to (9.4.8), use (9.4.6), (9.4.9) and (9.4.11) and choose L proportional to r, as we may, we obtain the full correlation scaling law

$$\Gamma(r,t,h) \simeq r^{-d+2-\eta} G\left(tr^{\phi}, \frac{h}{r^{\psi-d}}\right) \quad (r \to \infty; t, h \to 0). \tag{9.4.12}$$

Evidently the scale of r, and hence the correlation length, in zero field is determined by  $t^{-1/\phi}$  which leads to the identification

$$\nu = \frac{1}{\phi} = \nu'. \tag{9.4.13}$$

The relations (9.3.3) between  $\gamma$ ,  $\gamma'$ ,  $\eta$  and  $\nu$ ,  $\nu'$  are then a consequence of (9.4.11).

Now, choice of L proportional to  $t^{-\nu}$  in (9.65) shows that

$$\chi_T(t,h) \simeq t^{-\nu} X\left(\frac{h}{t^{\frac{1}{2}(d\nu+\gamma)}}\right) \tag{9.4.14}$$

where X is a function of a single variable. On integration from some  $h_1$ , where  $M(t, h_1)$  is non-singular, we obtain near the critical point,

$$M(t,h) \simeq t^{\frac{1}{2}(d\nu-\gamma)} Y\left(\frac{h}{t^{\frac{1}{2}(d\nu+\gamma)}}\right)$$
(9.4.15)

where Y is again a function of one variable. This is of precisely the form of the previous thermodynamic scaling relation (9.3.9) and we immediately make the further identifications  $2\beta = d\nu - \gamma$ 

and

$$\Delta = \Delta' = \frac{1}{2}(d\nu + \gamma) = \gamma + \beta \tag{9.4.16}$$

which should be compared with (9.3.9) and (9.2.11). Lastly, as in the original homogeneity analysis, we may integrate again to obtain the free energy and thence the final relations

$$d\nu = 2 - \alpha_{\rm s} = 2 - \alpha_{\rm s}',\tag{9.4.17}$$

which are to be compared with (9.3.12) and (9.3.15).

# Table 14. Summary of exponent relations and agreement with relative numerical data

	Formulae	d = 2	ng (d = 3)	Classical limit $(d = \infty)$
(a)	$ \begin{cases} \$ 9.1, 9.2 \\ \alpha_{s}' + 2\beta + \gamma' = 2 \\ \alpha_{s}' + \beta(1+\delta) = 2 \\ \delta = 1 + \gamma'/\beta = \Delta'/\beta \\ \Delta_{k}' = \beta + \gamma' = \Delta'  (k = 1, 2,) \end{cases} $	(~ _)		
	$\Delta_{2j} = 1 + \frac{1}{2}(\gamma - \alpha_{\rm s}) = \Delta$ $(j = 1, 2,)$	yes	yes	yes
(b)	$ \begin{cases} \$ 9.3, \ 9.4 \\ (2 - \eta) \nu = \gamma \\ (2 - \eta) \nu' = \gamma' \end{cases} $	yes	yes	yes
( <i>c</i> )	§ 9.1 $\delta = (2 - \alpha_{\rm s} + \gamma)/(2 - \alpha_{\rm s} - \gamma) = \Delta/(\Delta - \gamma)$	yes	(?)	yes
( <i>d</i> )	§§ 9.1, 9.2, 9.4	yes	?	yes
(e)	$\begin{split} & \$\$ 9.3, 9.4 \\ & d\nu' = \gamma' + 2\beta,  d\nu' = 2 - \alpha_{\rm s}' \\ & \eta = 2 - d\gamma'/(\gamma' + 2\beta) = 2 - d(\delta - 1)/(\delta + 1) \\ & d\nu = 2 - \alpha,  d\nu' = 2 - \alpha' \end{split}$	yes	?	no

## 9.5. Summary

The most important conjectural exponent relations discussed in this section are displayed in table 14 where they are grouped together in an order which represents roughly the weight of theoretical argument and evidence supporting them. The apparent consistency with the numerical values for the d = 2 and d = 3 Ising models and with the classical predictions, which it was argued should correspond to  $d \rightarrow \infty$ , is indicated by the comments in the appropriately headed columns (see also table 13; note that a query indicates serious doubts.)

