

Separation of the Interaction Potential into Two Parts in Statistical Mechanics. II. Graph Theory for Lattice Gases and Spin Systems with Application to Systems with Long-Range Potentials*

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The methods developed in a previous paper for treating systems with a pair potential of the form $v(r) = q(r) + w(r)$ are here applied to lattice gases (isomorphic to Ising systems). We chose $q(r)$ to be the "hard-core" potential preventing the multiple occupancy of a lattice site and $w(r)$ the interaction between two particles (or parallel spins) separated by r . The resulting graphical formalism is similar to that obtained by other authors exclusively for spin systems. We are thus able to connect their work with the general Mayer theory as it was originally applied to fluids and also to find new interpretations for some of the quantities appearing in the spin-system expansion. The formalism is then used in the case where $w(r)$ is a "Kac potential" of the form $w(r, \gamma) \sim \gamma^v \phi(\gamma r)$, where v is the dimensionality of the space considered and γ^{-1} is the range or w , assumed very large. We then obtain systematic expansions in γ for the correlation functions and thermodynamic properties of the system. These expansions are, however, invalid inside the two-phase region and near the critical point of the "van der Waals" system; i.e., a system with $\gamma \rightarrow 0$. To remedy this we introduce a new self-consistent type of approximation which is suggested by our graphical analysis of the γ expansion but is applicable also to systems with general interactions $w(r)$, not necessarily parametrized by γ . The spatially asymptotic behavior of the two-body correlation function at the critical point is then discussed using these graphical methods. From the expansion procedures it seems possible to find specific subsets of graphs which will give any desired asymptotic behavior of the two-body correlation function including known exact ones. However, we could find no *a priori* reason for the retention of these subsets of graphs to the exclusion of all others.

I. INTRODUCTION

IN Part I of this series¹ of papers, a systematic method was developed for investigating the correlation functions and the thermodynamic properties of a classical system of particles interacting via a pair potential $v(r)$, which may be usefully considered as composed of two distinct parts: a "short-range" part $q(r)$ and a "long-range" part $w(r)$,

$$v(r) = q(r) + w(r). \quad (1.1)$$

It is the purpose of this paper to apply these methods, with new extensions, to a system of particles whose positions are confined to a regular lattice, i.e., a lattice gas.

The motivation for dividing $v(r)$ into two parts is to take advantage of the fact that in many cases the properties of the reference system, i.e., a system for which the interparticle potential is $q(r)$, are better known than those of the actual system with interaction $v(r)$. As shown in I, we can express the

properties of the actual system in terms of $w(r)$ and the properties of the reference system by noting that the decomposition of $v(r)$ into the form (1.1) induces a corresponding decomposition of the correlation functions (i.e., the modified l -particle Ursell functions, \hat{F}_l) into short-ranged and long-ranged parts,

$$\hat{F}_l = \hat{F}_l^s + \hat{F}_l^L, \quad l = 2, 3, \dots$$

The full \hat{F}_l can be represented as a sum of graphs composed of "long-range" potential bonds that represent $\Phi(r) \equiv -\beta w(r)$, [$\beta = 1/kT$], and "hypervertices" that represent the \hat{F}_l^s . The latter functions can in turn be expressed in terms of Φ and the correlation functions of the reference system.

Applying to lattice gases the formalism developed in I for continuum fluids, we identify (unless otherwise stated) the short-range part of the interparticle potential $q(r)$ with the "hard-core" repulsion, which excludes the multiple occupation of a lattice site,

$$q(r) = \begin{cases} \infty, & r = 0, \\ 0, & r \neq 0. \end{cases} \quad (1.2)$$

$w(r)$ then represents the total *finite* interaction between two particles at different lattice sites. This identification of $q(r)$ and $w(r)$ greatly simplifies the structure of the "hypervertices," enabling us to

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¹ J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.* **6**, 1282 (1965); referred to as I; e.g., Eq. (I-3.1) refers to Eq. (3.1) in I.

develop new methods for their evaluation. It also makes this lattice gas, confined to a volume Ω (i.e., Ω lattice sites) at fugacity z isomorphic to a system of Ising spins² interacting with a pair potential $w(\mathbf{R} - \mathbf{R}')\sigma(\mathbf{R})\sigma(\mathbf{R}')$ and subject to a uniform external magnetic field H with

$$z \equiv \exp(\beta H + \frac{1}{2}\beta\alpha'). \quad (1.3)$$

Here, \mathbf{R} is a vector characterizing a particular lattice site, $\sigma(\mathbf{R})$ is a spin variable, $\sigma(\mathbf{R}) = \pm \frac{1}{2}$, and

$$\alpha' \equiv \sum_{\mathbf{R}'} w(\mathbf{R} - \mathbf{R}'). \quad (1.4)$$

Calling $\Xi(\beta, z, \Omega)$ the grand partition function of the lattice gas and $Q(\beta, H, \Omega)$ the canonical partition function of the spin system, we have

$$\Omega^{-1} \ln \Xi = \frac{1}{2} \ln z + \Omega^{-1} \ln Q - \frac{1}{8}\alpha'\beta. \quad (1.5)$$

In the thermodynamic limit $\Omega \rightarrow \infty$, (1.5) assumes the form

$$\beta p = \frac{1}{2} \ln z - \beta \Psi - \frac{1}{8}\alpha'\beta, \quad (1.6)$$

where p is the pressure of the lattice gas, and Ψ is the Helmholtz free energy per spin of the spin system.

The equality (1.5) is based on the relation between the microscopic density operator of the lattice gas $\rho(\mathbf{R})$, which can only assume the value zero or unity and the spin variable at the R th site $\sigma(\mathbf{R})$,

$$\rho(\mathbf{R}) = \sum_i \delta(\mathbf{R} - \mathbf{r}_i) = \sigma(\mathbf{R}) + \frac{1}{2} = (0, 1), \quad (1.7)$$

where \mathbf{r}_i is the position of the i th particle, and $\delta(\mathbf{r})$ is the Kroenecker delta function. It follows immediately from (1.7) that the one-particle distribution function of the lattice gas³ is

$$n_1(\mathbf{R}) = \langle \rho(\mathbf{R}) \rangle = \langle \sigma(\mathbf{R}) \rangle + \frac{1}{2},$$

$$\langle N \rangle = \sum_{\mathbf{R}} n_1(\mathbf{R}) = \rho \Omega = M + \frac{1}{2}\Omega, \quad (1.8)$$

where $\langle \sigma(\mathbf{R}) \rangle$ is the average magnetization at the site \mathbf{R} , $\langle N \rangle$ is the average number of particles in the system, and M is the total magnetization. Similarly,³

$$\hat{F}_2(\mathbf{R}, \mathbf{R}') \equiv \langle \rho(\mathbf{R})\rho(\mathbf{R}') \rangle - \langle \rho(\mathbf{R}) \rangle \langle \rho(\mathbf{R}') \rangle$$

$$= \langle \sigma(\mathbf{R})\sigma(\mathbf{R}') \rangle - \langle \sigma(\mathbf{R}) \rangle \langle \sigma(\mathbf{R}') \rangle, \quad (1.9)$$

and generally, $\hat{F}_l(\mathbf{R}_1, \dots, \mathbf{R}_l)$ is equal to the l th spin semi-invariant for $l \geq 2$. This isomorphism makes the entire formalism developed in I, specialized to lattice gases, immediately applicable to spin

systems and directly comparable with other formalisms developed specifically for the Ising problem. It is one of the aims of the present work to show the way in which our formalism is related to and generalizes a number of specific Ising spin (lattice-gas) results previously derived by other authors.⁴

Our work on lattice systems will be presented in two parts to be referred to as II (this paper) and III (a paper to follow), with II devoted to formally rigorous results, and III to approximation methods.

In Sec. II of this paper, we obtain the general graphical expressions for the correlation functions and thermodynamic properties of a lattice system in terms of graphs with Φ bonds and \hat{F}_i^* hypervertices. It is also shown there how to express the \hat{F}_i^* as functionals of Φ and of the density derivatives of \hat{F}_i^0 , the modified Ursell function of the reference system. For the situation considered here, with $q(\mathbf{r})$ given by (1.2), the reference system is an ideal lattice gas, making the \hat{F}_i^0 polynomials in the density ρ . Comparison with other work is also made here; the \hat{F}_i^* coinciding with the cumulants \bar{M}_i of Horwitz and Callen and of Englert.

While our expansions do not depend upon the introduction of any particular parametrization, they are especially well suited for use in the case in which $w(\mathbf{r})$ is a "Kac potential" containing a parameter γ

$$w(\mathbf{r}, \gamma) = \gamma^r \lambda \varphi(\gamma \mathbf{r}), \quad (1.10)$$

where r is the dimensionality of the space considered. The value of γ thus corresponds to the inverse range of $w(\mathbf{r}, \gamma)$. We are able to identify the terms in our expansions that contribute to any given order in γ , and explicitly give the expansion of the free energy in terms of Φ and ρ through terms of order $(\gamma')^2$ (as well as the prescription for finding $\ln \Xi$ to any order). The result to order $(\gamma')^2$ agrees with that of Coopersmith and Brout⁵; our general result cannot be directly compared with theirs. At $\rho = \frac{1}{2}$ we can also compare our explicit result with that of Siegert⁶ (who uses spin-system language and considers the case $H = 0$) and we find agreement.