Those relations involving the dimensionality directly seem most open to question, but it is remarkable that they are satisfied exactly by the planar Ising models. Furthermore, the discrepancies in three dimensions are rather small although at present they seem quite definite. This and the behaviour for  $d \rightarrow \infty$  might mean that in higher dimensions one also needs to introduce a characteristic area, volume, etc. (up to, perhaps, a (d-1)-dimensional manifold) with a temperature dependence not directly related to that of the correlation length and its powers. Some similar idea might also correct the droplet picture in the limit of large d and thereby also improve its representation of the values of  $\Delta$  in two and three dimensions. Whether such speculations are useful lines of thought for future progress remains to be seen, but it may be hoped that the heuristic arguments already developed will either be strengthened into real proofs or further analysed to reveal in detail why they fail. New and more powerful ideas are needed for the complete general calculation of the critical exponent values, recognizing their dependence on the crucial features of the interactions as well as on the dimensionality. Until this goal is achieved our theoretical understanding of critical phenomena will remain seriously incomplete.

# 10. Conclusions and outlook

In the foregoing sections we have discussed the theory of equilibrium critical phenomena with main emphasis on 'simple' systems characterized by a single dominant interaction of short range. In reviewing our conclusions and attempting to map future progress we shall also mention some aspects of the equilibrium behaviour that have been omitted or touched on only in passing. Finally, we shall highlight some of the problems of the theory of *non*-equilibrium critical phenomena which have not been considered at all in this article.

# 10.1. Equilibrium phenomena

Firstly, as to the successes of present theory, the close analogies between critical phenomena in different systems have been given a firm theoretical base and the way is open to understand the often relatively small quantitative differences of behaviour in terms of essential differences in the Hamiltonians. The defects of the classical treatments (and their limiting validity) have been thoroughly revealed and understood theoretically. Numerical calculations on the Ising and Heisenberg models have brought the predicted critical exponents very close to those observed experimentally, especially in the case of binary metallic alloys. One can be confident that the deviations now observed between theory and experiment are consequences of oversimplifications of the models (rather than deficiencies of calculation). The strong influence of dimensionality has been clearly demonstrated in connection with the Ising model. Indeed, while a solution for the two-dimensional Ising model in an arbitrary magnetic field would still be valuable, our knowledge of the analytic critical-point behaviour is already almost complete. In three dimensions any analytic results would, however, have great value if only as a check on the numerical extrapolations. Nevertheless, for the Ising model present numerical results are again almost complete and seem quite precise. The most notable conclusion to be drawn from them is the probable lack of symmetry of the critical exponents about  $T_{\rm e}$ . As discussed at length in the previous section, this casts doubt on the validity of the homogeneity and scaling theories of the critical point which otherwise look so promising. While we may expect further technical developments leading to longer series and improved extrapolation procedures, the differences around  $T_{\rm e}$  (if real) are sufficiently small that only rigorous analytical arguments seem likely to allay all reasonable doubts regarding the asymmetry (or on the contrary to prove that symmetry is actually realized). Experimentally, however, there remains much scope for resolving the question of symmetry for fluids, magnets, etc., by detailed measurements on carefully chosen single systems.

The dependence of the critical-point exponents on the Hamiltonian (as well as the dimensionality) is demonstrated by the results for the Heisenberg model. Although some light is thrown on these effects by the droplet picture, much remains to be elucidated and understood. One may expect that further numerical work will confirm present estimates above  $T_{\rm c}$  and reveal more clearly the dependence on spin and anisotropy (and hence yield interesting results for quantal lattice gases). Undoubtedly, however, the most urgent need is for a systematic approximation scheme for determining the critical behaviour of the Heisenberg model *below*  $T_{\rm c}$ .