In the limit $\gamma \rightarrow 0$, it was shown by Lebowitz and Penrose⁷ [for a wide class of potentials $q(\mathbf{r})$ and $\varphi(\mathbf{y})$] that the Helmholtz free energy per unit volume $a(\beta, \rho, 0+) = \lim_{\gamma \rightarrow 0} a(\beta, \rho, \gamma)$, from which the other thermodynamic properties of the system

⁴ See Refs. 12, 13, 17-19.

⁵ M. Coopersmith and R. Brout, Phys. Rev. 130, 2539 (1963).

⁶ A. J. F. Siegert, "On the Ising Model with Long-Range Interaction," Northwestern University preprint (1962).

⁷ J. L. Lebowitz and O. Penrose, J. Math. Phys. 7, 98 (1966).

² C. N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952).

³ J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 1495 (1963); cf. also Sec. II.

may be obtained, is given rigorously by applying the Gibbs double-tangent construction to the function

$$a_0(\beta, \rho) = a^0(\beta, \rho) + \frac{1}{2}\alpha\rho^2. \quad (1.11)$$

Here, $a^0(\beta, \rho)$ is the free energy per unit volume of the reference system corresponding to $w(\mathbf{r}, \gamma) = 0$, and

$$\begin{aligned} \alpha &= \lim_{\gamma \rightarrow 0} \sum_{\mathbf{R}'} w(\mathbf{R} - \mathbf{R}') \\ &= \lim_{\gamma \rightarrow 0} \alpha'(\gamma) = \int \varphi(\mathbf{y}) d\mathbf{y}. \end{aligned} \quad (1.12)$$

For the lattice gas considered here, we have

$$a^0(\beta, \rho) = \beta^{-1}[\rho \ln \rho + (1 - \rho) \ln (1 - \rho)]. \quad (1.13)$$

When these results are translated into spin language, we obtain the Weiss self-consistent theory of magnetism, which is thus proven rigorously for a spin-interaction potential of the form (1.10) in the limit $\gamma \rightarrow 0$. This generalizes the results of Baker,⁸ and Kac and Helfand,⁹ who proved the Weiss theory for a one-dimensional spin system with a special type of Kac potential $w(\mathbf{r}, \gamma) = \frac{1}{2}\alpha\gamma e^{-\gamma|\mathbf{r}|}$; $\alpha < 0$. (Baker also considered similar potentials in three dimensions, cf. Sec. III.)

When we carry through our expansion in γ , we obtain

$$a(\beta, \rho, \gamma) = a_0(\beta, \rho) + \sum_{n=1}^{\infty} a_n(\beta, \rho, \gamma), \quad a_n \sim O(\gamma^n). \quad (1.14)$$

For $\alpha < 0$, ferromagnetic interaction, the $a_n(\beta, \rho, \gamma)$ diverge for $n > \nu$ when β and ρ approach values corresponding to $(dp_0/d\rho)(\beta, \rho) = 0$, i.e., the boundary of the meta-stable region in the van der Waals-Maxwell (or Bragg-Williams) equation of state (cf. Fig. 1),

$$p_0(\beta, \rho) = \rho^2[d(a_0/\rho)/d\rho] = -\beta^{-1} \ln(1 - \rho) + \frac{1}{2}\alpha\rho^2. \quad (1.15)$$

The failure of the γ expansion inside the Bragg-Williams (BW) two-phase region, as well as in the vicinity of the BW critical point, leads us to propose in Sec. IV a nonperturbative self-consistent iterative approximation method for the evaluation of the \hat{F}_i^* occurring in the graphical expansion of \hat{F}_1 . To lowest order, this new method yields an \hat{F}_2 identical to that obtained from the (mean) spherical model

of Lewis and Wannier¹⁰ (this is a modification of the Berlin and Kac¹¹ spherical model). Explicit calculations with this approximation are carried out in III.

Higher-order approximations can be obtained in several ways, one of which involves an auxiliary function \hat{W} (Eq. 2.22) that has independently been considered by Stillinger¹² and by Abe.¹³ The latter used it in discussing the spatially asymptotic behavior of \hat{F}_2 at the critical point. Here we give a somewhat more general discussion than Abe's, pointing out the way in which various assumptions concerning the relationships between \hat{W} and \hat{F}_2 are related to the spatially asymptotic behavior of $\hat{F}_2(\mathbf{r}_{12})$ at the critical point.

II. GENERAL GRAPHICAL FORMALISM FOR THE CORRELATION FUNCTIONS AND THERMODYNAMIC POTENTIALS

In this part we summarize, for lattice systems, the graphical description given in I for the modified m -particle Ursell function $\hat{F}_m(\mathbf{r}_1, \dots, \mathbf{r}_m)$. The \hat{F}_m are defined³ in terms of the k -particle distribution functions $\hat{n}_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$ in the same way as the ordinary Ursell functions $F_m(\mathbf{r}_1, \dots, \mathbf{r}_m)$ are defined in terms of the ordinary distribution functions $n_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$. The $\hat{n}_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$ differ from the $n_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$ by being the probability densities of finding k particles, *not necessarily distinct*, at positions $\mathbf{r}_1, \dots, \mathbf{r}_k$ on the lattice. Thus

$$\begin{aligned} \hat{n}_1(\mathbf{r}_1) &= n_1(\mathbf{r}_1) = \langle \rho(\mathbf{r}_1) \rangle, \\ \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) &= \langle \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \rangle \\ &= n_2(\mathbf{r}_1, \mathbf{r}_2) + n_1(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2), \dots, \end{aligned} \quad (2.1)$$

with $\delta(\mathbf{r})$ denoting (for lattice systems) the Kronecker delta function. Correspondingly,

$$\begin{aligned} \hat{F}_1(\mathbf{r}_1) &= \hat{n}_1(\mathbf{r}_1) = F_1(\mathbf{r}_1), \\ \hat{F}_2(\mathbf{r}_1, \mathbf{r}_2) &= \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) - \hat{n}_1(\mathbf{r}_1)\hat{n}_1(\mathbf{r}_2) \\ &= F_2(\mathbf{r}_1, \mathbf{r}_2) + F_1(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2), \text{ etc.} \end{aligned} \quad (2.2)$$

Using the relationships (1.7) and (1.8) shows that

¹⁰ H. W. Lewis and G. H. Wannier, Phys. Rev. **88**, 682 (1952). An extension of this model to lattice gases for which $g(\mathbf{r})$, the infinitely repulsive potential, is not confined to $\mathbf{r} = 0$ (and are thus not isomorphic to spin systems) has been made recently by Lebowitz and Percus (Ref. 21). This exact model leads to an integral equation for the radial distribution function which remains valid also in the continuum limit and coincides when $w(\mathbf{r}) = 0$ with the Percus-Yevick integral equation.

¹¹ T. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).

¹² F. H. Stillinger, Phys. Rev. **135**, A1646 (1964).

¹³ R. Abe, Progr. Theoret. Phys. (Kyoto) **33**, 600 (1965).

⁸ G. A. Baker, Jr., Phys. Rev. **126**, 2071 (1962).

⁹ M. Kac and E. Helfand, J. Math. Phys. **4**, 1078 (1963).

\hat{F}_l is equal to the l th semi-invariant of the spin system for $l \geq 2$. Thus, [cf. (1.9)],

$$\begin{aligned} \hat{F}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \hat{n}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - \hat{n}_1(\mathbf{r}_1)\hat{n}_2(\mathbf{r}_2, \mathbf{r}_3) \\ &\quad - \hat{n}_1(\mathbf{r}_2)\hat{n}_2(\mathbf{r}_1, \mathbf{r}_3) - \hat{n}_1(\mathbf{r}_3)\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad + 2\hat{n}_1(\mathbf{r}_1)\hat{n}_1(\mathbf{r}_2)\hat{n}_1(\mathbf{r}_3) = \langle \sigma(\mathbf{r}_1)\sigma(\mathbf{r}_2)\sigma(\mathbf{r}_3) \rangle \\ &\quad - \langle \sigma(\mathbf{r}_1) \rangle \langle \sigma(\mathbf{r}_2)\sigma(\mathbf{r}_3) \rangle - \langle \sigma(\mathbf{r}_2) \rangle \langle \sigma(\mathbf{r}_1)\sigma(\mathbf{r}_3) \rangle \\ &\quad - \langle \sigma(\mathbf{r}_3) \rangle \langle \sigma(\mathbf{r}_1)\sigma(\mathbf{r}_2) \rangle + 2\langle \sigma(\mathbf{r}_1) \rangle \langle \sigma(\mathbf{r}_2) \rangle \langle \sigma(\mathbf{r}_3) \rangle. \end{aligned} \quad (2.3)$$

Starting with the usual representation of the $\hat{F}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ in terms of composite graphs with density ρ , or fugacity z vertices, and two type of bonds: "short-range" K -bonds, $K(\mathbf{x}_{12}) \equiv \{\exp[-\beta q(\mathbf{x}_{12})] - 1\}$ and "long-range" Φ -bonds, $\Phi(\mathbf{x}_{12}) \equiv -\beta w(\mathbf{x}_{12})$, cf. (I-2.8), we now divide each \hat{F}_l into two parts; \hat{F}_l^s (\hat{F}_l^s short-range) and \hat{F}_l^L (\hat{F}_l^L long-range),

$$\hat{F}_l(\mathbf{r}_1, \dots, \mathbf{r}_l) = \hat{F}_l^s(\mathbf{r}_1, \dots, \mathbf{r}_l) + \hat{F}_l^L(\mathbf{r}_1, \dots, \mathbf{r}_l). \quad (2.4)$$