To go forward it is now also necessary to try to calculate reliably for somewhat more realistic models. It seems premature to hope for rapid progress on the continuum-gas models in the critical region, although the deviations of the observed critical exponents from the lattice-gas results make this very desirable. As a first step, lattice gases with hard cores of larger size (relative to the lattice spacing) as well as attractive interactions might well be studied, although the intervention of crystalline lattice ordering will probably still complicate the problem.<sup>†</sup> For ferromagnets and antiferromagnets an important but difficult task is the development of the theory of band- or spin-delocalized itinerant-electron magnetic models to the point where useful critical-point predictions can be made. Present theories have essentially not gone beyond the mean field approach (e.g. Izuyama and Kubo 1964, Fedders and Martin 1966). On the other hand, less realistic, but mathematically more tractable, models should still be devised and pursued since their properties, if accurately determined, will doubtless be useful in deepening our understanding of the interplay between dimensionality and the specific features of the model Hamiltonian even if these are not too realistic.

In this connection we have already discussed briefly in §2.9 the characteristically different critical behaviour of superconductors and ferroelectrics. We did not, however, consider separately 'dipolar magnets' in which the long-range magnetic dipole-dipole interactions play a significant role in the ordering. Since such systems have very low critical temperatures they can be studied experimentally in relatively large (on the scale  $k_{\rm B}T_{\rm c}/g\beta_{\rm B}$ ) magnetic fields. Wolf and co-workers (e.g. Wolf and Wyatt 1964) have done notable work on the highly anisotropic (Ising-like) antiferromagnet dysprosium aluminium garnet. Although the changes, if any, in the critical exponents have not yet been fully determined, the existence of

<sup>&</sup>lt;sup>†</sup> It may be mentioned that lattice gases with hard cores of increased size but with *no* attractive interactions have been studied in some detail (Gaunt and Fisher 1965, Runnels 1965, Bellemans and Nigam 1966, Ree and Chesnut 1966). These results are presumably relevant to the 'melting' of continuum hard-core fluids studied extensively by Monte Carlo and direct computer simulations (e.g. Alder and Wainwright 1960, 1962, Wood and Jacobson 1957), but not to critical phenomena.

a lambda line of critical points terminating at a 'hypercritical' point where the transition becomes first order has been clearly revealed (Keen *et al.* 1966). The extension and testing of the homogeneity laws for such transition points present an interesting problem.

A related general question concerns the effects on the critical point of interactions with 'background' degrees of freedom, particularly the mechanical-elastic modes of motion. Thus in certain cases a dependence of the magnetic coupling parameter J on the lattice spacing can apparently 'split' the ferromagnetic Curie point into two critical points at fields  $\pm H_c$  leaving a first-order transition point (actually a triple point) in zero field.<sup>†</sup>

The effects on critical points of 'secondary' external fields (which are not directly related to the ordering) are of general theoretical interest and also of value because of the insight into the microscopic mechanisms that may be obtained. Gravitational fields have been investigated in connection with gas-liquid critical points (where they are essentially unavoidable) by, notably, Schneider, Schmidt and Lorentzen.<sup>‡</sup> Non-local effects seem not yet to have been detected but might be expected theoretically very close to  $T_{\rm e}$ . Recently Debye and Kleboth (1965) have measured the change in light scattering from a binary fluid critical mixture under an external *electric* field; so far their results have been interpreted satisfactorily by a classical theory but, with developments of the technique, new aspects of non-classical behaviour should be revealed.

A different type of external field is that associated with the boundaries or walls of a system. Theoretically the boundary free energies have been calculated explicitly for the plane Ising lattice and are found to exhibit strong critical anomalies (Fisher and Ferdinand 1967). Intimately related to the direct boundary effects are the limitations on the magnitudes of the specific heat and other ideally infinite anomalies by the finite size of a system (Domb 1965 a, b, c, Fisher and Ferdinand 1967). As already mentioned, this may be one factor in the unexplained rounding of observed magnetic specific-heat anomalies and merits further theoretical and experimental exploration.