Here, \hat{F}_l^s is the subset of all composite graphs in \hat{F}_l in which there is a path, consisting of K -bonds alone, connecting the labeled points $\mathbf{r}_1, \dots, \mathbf{r}_l$. The central graphical result in I, (I-2.15), states

$$\begin{aligned} \hat{F}_l(\mathbf{r}_1, \dots, \mathbf{r}_l) &= \text{the sum of all irreducible} \\ &\text{graphs, with } \Phi \text{ bonds and } \hat{F}_k^s(\mathbf{x}_1, \dots, \mathbf{x}_k) \\ &\text{hypervertices, having } l \text{ white circles labeled} \\ &\text{by } 1, 2, \dots, l, \text{ respectively.} \end{aligned} \quad (2.5)$$

A hypervertex of order k , which represents a function $w_k(\mathbf{x}_1, \dots, \mathbf{x}_k)$, can be pictured as a large circle, along the circumference of which are attached k vertices (or points). The small vertices can be either black or white and correspond, respectively, to field points over which summations are performed, and to labeled points (root points). Each field point has one and only one Φ bond coming out of it going to another vertex. A graph is associated with its corresponding sum (over the field points) in the usual way (treating each hypervertex as a point for the purpose of counting). In (2.5), *irreducible* means that there are no articulation hypervertices. Also $\hat{F}_l^s(\mathbf{r}_1, \dots, \mathbf{r}_l)$ is represented by a single hypervertex, e.g.,

$$\begin{aligned} &\text{Diagram: A circle with four vertices labeled 1, 2, 3, 4. Vertices 1 and 2 are black, 3 and 4 are white.} \\ &\quad = \hat{F}_4^s(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \quad \text{and} \\ &\text{Diagram: Two circles connected by a line. The left circle has two black vertices, the right circle has two white vertices.} \\ &\quad = \sum_{\mathbf{x}_1} \sum_{\mathbf{x}_2} \hat{F}_2^s(\mathbf{r}_1, \mathbf{x}_1) \Phi(\mathbf{x}_{12}) \hat{F}_2^s(\mathbf{x}_2, \mathbf{r}_3). \end{aligned}$$

For lattice gases with a short-range potential $q(\mathbf{r})$, defined in (1.2), $K(\mathbf{r}) \equiv -\delta(\mathbf{r})$, and hence the $\hat{F}_k^s(\mathbf{x}_1, \dots, \mathbf{x}_k)$ can differ from zero only when all the k points coincide. We have $\hat{F}_1^s = \hat{F}_1^L = \nu_1 = \rho$ and $\hat{F}_k^s(\mathbf{x}_1, \dots, \mathbf{x}_k) = \nu_k \delta(\mathbf{x}_1 - \mathbf{x}_2)$

$$\times \delta(\mathbf{x}_1 - \mathbf{x}_3) \cdots \delta(\mathbf{x}_1 - \mathbf{x}_k), \quad k \geq 2. \quad (2.6)$$

This greatly simplifies the graphical description (2.5), since the hypervertices now become ordinary point vertices albeit with values ν_k depending on their order. (We therefore represent them as simple points when there is no danger of confusion.) It should be noted also that the ν_k depend on the interaction potential $w(\mathbf{r})$, since only the labeled (root) points in a hypervertex have to be connected by a path consisting of K bonds. In the reference system $w(\mathbf{r}) = 0$ the \hat{F}_k and the ν_k then assume simple values ν_k^0 ,

$$\hat{F}_k^0(\mathbf{r}_1, \dots, \mathbf{r}_k) = \nu_k^0 \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_3) \cdots \delta(\mathbf{r}_1 - \mathbf{r}_k). \quad (2.7)$$

The values of ν_k^0 can be obtained easily from the definition of the \hat{n}_k as expectation values of products of the microscopic density variable $\rho(\mathbf{x}_i)$ by noting from the definition of $\rho(\mathbf{x}_i)$, (1.7), that, independent of w , $\hat{n}_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$ for $\mathbf{r}_1 = \dots = \mathbf{r}_k$,

$$\hat{n}_k(\mathbf{r}_1, \dots, \mathbf{r}_k) \equiv \langle [\rho(\mathbf{r}_1)]^k \rangle = \langle \rho(\mathbf{r}_1) \rangle^k = \rho^k, \quad (2.8)$$

with the last equality holding for a uniform system. Hence, considered as functions of ρ ,

$$\begin{aligned} \nu_1^0 &= \hat{F}_1^0(\mathbf{r}_1) = \rho = \langle \sigma \rangle + \frac{1}{2}, \\ \nu_2^0 &= \hat{F}_2^0(\mathbf{r}_1, \mathbf{r}_1) = \nu_2 + \hat{F}_2^L(\mathbf{r}_1, \mathbf{r}_1) \\ &= \rho(1 - \rho) = \frac{1}{4} - \langle \sigma \rangle^2, \quad (2.9) \\ \nu_3^0 &= \hat{F}_3^0(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_1) = \nu_3 + \hat{F}_3^L(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_1) \\ &= \rho(1 - \rho)(1 - 2\rho) = [\langle \sigma \rangle^2 - \frac{1}{4}]\langle \sigma \rangle, \text{ etc.} \end{aligned}$$

It follows from the definition of the \hat{F}_k^s 's, $k \geq 2$, that they (and thus also the ν_k^0) are even/odd functions of $\rho - \frac{1}{2}$, (i.e., $\langle \sigma \rangle$) for k even/odd. The same symmetry properties hold also for the ν_m . This can be proved as follows: The $\hat{F}_m^s(\mathbf{r}_1, \dots, \mathbf{r}_m)$, when expressed graphically by (2.5), are functions of the ν_k 's and Φ . Hence, we can write from (2.9),

$$\nu_m^0(\rho) = f_m(\nu_2, \nu_3, \nu_4, \dots), \quad m = 2, 3, \dots \quad (2.10)$$

Equations (2.10) then provide solutions for the ν_k in terms of ρ . We now note that every graph in \hat{F}_m which has l Φ -bonds and s_k vertices ν_k ($k = 2, 3, \dots$), satisfies the relation $\sum_k k s_k = 2l + m$. Therefore

$$(-1)^m = (-1)^{\sum k s_k} = (-1)^{2l + m}. \quad (2.11)$$

Now, $\hat{W}(\mathbf{r}) = \hat{W}^s(\mathbf{r}) + \hat{W}^L(\mathbf{r})$ (with $\hat{W}^s = \hat{F}_2^s$) has the same graphical expansion as $\hat{F}_2(\mathbf{r})$, Eq. (2.5) or Eq. (2.16), with the *additional* restrictions that no graph contain any cutting bonds, i.e., bonds whose removal separates the graph into two parts, each of which contains a white vertex.

In the case of a field-free ($H = 0$) lattice system, the function $\hat{W}(\mathbf{r})$ reduces (when $r \neq 0$) to the function $\frac{1}{2}[w(\mathbf{r})]$ introduced by Stillinger,¹² and coincides with the function $I(\mathbf{r})$ introduced by Abe.¹³ (Both authors consider only the field-free case.)

B. Thermodynamic Properties

The thermodynamic properties of our system may be obtained from \hat{F}_2 in several ways (cf. Sec. VI of I), chief among these being the fluctuation-compressibility relation¹⁵

$$\rho/\beta(dp/d\rho) = \sum \hat{F}_2(\mathbf{r}) = \bar{F}_2(0), \quad (2.24)$$

and the energy relation

$$u(\beta, \rho) = \frac{1}{2}\rho^2\alpha' + \frac{1}{2} \sum w(\mathbf{r})\hat{F}_2(\mathbf{r}) \\ = \partial\beta a(\beta, \rho)/\partial\beta, \quad (2.25)$$

where $u(\beta, \rho)$ and $a(\beta, \rho)$ are the internal and Helmholtz free energies per unit volume, and use has been made of the fact that $w(0) = 0$. All the thermodynamic properties of the system follow from $a(\beta, \rho)$, with

$$a(\beta, \rho) = a_0'(\beta, \rho) + \frac{1}{2}\beta^{-1} \sum w(\mathbf{r}) \\ \times \int_0^\beta \hat{F}_2(\mathbf{r}; \beta', \rho) d\beta', \quad (2.26)$$

where

$$a_0'(\beta, \rho) = a^0(\beta, \rho) + \frac{1}{2}\alpha'\rho^2$$

with a^0 given in (1.13) and α' defined in (1.4).

An explicit graphical representation for $\beta p = \Omega^{-1} \ln \Xi$ was derived in Appendix C of I, which yields, for lattice systems,

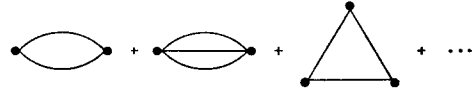
$$\ln \Xi = \Omega\beta p = \Omega\beta p_0 + S \\ - \sum_{n \geq 2} \nu_n G_n(\mathbf{r}_1, \dots, \mathbf{r}_n)|_{\mathbf{r}_1, \dots, \mathbf{r}_n}, \quad (2.27)$$

where

$$G_n(\mathbf{r}_1, \dots, \mathbf{r}_n) \\ = \frac{1}{n!} \sum_{\mathbf{x}_i} \prod_i \Phi(\mathbf{r}_i, \mathbf{x}_i) \hat{F}_n(\mathbf{x}_1, \dots, \mathbf{x}_n) \quad (2.28)$$

and

S = the sum of all irreducible unrooted graphs, consisting of Φ -bonds and at least two ν_k -hypervertices and two Φ -bonds =



and $\beta p_0 = -\ln(1 - \rho) + \frac{1}{2}\beta\alpha'\rho^2$, as given by (1.15). (2.29)

C. Evaluation of the ν_k

In order to be able to use Eqs. (2.5) and (2.27) to express the \hat{F}_n and $\ln \Xi$ in terms of Φ and quantities that refer only to the reference system, it is necessary to have a prescription that enables us to express the ν_k in such terms. The Eq. (I-2.18), derived and discussed in I, yields this prescription when combined with (2.5). For our lattice system (I-2.18) can be written as

$$\nu_l = \mathfrak{N} \exp \left\{ \sum_{k \geq 2} \left(\frac{1}{k!} \right) [\hat{F}_k^{\nu L}(0)] \frac{\partial^k}{\partial \rho^k} \right\} \nu_l^0, \quad (2.30)$$

where \mathfrak{N} indicates a normal order in which all derivatives go to the right before evaluation, and $\hat{F}_k^{\nu L}(0) = \hat{F}_k^{\nu L}(\mathbf{r}_1, \dots, \mathbf{r}_k)$ for $\mathbf{r}_1 = \dots = \mathbf{r}_k$ with $\hat{F}_k^{\nu L}$ the "very long"-range part of \hat{F}_k defined as

$\hat{F}_k^{\nu L}$ is given by the same graphs, Eq. (2.5), that we use for \hat{F}_k itself *except* that we exclude all graphs in which any two labeled circles are shared by a single hypervertex. (2.31)

(For $k = 2$, $\hat{F}_k^{\nu L}$ and \hat{F}_k^L coincide.) Actually, for our lattice system the right-hand side of (2.30) contains only a finite number of terms for every l , since ν_k^0 is a polynomial in ρ of order k , so that $\partial^l \nu_k^0 / \partial \rho^l = 0$ for $l > k$. As a result we have

$$\nu_2 = \nu_2^0 + \frac{1}{2}(\partial^2 \nu_2^0 / \partial \rho^2) \hat{F}_2^L(0) = \nu_2^0 - \hat{F}_2^L(0), \\ \nu_3 = \nu_3^0 + \frac{1}{2}(\partial^2 \nu_3^0 / \partial \rho^2) \hat{F}_2^L(0) + \frac{1}{6}(\partial^3 \nu_3^0 / \partial \rho^3) \hat{F}_3^{\nu L}(0) \\ = \nu_3^0 - 3(1 - 2\rho) \hat{F}_2^L(0) + 2\hat{F}_3^{\nu L}(0). \quad (2.32)$$

We can also get the above equations for ν_k by using (2.9) and (2.10) to solve for the ν_k in terms of the ν_n^0 , but (2.30) is more direct and comes from the general relation Eq. (I-2.18).

The equations considered in this section are not based on any particular parameterization or ordering scheme. Nevertheless, the detailed results of eliminating the ν_k in favor of ν_k^0 and $\partial^l \nu_k^0 / \partial \rho^l$ through the use of (2.30) are only of use if we have some means of estimating the relative importance of the terms in the series that we finally obtain. One such

means involves the use of a range parameter γ , which we discuss in the next section.

D. Use of Fugacity, (or H), as the Independent Variable

The functions ν_k and ν_k^0 are natural functions to use when the properties of the system are to be expressed in terms of ρ and Φ or, in spin-system language, $\langle\sigma\rangle$ and Φ . However, H or z rather than $\langle\sigma\rangle$ is more likely to be the independent variable of interest when the system is being used as a model for a magnet. To obtain expansions in terms of z and Φ , we use the expansions in I that contain \hat{F}'_k hypervertices instead of \hat{F}^*_k hypervertices. Applying the results of I to a lattice system then yields, instead of (2.5),

\hat{F}'_l = the sum of all connected graphs with Φ bonds and \hat{F}'_k hypervertices, having l white circles labeled by $1, 2, \dots, l$, respectively. (2.33)

Here, $\hat{F}'_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$ is the subset of all composite graphs with z -vertices and K and Φ -bonds in \hat{F}'_k , in which there is a path consisting of K -bonds alone, connecting every pair of points in the graph. The last requirement implies that, for the lattice gases considered here, $K(\mathbf{r}) = -\delta(\mathbf{r})$, all the z -vertices in \hat{F}'_k must coincide. Hence, since we have assumed that $\Phi(0) = 0$, \hat{F}'_k , considered as a function of the fugacity z , must be equal to its value in the reference system

$$\hat{F}'_k(\mathbf{r}_1, \dots, \mathbf{r}_k; z) = \hat{F}^0_k(\mathbf{r}_1, \dots, \mathbf{r}_k; z) = \mu_k(z) \delta(\mathbf{r}_2 - \mathbf{r}_1) \dots \delta(\mathbf{r}_k - \mathbf{r}_1). \quad (2.34)$$

The μ_k may now be found directly from the properties of the reference system (ideal lattice gas). Introducing the variable $x = \ln z = \beta H + \frac{1}{2}\beta\alpha'$, we have

$$\begin{aligned} \mu_k &= \partial^k [\ln(1+z)] / \partial(\ln z)^k \\ &= (\partial^k / \partial x^k) [\ln(2 \cosh x/2) + x/2], \end{aligned} \quad (2.35)$$

so

$$\partial^i \mu_k / \partial x^i = \mu_{k+i} \quad (2.36)$$

and

$$\begin{aligned} \mu_1 &= z/1 + z = \frac{1}{2} \tanh(\frac{1}{2}x) + \frac{1}{2}, \\ \mu_2 &= z/(1+z)^2 = \frac{1}{4} \operatorname{sech}^2(\frac{1}{2}x), \\ \mu_3 &= z(1-z)/(1+z)^3 = -2(\mu_1 - \frac{1}{2})\mu_2, \dots \end{aligned} \quad (2.37)$$

Instead of (2.30) we have [from (I-C-6)]

$$\nu_i = \Re \{ \exp [\sum_{k \geq 1} G_k(0) (\partial^k / \partial x^k)] \} \mu_i, \quad (2.38)$$

where G_k is defined in (2.28) and

$$G_k(0) = G_k(\mathbf{r}_1, \dots, \mathbf{r}_k) \quad \text{for } \mathbf{r}_1 = \dots = \mathbf{r}_k. \quad (2.39)$$

Finally, instead of (2.27), we have [from (I-C-3)]

$$\ln \Xi = (\ln \Xi)^0 + \text{the sum of all connected graphs with } \Phi \text{ bonds and at least two unlabeled } \mu_k \text{ hypervertices}, \quad (2.40)$$

where

$$\Omega^{-1}(\ln \Xi)^0 = \ln(1+z), \quad (2.41)$$

so that, from (1.2), we have the expression that gives the free energy of the spin system:

$$\begin{aligned} \ln Q &= \ln(1+z) - \frac{1}{2} \ln z \\ &+ \text{the sum of Eq. (2.40)}. \end{aligned} \quad (2.42)$$

E. Comparison with Other Work

Having obtained the μ_k -hypervertex and ν_k -hypervertex expressions from the general results of I, we can make contact with the spin-system expansions of others.

Although Eq. (2.40) and (2.33) have the same graphical structure as the "unrenormalized" linked-cluster expansions that have been derived by others⁴ especially for spin systems, they are not identical, graph by graph, to the latter owing to a difference in the functions represented by the hypervertices. The semi-invariants used most often in discussing the spin systems—for example, Englert's¹⁷ $M_k^0(x')$ or Stillinger's D_k —are somewhat different functions [e.g., after adjusting the units, $M_1^0(x') = \frac{1}{2} \tanh(x'/2)$ instead of $\mu_1 = \frac{1}{2} \tanh(x/2) + \frac{1}{2}$] of somewhat different arguments ($x' = \beta H$ instead of $x = \beta H + \frac{1}{2}\beta\alpha'$), the general relation being

$$\mu_k(x) = M_k^0(x' + \frac{1}{2}\beta\alpha') + \frac{1}{2} \delta_{k,1}. \quad (2.43)$$

These two differences just compensate one another to lead to the same final graphical prescription whether the hypervertices represent the μ_k 's or the M_k^0 's.

On the other hand, in comparing the ν_k 's with the "renormalized" semi-invariants—for example, Englert's M_k —these differences are no longer found. There is, at most, only the trivial difference of notation; in a spin system, it is natural to express the ν_k as a polynomial in the long-range order $R = 1 - 2\rho$ instead of ρ itself.⁵ Whether ν_k is expressed as the function $\nu_k(\rho)$ or as $M_k(R)$, each graph in the expansion (2.16) represents the same function of ρ and Φ .

¹⁷ F. Englert, Phys. Rev. 129, 567 (1963).

The \bar{M}_k of Horwitz and Callen¹⁸ would also coincide with ν_k if their renormalization procedure to obtain \bar{M}_k to all orders were explicitly carried through (which is indeed what Englert did) and in the field-free case ($H = 0$) our ν_k also appear to reduce to Stillinger's \bar{D}_k .

Our ν_k^* are related to the vertex functions appearing in the expansions of Brout,¹⁹ and of Coopersmith and Brout,⁵ in the sense that they depend explicitly on ρ or R rather than on z or H , but there is a technical difference resulting from our use of the $\partial^k \nu_i^0 / \partial \rho^k$ instead of the combinations of Kronecker δ 's and ν_k^0 's that appear in the expansions of those authors.