The inhomogeneous region near a wall is, at least superficially, similar to the *interfacial* region between two conjugate phases below a critical point. The close link between the interfacial free energy (surface tension) and the other thermodynamic properties near the critical point has already been seen in the discussion of the droplet picture (§9.1). For the plane-lattice Ising model, as mentioned, the surface free energy is known (Onsager 1944, Fisher and Ferdinand 1967). The classical theory of the interface due to van der Waals has been extended by Widom (1965 b) to allow for general values of the thermodynamic exponents. A scaling hypothesis, which is again checked by the Ising model in two dimensions, leads to a prediction for the sharp growth of the interfacial thickness as  $T_{\rm e}$  is approached.

<sup>†</sup> See Bean and Rodbell (1962), de Blois and Rodbell (1963) and the conference paper by Garland and Renard and the subsequent discussion (in Green and Sengers 1966), where references to earlier theoretical and experimental work are given. So far only more or less classical theoretical treatments have been developed.

<sup>‡</sup> See Weinberger and Schneider (1952), Schneider and Habgood (1953), E. H. W. Schmidt (in Green and Sengers 1966), and Lorentzen (1965). Lorentzen and Hanson (in Green and Sengers 1966) and Voronel' and Giterman (1965) have studied the gravitational effects on binary fluid systems.

This in turn has recently been tested experimentally by Gilmer *et al.* (1965). Further developments, both experimental and theoretical<sup>†</sup>, along these lines may be expected and should yield valuable insight into the effects of dimensionality. (Experimental studies of *surface* phases and their one-dimensional interfaces would also be most instructive.)

Finally, under equilibrium phenomena one should note the 'dilution' effects that occur when, for example, a second molecular species is added near a gas-liquid critical point. In this connection Chashkin *et al.* (1965) have reported peculiar structure in the specific-heat anomalies which, if not an artefact, demands a theoretical interpretation. The three-component or ternary fluid system presents a somewhat similar case. The critical behaviour of dilute ferromagnetic alloys (e.g. iron plus a non-magnetic metal) has been studied to some extent experimentally (e.g. Craig *et al.* 1965) but theoretical work has so far been confined mainly to estimating the lowering of the critical temperature on dilution (see, for example, Morgan and Rushbrooke 1963).

#### 10.2. Non-equilibrium phenomena

Non-equilibrium phenomena near critical points may be divided roughly into macroscopic and microscopic aspects. Under the former heading is the question of the existence and nature of critical anomalies in the transport coefficients, for example the viscosity, the thermal conductivity, the diffusion coefficients, etc. Under the latter heading may be placed the behaviour of relaxation times for atomic and molecular processes, resonance linewidths, ultrasonic attenuation and inelastic scattering, particularly by light and by neutrons. Theoretically it is now clear that in all these cases it is the time and space (or frequency and wave-number) dependence of the underlying correlation functions for two (or sometimes a few) particles, spins, etc., that is relevant. Thus Van Hove (1954 a, b) has shown how the inelastic scattering from a fluid is determined by the function

$$S(\mathbf{k},\omega) = \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp\left\{i(\mathbf{k}\cdot\mathbf{r}-\omega t)\right\} G(\mathbf{r},t)$$
(10.2.1)

where  $G(\mathbf{r}, t)$  is the correlation between a particle at the origin at time t = 0 and one at  $\mathbf{r}$  at time t. The development of formal expressions for the transport coefficients as integrals over time-correlation functions (see the excellent review by Zwanzig (1965)), demonstrates that macroscopic non-equilibrium phenomena are to be understood in principle from the same standpoint. Most existing theories, however, have not advanced far beyond macroscopic and semi-phenomenological descriptions of the type found to be unsatisfactory for equilibrium phenomena. Thus, in their original discussion of Brillouin scattering in fluids, Landau and Placzek<sup>‡</sup> assumed that the microscopic fluctuations obeyed the bulk hydrodynamic equations. This implies that fluctuations of wave vector  $\mathbf{k}$  propagate essentially as independent normal modes but subject to exponential damping with decay times  $\tau(\mathbf{k})$ . Corresponding to the assumed exponential decay, frequency line shapes are

<sup>&</sup>lt;sup> $\dagger$ </sup> A more detailed theoretical interpretation of the diffuse interface in terms of capillary waves has been advanced by Buff *et al.* (1965).