We have thus established the connection between the general expansions that were derived in I for an arbitrary decomposition of a potential into two parts and the Ising spin-system expansions heretofore derived by means of procedures that are immediately applicable only to those systems. The connection is made via lattice systems for which the reference potential is identified with the exclusion of multiple occupancy of a single site (i.e., the association of a single spin to each site). Our method has the advantage of giving a simple direct interpretation to the hypervertices ν_k in terms of the short-range part of \hat{F}_k , as well as suggesting some new generalizations.

One natural generalization that our expansions suggest is the consideration of a wider class of reference systems. One might, for example, use the exactly solvable 2-dimensional Ising model with nearest-neighbor interaction as a reference system, and introduce a further interaction as a perturbation. Alternatively, the nearest-neighbor potential itself could be considered as part reference potential and part perturbing potential to facilitate the development of new approximation schemes. This is the starting point of an approximation scheme developed by G. Horwitz.²⁰ For such reference systems, the \hat{F}_k^* no longer have the simple form (2.6), but all our formal results immediately apply.

III. LONG-RANGE KAC POTENTIALS

Following the analysis developed in I, we now consider the case where $w(r)$, which was arbitrary so far, contains an inverse range parameter γ which can approach zero (after the size of the system has become infinitely large). Following Baker,⁸ we shall

use, for lattice systems, a slightly modified "Kac potential" of form (1.10) for $w(r, \gamma)$,

$$w(r, \gamma) = \begin{cases} \gamma^\nu \lambda(\gamma) \varphi(r), & r \neq 0, \\ 0, & r = 0, \end{cases} \quad (3.1)$$

where ν is the dimensionality of the space considered,¹⁴ and $\lambda(\gamma)$ is so chosen that

$$\lim_{\gamma \rightarrow 0} \lambda(\gamma) = 1 \quad (3.2)$$

and the "integrated strength" of the long-range potential

$$\sum w(r, \gamma) \equiv \alpha' = \lambda(\gamma) \sum' \varphi(r) \gamma^\nu = \alpha \quad (3.3)$$

is independent of γ . The last summation is over an infinite lattice with the $r = 0$ term omitted. We assume for simplicity¹⁴ that we are dealing with simple cubic lattices of unit spacing, so that in the limit $\gamma \rightarrow 0$, (3.3) becomes the integral of $\varphi(x)$ over all space, coinciding with (1.12). [The advantage of introducing the multiplying factor $\lambda(\gamma)$ which has only trivial effects for $\gamma \rightarrow 0$ is that it permits simultaneous consideration also of very large γ , in which case $w(r, \gamma)$ becomes a nearest-neighbor potential with the "integrated strength" of the potential remaining fixed.] We generally leave λ as a parameter and consider its explicit dependence on γ only at the end. It was shown in I how to obtain an expansion of \hat{F}_2 (and other \hat{F}_i) in powers of γ [for well-behaved $\varphi(y)$'s, cf. (I-3.1) and (I-3.3)]. For this purpose, it is necessary to treat $\hat{F}_2^*(r, \gamma)$ and $\hat{F}_2^L(y, \gamma)$ differently, considering them, respectively, as functions of r and γ , and as functions of y and γ ; $y \equiv \gamma r$. This difference is completely obvious for the lattice systems considered here, where $\hat{F}_2^*(r, \gamma) = \nu_2(\gamma) \delta(r)$, and need not, therefore, always be kept track of explicitly, as long as we use the convention that $\delta(y) = \delta(r)$.

To facilitate the γ expansion of \hat{F}_i , two kinds of ordering, γ and Γ ordering, of the graphs entering into \hat{F}_i , were introduced in I. In the γ -ordering, we classify all composite graphs with *density vertices*, and Φ - and K -bonds according to the difference between the number t of Φ -bonds and the number of free integrations m occurring in the graph. The number of free integrations in a graph is found by deleting all the Φ -bonds in a graph for \hat{F}_i and counting the number of separate pieces not connected to any root point by a K -bond. All such graphs are then of $O(\gamma')^{t-m}$. We then have

$$\hat{F}_i = \hat{F}_{i|0|} + \hat{F}_{i|1|} + \cdots \quad (3.4)$$

¹⁸ G. Horwitz and H. B. Callen, Phys. Rev. 124, 1757 (1961).

¹⁹ R. Brout, Phys. Rev. 115, 824 (1959); *ibid.* 118, 1009 (1960).

²⁰ G. Horwitz (to be published).

with

$$\hat{F}_{l[k]}, \quad k \equiv t - m \text{ of } 0(\gamma)^k,$$

$$\hat{F}_{l[k]} = \sum_{i=1}^{\infty} \gamma^i \hat{F}_{l[k]i}. \quad (3.5)$$

The Γ ordering applies directly to graphs with Φ -bonds (or \mathcal{C} -bonds) and \hat{F}_i^* hypervertices entering \hat{F}_l in (2.5). These are ordered according to the difference j between the number of Φ bonds (or \mathcal{C} bonds) and the number of hypervertices containing no labeled vertices in the graph. Calling such a subset $\Gamma_j^{(1)}$, we have

$$\hat{F}_2 = \text{diagram 1} + \left(\text{diagram 2} \right) + \left(\text{diagram 3} \right) + \dots$$

$$= \Gamma_0(\mathbf{r}_{12}, \gamma) + \Gamma_1(\mathbf{y}_{12}, \gamma; \nu_2) + \Gamma_2(\mathbf{y}_{12}, \gamma; \nu_2, \nu_3) + \dots, \quad (3.6)$$

$$\hat{F}_3 = \text{diagram 4} + \left(\text{diagram 5} \right) + \dots$$

$$= \Gamma_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \gamma) + \Gamma_1^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \gamma; \nu_2, \nu_3) + \dots, \quad (3.7)$$

where we have set $\Gamma_j^{(2)} = \Gamma_j$. Writing out the first few terms more explicitly yields

$$\hat{F}_2^*(\mathbf{r}) = \Gamma_0(\mathbf{r}, \gamma) = \nu_2(\gamma) \delta(\mathbf{r}), \quad (3.8)$$

$$\Gamma_1(\mathbf{y}, \gamma) = \nu_2^2 \mathcal{C}(\mathbf{y}, \gamma)$$

$$= \left(\frac{\gamma}{2\pi} \right)^2 \int_{-\pi/\gamma}^{\pi/\gamma} \dots \int e^{i\mathbf{x} \cdot \mathbf{y}} \frac{\nu_2^2 \tilde{\Phi}(\mathbf{x}, \gamma)}{1 - \nu_2 \tilde{\Phi}(\mathbf{x}, \gamma)} d\mathbf{x}, \quad (3.9)$$

with

$$\tilde{\Phi}(\mathbf{x}, \gamma) = \sum_{\mathbf{y}} e^{-i\mathbf{x} \cdot \mathbf{y}} \Phi(\mathbf{y}) = -\beta \lambda(\gamma) \sum_{\mathbf{y}} e^{-i\mathbf{x} \cdot \mathbf{y}} \varphi(\mathbf{y}) \gamma^r$$

$$\rightarrow -\beta \int e^{-i\mathbf{x} \cdot \mathbf{y}} \varphi(\mathbf{y}) d\mathbf{y} = \tilde{\Phi}(\mathbf{x}), \quad (3.10)$$

the summation over $\mathbf{y} = \gamma \mathbf{r}$ being over a lattice with spacing γ , and the integration over $\mathbf{x} \equiv \gamma^{-1} \mathbf{k}$ having a range $-\pi/\gamma$ to π/γ (after taking the thermodynamic limit $\Omega \rightarrow \infty$). $\tilde{\Phi}(\mathbf{x}, \gamma)$ is equal to $\tilde{\Phi}(\mathbf{k}) = -\beta \tilde{w}(\mathbf{k})$ defined in (2.15), which we shall also write sometimes as $\tilde{\Phi}(\mathbf{k}, \gamma) = -\beta \tilde{w}(\mathbf{k}, \gamma)$; the range of $\mathbf{k} = \gamma \mathbf{x}$ always being $-\pi$ to π . When we

go to the limit $\gamma \rightarrow 0$, $\tilde{\Phi}(\mathbf{x}, \gamma) \rightarrow \tilde{\Phi}(\mathbf{x})$ which coincides with the continuum Fourier transform of $-\beta \varphi(\mathbf{y})$ used in I. Similarly,

$$\Gamma_2(\mathbf{y}, \gamma) = \frac{1}{2!} \left(\frac{\gamma}{2\pi} \right)^2$$

$$\times \int_{-\pi/\gamma}^{\pi/\gamma} \dots \int d\mathbf{x} \frac{e^{i\mathbf{x} \cdot \mathbf{y}} \nu_2^2 \tilde{\Phi}(\mathbf{x}, \gamma)}{[1 - \nu_2 \tilde{\Phi}(\mathbf{x}, \gamma)]^2}, \quad (3.11)$$

where $\tilde{\Phi}$, the Fourier transform of $\mathcal{C}^2(\mathbf{y}, \gamma)$, is given by

$$\tilde{\Phi}(\mathbf{x}, \gamma) = \left(\frac{\gamma}{2\pi} \right) \int d\mathbf{x}' \tilde{\mathcal{C}}(\mathbf{x} - \mathbf{x}', \gamma) \tilde{\mathcal{C}}(\mathbf{x}', \gamma) \quad (3.12)$$

with

$$\tilde{\mathcal{C}}(\mathbf{x}, \gamma) = \tilde{\Phi}(\mathbf{x}, \gamma) / [1 - \nu_2 \tilde{\Phi}(\mathbf{x}, \gamma)]. \quad (3.13)$$

Also,

$$\Gamma_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \nu_3 \delta(\mathbf{r}_{12}) \delta(\mathbf{r}_{23}), \quad (3.14)$$

$$\Gamma_1^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \gamma) = \nu_3 \nu_2 [\delta(\mathbf{r}_{12}) \mathcal{C}(\mathbf{y}_{13}, \gamma) + \delta(\mathbf{r}_{13}) \mathcal{C}(\mathbf{y}_{12}, \gamma) + \delta(\mathbf{r}_{23}) \mathcal{C}(\mathbf{y}_{13}, \gamma)]. \quad (3.15)$$

The Γ ordering may also be applied directly to the function \hat{W} introduced in Eq. (2.22), where the first few terms become particularly simple since there are no cutting bonds in \hat{W} ,

$$\hat{W} = \text{diagram 6} + \left(\text{diagram 7} \right) + \left(\text{diagram 8} \right) + \dots$$

$$= \hat{W}_0(\mathbf{r}_{12}, \gamma) + \hat{W}_2(\mathbf{y}_{12}, \gamma; \nu_3)$$

$$+ \hat{W}_3(\mathbf{y}_{12}, \gamma; \nu_3, \nu_4) + \dots \quad (3.16)$$

with

$$\hat{W}_0(\mathbf{r}) = \nu_2 \delta(\mathbf{r}), \quad \hat{W}_2(\mathbf{y}, \gamma) = \nu_3^2 \mathcal{C}^2(\mathbf{y}, \gamma), \text{ etc.} \quad (3.17)$$

It is clear from the Γ -ordering scheme mentioned before that $\Gamma_i^{(1)}$ and W_i are of $O(\gamma^i)$,

$$\Gamma_i^{(1)} = \gamma^i [\Gamma_{i,0}^{(1)} + \gamma \Gamma_{i,1}^{(1)} + \dots], \quad (3.18)$$

$$W_i = \gamma^i [W_{i,0} + \gamma W_{i,1} + \dots].$$

Thus, to different orders in γ ,

$$\hat{F}_2(\mathbf{r}) = \nu_2 \delta(\mathbf{r}) + O(\gamma^r)$$

$$= [\nu_2^0 + \gamma \nu_{2,1} + \dots] \delta(\mathbf{y}) + O(\gamma^r), \quad (3.19)$$

where $\delta(\mathbf{y}) = 0$ unless $\mathbf{r} = \gamma^{-1}\mathbf{y} = 0$, and generally;

$$\begin{aligned}\hat{F}_2(\mathbf{y}) &= \nu_2 \delta(\mathbf{y}) + \Gamma_1(\mathbf{y}, \gamma) + \cdots \\ &+ \Gamma_i(\mathbf{y}, \gamma) + O(\gamma^{i+1}) \\ &= \left(\frac{\gamma}{2\pi}\right)^r \int_{-\pi/\gamma}^{\pi/\gamma} \cdots \int e^{i\mathbf{x}\cdot\mathbf{y}} \\ &\times [\nu_2^{-1} - \tilde{\Phi}(\mathbf{k}, \gamma)]^{-1} d\mathbf{k} + O(\gamma^{2r}) \\ &\equiv \left(\frac{\gamma}{2\pi}\right)^r \int_{-\pi/\gamma}^{\pi/\gamma} \cdots \int e^{i\mathbf{x}\cdot\mathbf{y}} \\ &\times [\bar{W}_0 - \tilde{\Phi}(\mathbf{k}, \gamma)]^{-1} d\mathbf{k} + O(\gamma^{2r}).\end{aligned}\quad (3.20)$$

Alternatively,

$$\begin{aligned}\hat{F}_2(\mathbf{y}) &= \left(\frac{\gamma}{2\pi}\right)^r \int_{-\pi/\gamma}^{\pi/\gamma} \cdots \int e^{i\mathbf{x}\cdot\mathbf{y}} \\ &\times \{[\bar{W}_0 + \bar{W}_2(\mathbf{k}, \gamma) + \cdots + \bar{W}_i(\mathbf{k}, \gamma)]^{-1} \\ &- \tilde{\Phi}(\mathbf{k}, \gamma)\}^{-1} d\mathbf{k} + O(\gamma^{i+1}),\end{aligned}\quad (3.21)$$

where we have used Eq. (2.23) to express \hat{F}_2 in terms of \bar{W} . This ordering of \hat{F}_2 on the basis of the Γ ordering of \bar{W} turns out to be very convenient later when we consider self-consistent type approximations for \hat{F}_2 .

A. Expansion of the ν_k

A function that appears often in our results is the chain with ν_2^0 as a vertex-function instead of ν_2 ; we denote this as $\mathcal{C}_0(\mathbf{y}; \gamma)$ or simply $\mathcal{C}_0(\mathbf{y})$,

$$\mathcal{C}_0(\mathbf{y}) = \left(\frac{\gamma}{2\pi}\right)^r \int_{-\pi/\gamma}^{\pi/\gamma} \cdots \int d\mathbf{k} \frac{\tilde{\Phi}(\mathbf{k}, \gamma) e^{-i\mathbf{x}\cdot\mathbf{y}}}{1 - \nu_2^0 \tilde{\Phi}(\mathbf{k}, \gamma)}. \quad (3.22)$$

We also find it useful to introduce the functions

$$\begin{aligned}\Delta_i &= \nu_i - \nu_i^0, \quad S_0(\mathbf{y}) = \mathcal{C}_0^2(\mathbf{y}), \\ T_0(\mathbf{y}) &= \mathcal{C}_0^3(\mathbf{y}), \quad Q_0(\mathbf{y}) = \mathcal{C}_0^4(\mathbf{y}),\end{aligned}\quad (3.23)$$

and the identities

$$\tilde{\mathcal{C}}(\mathbf{k}; \gamma) = \tilde{\mathcal{C}}_0(\mathbf{k}; \gamma) / [1 - \Delta_2 \tilde{\mathcal{C}}_0(\mathbf{k}, \gamma)], \quad (3.24)$$

$\ln [1 - \nu_2 \tilde{\Phi}]$

$$= \ln [1 - \nu_2^0 \tilde{\Phi}] + \ln [1 - \Delta_2 \tilde{\mathcal{C}}_0]. \quad (3.25)$$

From (2.30) and (2.31), making use of (3.23) and (3.24), we find

$$\begin{aligned}\nu_2 &= \nu_2^0 - (\nu_2^0)^2 \mathcal{C}_0(0) + [2(\nu_2^0)^3 - (\nu_2^0)^2] S_0(0) \\ &+ (\nu_2^0)^4 \mathcal{C}_0(0) \tilde{S}_0(0) - \frac{(\nu_2^0)^2 (\nu_2^0)^2}{2} \\ &\times \left\{ \frac{1}{(2\pi)^r} \int \tilde{S}_0(\mathbf{k}) [\tilde{\mathcal{C}}_0(\mathbf{k})]^2 d\mathbf{k} \right\} \\ &- (\nu_2^0) (\nu_2^0)^2 \tilde{T}_0(0) + O(\gamma^{2r}).\end{aligned}\quad (3.26)$$

For arbitrary ρ , the next higher order in γ^r already includes a considerable number of terms. For $\rho = \frac{1}{2}$, however, there is appreciable simplification owing to the fact that $\partial^k \nu_l^0 / \partial \rho^k = 0$ when $\rho = \frac{1}{2}$ if $k + l$ is odd.

We have for $\rho = \frac{1}{2}$

$$\begin{aligned}\nu_2 &= \frac{1}{4} - \frac{1}{16} \mathcal{C}_0(0) + \frac{1}{256} \mathcal{C}_0(0) \tilde{S}_0(0) + \frac{1}{32} S_0(0) \\ &- \frac{17}{768} T_0(0) - \frac{1}{768} \tilde{Q}_0(0) - \frac{1}{6144} \\ &\times \left\{ \frac{1}{(2\pi)^r} \int [\tilde{\mathcal{C}}_0(\mathbf{k})]^2 \tilde{T}(\mathbf{k}) d\mathbf{k} \right\} - \frac{1}{4096} S_0(0) \\ &\times \left\{ \frac{1}{(2\pi)^r} \int [\tilde{\mathcal{C}}_0(\mathbf{k})]^3 d\mathbf{k} \right\} - \frac{3}{512} S_0(0) \tilde{S}_0(0) \\ &- \frac{1}{4096} \mathcal{C}_0(0) [\tilde{S}_0(0)]^3 + O(\gamma^{4r}).\end{aligned}\quad (3.27)$$