<sup>‡</sup> See, for example, Frenkel (1964 b), Landau and Lifshitz (1959, 1960).

commonly predicted to be of characteristic Lorentzian shape, i.e. proportional to  $(1 + \tau^2 \omega^2)^{-1}$ .

This picture of the fluctuations, which is a natural generalization of the Ornstein-Zernike theory, works very well in normal circumstances but might be expected to break down near a critical point. In some respects this has already been found. Thus in a fluid the lifetime  $\tau(\mathbf{k})$  of the diffusive (non-propagating) mode is found theoretically to vary as  $\rho C_{\rm p}/\lambda k^2$  where  $\lambda$  is the thermal conductivity which is presumed to remain constant through the critical region. Since  $C_p$  diverges like  $K_T$ , i.e. as  $(T - T_c)^{-\gamma}$  when  $\rho = \rho_c$ , a marked 'thermodynamic slowing down' of the fluctuations is predicted near  $T_{\rm e}$ . This is indeed observed, but, at the same time, the thermal conductivity  $\lambda$  is also found to be divergent although more weakly than  $C_{\rm p}$  (see Michels *et al.* (1962) who discovered that  $\lambda$  varies approximately as  $C_{\rm v} \sim -\ln|T - T_{\rm c}|$ .) In the analogous theory for a ferromagnet (Van Hove 1954 a, b) a similar thermodynamic slowing down is predicted since  $\tau(\mathbf{k})$  should now vary as  $\chi_{\tau}(T)/k^2$ . Consequently the *inelastic* part of the critical scattering of neutrons is expected to vanish as  $T \rightarrow T_c$ . However, Jacrot *et al.* (1962) and Passel *et al.* (1965) have found that the inelastic linewidth for iron remains finite and essentially constant up to the Curie point. At present the reason for this marked discrepancy is not really understood.

Again the extent to which different systems have, or should have, analogous non-equilibrium critical behaviour is not clear. Thus, Sengers (in Green and Sengers 1966) has pointed out that while the thermal conductivity of simple fluids has a definite critical anomaly the viscosity exhibits at most a very minor one. Conversely for binary fluid mixtures large anomalies have been found in the viscosity of several systems but none has been seen in the thermal conductivities.

Added impetus to the development of improved theories has been given recently by the development of new and very precise experimental techniques. Most notable is the use of lasers by Ford and Benedek (1965) and Alpert *et al.* (1965) to study inelastic light scattering at the critical points of pure fluids and binary mixtures. Nuclear magnetic resonance methods have also given valuable information very close to critical points (e.g. Heller and Benedek 1962, Heller 1966, Noble and Bloom 1965). For recent surveys of these and other techniques the reader should consult the *Proceedings of the Washington Conference on Phenomena in the Neighborhood of Critical Points* (Green and Sengers 1966), to which we have already referred on numerous occasions. The *Proceedings* also contains theoretical discussions of relaxation and inelastic processes in magnets by Marshall and by Heller. A theory of non-equilibrium critical processes in fluids, particularly ultrasonic absorption, has been presented and reviewed by Fixman (1964). Attention should also be drawn to more recent theoretical work by Kawasaki (1966 a, b, c).

In conclusion it is fair to say that both the theoretical and experimental situation for non-equilibrium critical phenomena is some one to two decades behind that for the equilibrium phenomena—perhaps more, since already over twenty years have passed since Onsager's exact solution for the square Ising lattice which opened the modern era of critical-point studies. Optimistically we may hope that the next decade may bring comparable progress in the study of time-dependent phenomena. Although the problems seem hard there is no doubt that the challenge should be accepted.
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## Exponent definitions and values