The expansion of ν_k for $k > 2$ is similar. In order to find $\ln \Xi$ through $O(\gamma^{3r})$ for arbitrary ρ , and $O(\gamma^{4r})$ for $\rho = \frac{1}{2}$, we need only

$$\begin{aligned}\nu_3 &= \nu_3^0 + \frac{1}{2} (\partial^2 \nu_3^0 / \partial \rho^2) (\nu_2^0)^2 \mathcal{C}_0(0) + O(\gamma^{2r}), \quad \rho \text{ arbitrary,} \\ \nu_4 &= \nu_4^0 + \frac{1}{2} (\partial^2 \nu_4^0 / \partial \rho^2) (\nu_2^0)^2 \mathcal{C}_0(0) + O(\gamma^{2r}), \quad \rho \text{ arbitrary,}\end{aligned}\quad (3.28)$$

where

$$\nu_3^0 = \rho(1 - \rho)(1 - 2\rho)$$

and

$$\nu_4^0 = \frac{1}{2} \rho(1 - \rho)[(2\rho - 1)^2 - 1].$$

A general Φ -bond, $(\partial^k \nu_l^0 / \partial \rho^k)$ -hypervertex expansion of the ν_k can be obtained by repeated use of (2.31) to eliminate the \hat{F}^{1L} in (2.30). This expansion, which can easily be re-expressed in terms of \mathcal{C}_0 instead of Φ , gives the general term in (3.27) and, when used with (3.24), (2.16), and (2.29), also yields the full expansion of $\ln \Xi$ in terms of \mathcal{C}_0 and $\partial^i \nu_k^0 / \partial \rho^i$. In characterizing the \mathcal{C}_0 -bonds $(\partial^i \nu_k^0 / \partial \rho^i)$ -hypervertex expansion of ν_k and $\ln \Xi$ graphically, the distinction between those lines incident upon a hypervertex that are associated with the index “ l ” and those lines associated with the “ k ” is important; in Appendix B of I we used the designations “in” and “out” in considering the “ l ’s” and “ k ’s”, and we refer the reader to that paper for the graphological details. These expansions are simple enough to be written out explicitly through one higher order of γ^r beyond (3.26), (3.27), and (3.28) without undue labor. Beyond that, the large number of terms makes explicit enumeration awkward.

B. Expansion of the Free Energy

The ordering of \hat{F}_2 combined with the expansion of the ν_k introduces, using (2.26), a corresponding expansion of the Helmholtz free energy. We find in analogy with (I-6.14)

$$\beta a = \beta a_0(\beta, \rho) + \frac{1}{2} \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} \ln [1 - \nu_2^0 \tilde{\Phi}(\mathbf{k}, \gamma)] d\mathbf{k} - \frac{1}{4} \{ (\nu_2^0)^2 \sum_y T_0(y) - (\nu_2^0)^2 S_0(0) \} + O(\gamma^{2\nu+1}). \quad (3.29)$$

Brout¹⁹ seems to have been the first to suggest developing a formal program using γ as an ordering parameter to investigate the free energy, and he considered the results of retaining only zero and first-order terms (i.e., of dropping ν_k for $k \geq 3$), and evaluating the ν_2 by means of a spherical model-like approximation that we discuss in detail later. A similar analysis can be made of expansions in terms of H and Φ rather than ρ and Φ , and subsequent to Brout's initial work Horwitz and Callen¹⁸ suggested an approximation obtainable by retaining the zero and first-order terms in such expansions. Equation (3.29) agrees with the result obtained from the prescription of Coopersmith and Brout.⁵

C. Illustrative Examples

1. Exponential Potential in One Dimension

We consider a one-dimensional system where $\varphi(y)$ of (3.1) has the form $\frac{1}{2}\alpha e^{-|y|}$. We then have

$$\tilde{\Phi}(k, \gamma) = -\beta(\alpha/2)\lambda\gamma [\sinh \gamma / (\cosh \gamma - \cos k) - 1], \quad (3.30)$$

where

$$\lambda(\gamma) = \gamma^{-1}(e^\gamma - 1) \xrightarrow{\gamma \rightarrow 0} 1 \quad (3.31)$$

making α the integrated strength of w , $w(0) = \alpha$. This gives to second order in γ [see (3.6)]

$$\hat{F}_2(y, \gamma; \nu_2) = \nu_2 \delta(r) + (\nu_2^0)^2 \mathcal{C}_0(y, \gamma; \nu_2^0) + O(\gamma^3), \quad (3.32)$$

where, from (3.9) and (3.22),

$$(\nu_2^0)^2 \mathcal{C}_0(y, \gamma; \nu_2^0) = \nu_2^0 \left[\frac{1}{1 - \beta(\alpha/2)\lambda\gamma\nu_2^0} - 1 \right] \delta(r) - \beta\lambda \frac{\alpha}{2} \gamma \left[\frac{\nu_2^0}{1 - \beta(\alpha/2)\lambda\gamma\nu_2^0} \right]^2 \frac{\sinh \gamma}{\sinh(\gamma s)} e^{-s|y|}, \quad (3.33)$$

s being determined by the relation

$$\cosh(\gamma s) = \cosh \gamma + \frac{\beta(\alpha/2)\lambda\gamma\nu_2^0}{1 - \beta(\alpha/2)\lambda\gamma\nu_2^0} \sinh \gamma, \quad (3.34)$$

yielding

$$s = (1 + \beta\alpha\nu_2^0)^{\frac{1}{2}} + O(\gamma), \quad (3.35)$$

and ν_2 is given in terms of ν_2^0 by means of (2.9), (2.30), (3.9), and (3.23):

$$\nu_2 = \nu_2^0 - (\nu_2^0)^2 \mathcal{C}_0(0, \gamma; \nu_2^0) + O(\gamma^2). \quad (3.36)$$

In a way similar to (3.33), we get with (3.34)

$$\nu_2 = \nu_2^0 \{ 1 - \nu_2^0 \beta(\alpha/2) \lambda \gamma [1 - s^{-1}] \} + O(\gamma^2). \quad (3.37)$$

After expanding (3.33) to second order in γ , we obtain

$$\Gamma_1(y, \gamma; \nu_2^0) = (\nu_2^0)^2 \beta(\alpha/2) \lambda \gamma [\delta(r) - s^{-1} \times \exp[-s|y|]] + O(\gamma^2), \quad (3.38)$$

and finally,

$$\hat{F}_2(y, \gamma; \nu_2^0) = \nu_2^0 \delta(r) + (\nu_2^0)^2 \beta(\alpha/2) \lambda \gamma \times [\delta(r) - \exp[-s|y|]] s^{-1} + O(\gamma^2). \quad (3.39)$$

This expression coincides with the one derived by Kac and Helfand⁹ [their (5.8)] for $r \neq 0$, and $\rho = \frac{1}{2}$.

For the same one-dimensional potential we obtain, for the free energy per unit volume given by (3.29), the expression

$$\begin{aligned} \beta a(\beta, \rho, \gamma) &= \rho \ln \rho + (1 - \rho) \ln(1 - \rho) \\ &+ \beta(\alpha/2) \rho^2 - \frac{\gamma}{2} \{ 1 + \beta(\alpha/2) \lambda \rho - [1 + \beta\alpha\lambda\rho(1 - \rho)^{\frac{1}{2}}] \} \\ &+ \frac{\gamma^2}{2} \frac{[\beta(\alpha/2) \lambda \rho(1 - \rho)]^2}{1 + \beta\alpha\lambda\rho(1 - \rho)} \left\{ \frac{1}{2} + \frac{1}{9} \beta(\alpha/2) \lambda (1 - 2\rho)^2 \right. \\ &\times \left. \frac{1}{[1 + \beta\gamma\alpha\rho(1 - \rho)]} \right\} + O(\gamma^3). \end{aligned} \quad (3.40)$$

This free energy may be compared after expanding λ , (3.31), in powers of γ with the one derived for a continuum in (I-6.15). Both can be written as

$$\begin{aligned} \beta a(\beta, \rho) &= \beta a^0(\beta, \rho) + \beta(\alpha/2) \rho^2 - (\gamma/2) \\ &\times \{ 1 + \beta(\alpha/2) \rho - [f(\beta, \rho)]^{\frac{1}{2}} \} + f^{-1}(\beta, \rho) O(\gamma^2), \end{aligned} \quad (3.41)$$

where $f(\beta, \rho) = 0$ is the boundary of the meta-stable region in the van der Waal-Maxwell equation of state [cf. Eq. (4.1) and Fig. 1], and follows from (1.15) for the lattice and from (I-1.2) for the continuum system.

Equation (3.39) can also be compared, after the appropriate transcription, with the free energy per lattice site of the spin system, and it coincides at $\rho = \frac{1}{2}$ with the free-field expression derived by Siebert,⁶ including the terms of $O(\gamma^2)$.

2. Exponential Potential in Two and Three Dimensions

Following Baker⁸ we consider a potential $w_r(\mathbf{r}, \gamma)$, $\nu = 2, 3$, as given by (3.1) of the explicit form

$$w_r(\mathbf{r}, \gamma) = \alpha \gamma^{\frac{\lambda_r(\gamma)}{2}} \prod_{i=1}^{\nu} e^{-\gamma |r_i|} \quad (3.42)$$

for $\mathbf{r} \neq 0$ and vanishes for $\mathbf{r}=0$, where $\mathbf{r} = (r^1, \dots, r^\nu)$ and

$$\lambda_2(\gamma) = \gamma^{-2}(e^\gamma - 1)^2/e^\gamma \rightarrow 1, \quad (3.43)$$

$$\lambda_3(\gamma) = 8\gamma^{-3}[(e^\gamma - 1)^3/(6e^{2\gamma} + 2)] \rightarrow 1. \quad (3.44)$$

Then

$$\Phi_r(\mathbf{k}, \gamma) = -\beta \alpha \frac{\gamma^{\lambda_r(\gamma)}}{2^{\nu}} \left[(e^{2\gamma} - 1)^{\nu} - \prod_{i=1}^{\nu} (1 + e^{2\gamma} - 2e^{\gamma} \cos k_i) \right] / \prod_{i=1}^{\nu} (1 + e^{2\gamma} - 2e^{\gamma} \cos k_i), \quad (3.45)$$

where $\mathbf{k} = (k_1, \dots, k_\nu)$ and $w_r(0) = \alpha$.