Exponent	Definitions and experimental data		Exact and approximate theoretical values					
	$\Delta T = \mid T$ Gas–liquid	- T <sub>c</sub>   Ferromagnet	Classical theory	Ising $(d = 2)$	Ising $(d = 3)$	Heisenberg (d = 3) $(S = \infty)$	Heisenberg (d = 3) $(S = \frac{1}{2})$	Exponent
below $T_{\rm e}$	at coexistence $T \rightarrow T_c - T_c$	$H = 0, T \rightarrow T_{\rm c} -$						below $T_{\rm c}$
α'	$C_V \sim \Delta T^{-lpha' \simeq 0(\log)}$	$C_H \sim \Delta T^{-\alpha' \simeq 0 (\log)}$	0 (discon.)	0 (log)	$\frac{1}{16}$ +0.16 16 -0.035			α'
β	$ ho_{ m L} -  ho_{ m G} \sim \Delta T^{eta \simeq 0.34}$	$M_0(T) \sim \Delta T^{\beta \simeq  0.33}$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{5}{16} + 0.003$			β
$\gamma'$	$K_T \sim \Delta T^{-\gamma' \gtrsim 1\cdot 2}$	$\chi_T \sim \Delta T^{-\gamma'}$	1	$1\frac{3}{4}$	$1\frac{5}{16}$ $\frac{+0.03}{-0.05}$			γ
ν'	$\kappa(T) \sim \Delta T^{\nu'}$	$\kappa(T) \sim \Delta T^{\nu'}$	$\frac{1}{2}$	1	$(0.675 \substack{+0.02\\-0.03})$			$\nu'$
$\Delta'$	$\hat{\partial}^{3} p / \hat{\partial} \mu^{3} \sim \partial K_{T} / \hat{\partial} p \sim \Delta T^{-\gamma' - \Delta'}$	$\partial^3 F/\partial H^3 \sim \Delta T^{-\gamma'-\Delta'}$	1 <del>1</del>	17				$\Delta'$
at $T = T_{\rm c}$	$ ho  ightarrow  ho_{ m c}$	$M \rightarrow 0$						at $T = T_{\rm c}$
δ	$ p-p_{\rm c}  \sim  \rho-\rho_{\rm c}^{\delta \simeq 4\cdot 2} $	$ H  \sim  M ^{\delta^{\gtrsim 4\cdot 2}}$	3	15	$5\frac{1}{5} \pm 0.15$			δ
η	$I_{\rm c}({f k})/I_0({f k}) \sim 1/k^{2-\eta}$	$oldsymbol{\hat{\chi}_{c}}(\mathbf{k}) \sim 1/k^{2-\eta}$	0	14	$\frac{1}{18} \pm 0.008$	$0.075 \pm 0.035$	$\simeq 0.08$	η
	$G_{\mathbf{c}}(\mathbf{r}) \sim r^{-(d-2+\eta)}  \eta \gtrsim 0$	$\langle S_{0^{\mathbf{z}}} S_{\mathbf{r}^{\mathbf{z}}} \rangle \sim r^{-(d-2+\eta)}  \eta \gtrsim 0$						
above $T_{ m c}$	$ ho =  ho_{ m c}, \ T  ightarrow T_{ m c} +$	$H = 0, T \rightarrow T_{\rm c} +$						above $T_{ m c}$
α	$C_V \sim \Delta T^{-\alpha \ge 0}$	$C_H \sim \Delta T^{\alpha \simeq 0}$	0 (discon.)	0 (log)	$\frac{1}{8} \pm 0.015$	≃0 (?)	≃0 (?)	α
γ	$K_T \sim \Delta T^{-\gamma \gtrsim 1 \cdot 2}$	$\chi_T \sim \Delta T^{-\gamma \simeq 1.35}$	1	1 <u>3</u>	$1\frac{1}{4} \pm 0.003$	$1.33 \pm 0.01$	$1.43 \pm 0.04$	γ
ν	$\kappa(T) \sim \Delta T^{-\nu \ge 0.6}$	$\kappa(T) \sim \Delta T^{-\nu \gtrsim 0.66}$	$\frac{1}{2}$	1	$\frac{9}{14} \pm 0.0025$	$0.692 \pm 0.012$	$\simeq 0.74$	ν
Δ		$\partial^4 F / \partial H^4 \sim \Delta T^{-\gamma - 2\Delta}$	11	1 <del>7</del>	$1\frac{9}{16} \pm 0.03$		$1.81 \pm 0.05$	Δ