For the free energy per unit volume we obtain from (3.29), after expanding in powers of γ , the expression

$$\beta a_r(\beta, \rho) = \beta a^0(\beta, \rho) + \frac{1}{2} \beta \alpha \rho^2 - \frac{1}{2} \gamma^{\nu} \int_0^{\nu\pi} d\xi I_r(\xi) + O(\gamma^{\nu+1}), \quad (3.46)$$

where the form of the integrand $I_r(\xi)$ depends explicitly on the dimension ν .

Two-dimensions ($\nu = 2$). In analogy to the result obtained by Baker⁸ for the corresponding $I_2(\xi)$, we have for $\alpha < 0$,

$$\beta a(\beta, \rho) = \beta a^0(\beta, \rho) + \frac{1}{2} \beta \alpha \rho^2 - \frac{1}{4} \beta \alpha \gamma^2 \times \left[\frac{1}{2} \rho (2 - \rho) - \frac{1}{\pi} \int_0^{\nu\pi} d\xi \mathbf{K}(\beta |\alpha| \xi) \right] + O(\gamma^3), \quad (3.47)$$

where $\mathbf{K}(k)$ is the complete elliptic integral of the first kind which diverges as $k \rightarrow 1$, i.e., under an appropriate upper limit in (3.47), when the relation $\beta |\alpha| \nu_2^0 = 1$ holds. However, the integral in (3.47) is still finite in this case as one can see from the expansion of $\mathbf{K}(k)$ for k near 1. The same expansion allows also to see that the coefficient of γ^3 is already divergent under the same relation. Therefore, we obtain the behavior of the free energy predicted after (1.14). Finally, from the properties of elliptic integrals, it can be seen that for $\beta |\alpha| \nu_2^0 \rightarrow 1$ there is a singularity in the γ^2 term of the specific heat at constant density for $\rho = \frac{1}{2}$, of the form $(T - T_c)^{-1}$, where T_c is the van der Waals-Maxwell critical temperature $\beta_c = -(\nu_2^0 \alpha)^{-1} = -4/\alpha$.

Three Dimensions ($\nu = 3$). In this case the expression for the free energy per unit volume differs from (3.47) in that the integral in (3.46) has the form⁸

$$\frac{\gamma^3}{\pi^2} \int_0^{\nu\pi} d\xi \int_0^{\pi} dk_3 \mathbf{K} \left(\frac{\gamma^2 \beta |\alpha| \xi}{1 + e^{2\gamma} - 2e^{\gamma} \cos k_3} \right) / (1 + e^{2\gamma} - 2e^{\gamma} \cos k_3),$$

giving again a finite result for the coefficient of γ^7 even when $\beta |\alpha| \nu_2^0 \rightarrow 1$.

IV. DISCUSSION OF γ -EXPANSION AND SELF-CONSISTENT APPROXIMATIONS

Before discussing the usefulness of the γ -expansion developed in the last section, we discuss first the known, or conjectured, behavior of our system for different values of γ . In the van der Waals limit $\gamma \rightarrow 0$, the free energy per unit volume $a(\beta, \rho, 0+) = \lim_{\gamma \rightarrow 0} a(\beta, \rho, \gamma)$ is obtained⁷ by applying the double-tangent construction to the generalized van der Waals free energy $a_0(\beta, \rho) = a^0(\beta, \rho) + \frac{1}{2} \beta \alpha \rho^2$. The latter is, of course, the zero-order term in our expansion of $a(\rho, \gamma)$ in powers of γ . In Fig. 1 the exterior of curve I is the region in which $a_0(\beta, \rho) = a(\beta, \rho, 0+)$ for $\alpha < 0$. [For $\alpha \geq 0$, $a(\beta, \rho, 0+)$ coincides with $a_0(\beta, \rho)$ for all β and ρ .] Inside curve I, the system will exist in two phases and have its

thermodynamic properties described by $a(\rho, 0+)$, a linear combination of its properties in the two phases; $a_0(\rho)$, on the other hand, describe the properties of the system when the system is in a state

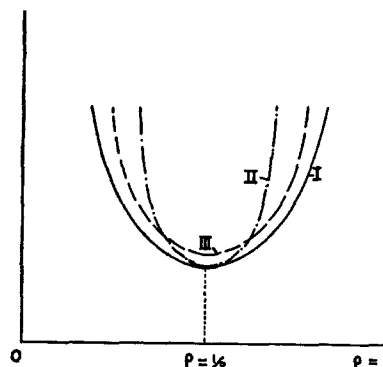


Fig. 1. I. Boundary of two-phase region for $\gamma \rightarrow 0$. II. Boundary of metastable region for $\gamma \rightarrow 0$. III. "Expected" boundary of two-phase region for small γ in two and three dimensions.

of uniform density. This coincides with the metastable state in the region between curve I and curve II. This latter curve is determined by the equation

$$\beta = -[\nu_2^0 \bar{w}(0)]^{-1} = -[\rho(1 - \rho)\alpha]^{-1}. \quad (4.1)$$

We have also drawn in Fig. 1 the "expected" two-phase region of the system in two and three dimensions for some fixed small γ (keeping the integrated strength of the potential α fixed). (In one dimension there will be no transition for $\gamma \neq 0$.)

Now, the coefficients of the expansion in γ [of $a(\beta, \rho, \gamma)$ or $\hat{F}_2(\gamma, \gamma)$] will diverge as the boundary of the metastable region, curve II, is approached from the outside and will be meaningless inside curve II, where $dp_0(\rho)/d\rho$ is negative, cf. (3.40). The expansion in γ can therefore be meaningful, as an approximation to the real state of the system, only outside curve I. Inside curve I, the correct $a(\beta, \rho, \gamma)$ is not analytic in γ for small γ . The coefficients of our expansion will become large as the boundary of curve II is approached (this curve coincides with curve I at the critical density $\rho = \frac{1}{2}$).

The first few terms in the expansion may therefore be used as an approximation to the properties of the system for small values of γ only in the region—call it R —outside curve I, and not too close to the critical point [outside a region of $O(\gamma^1)$ in one dimension⁹]. In the region R , the expansion in γ is straightforward (we have not, however, investigated the question of the convergence of the expansion at all).

The above analysis indicates that the straightforward γ -expansion is incapable of yielding reliable information inside the critical (or two-phase) region for finite γ . In order to overcome this limitation on the γ -expansion, as well as to consider situations where γ is not very small, one can use approximation methods for \hat{F}_1 which do not assume analyticity in γ ; $a(\rho, \gamma)$ may then be obtained from \hat{F}_2 via (2.26). Now, our expansion procedure in the last section consisted of two parts: (1) Γ ordering of the graphs

$$\hat{F}_1(\mathbf{r}_1, \dots, \mathbf{r}_l) \\ = \sum_{k=0}^{\infty} \Gamma_k^l(\mathbf{r}_1, \dots, \mathbf{r}_l; \gamma, \nu_2, \dots, \nu_{k+l}) \quad (4.2)$$

and (2) an expansion of each Γ_k^l in powers of γ . It was this second step, which involved the expansion of the ν_k in powers of γ , that led to the singularities discussed before. It seems therefore sensible to avoid the expansion of the Γ_k^l in powers of γ . This requires some method for evaluating the ν_k to each order in the Γ ordering (without any reference to γ at all).

We shall now describe such a method but leave its detailed analysis to Part III of this series.

A. Self-Consistent Method for the Determination of the ν_k

Since our interest lies primarily in \hat{F}_2 , and the thermodynamic properties which may be computed from it, we consider the following iterative self-consistent method for the evaluation of the ν_k appearing in \hat{F}_2 . [This method is based on Γ ordering but does not make any explicit reference to the range of $w(\mathbf{r})$.] The first-order step in our approximation scheme consists of retaining *only* the Γ_0 and Γ_1 graphs in \hat{F}_2 and evaluating the ν_2 appearing in them from the exact relation (2.9),

$$\begin{aligned} \nu_2(\rho) &\equiv \rho(1 - \rho) = \Gamma_0(\mathbf{r}_1, \mathbf{r}_1; \nu_2) + \Gamma_1(\mathbf{r}_1, \mathbf{r}_1; \nu_2) \\ &= \Omega^{-1} \sum_{\mathbf{k}} \frac{\nu_2}{1 - \nu_2 \bar{w}(\mathbf{k})}. \end{aligned} \quad (4.3)$$

In the next order of our approximation we retain the Γ_0 , Γ_1 , and Γ_2 graphs in \hat{F}_2 and the Γ_0^3 and Γ_1^3 graphs in \hat{F}_3 . We then determine the ν_2 and ν_3 which appear in these graphs from the set of two coupled equations taken from (2.9),

$$\nu_2(\rho) = \nu_2 + \Gamma_1(\mathbf{r}_1, \mathbf{r}_1; \nu_2) + \Gamma_2(\mathbf{r}_1, \mathbf{r}_1; \nu_2, \nu_3), \quad (4.4)$$

$$\nu_3(\rho) = \nu_3 + \Gamma_1^3(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_1; \nu_2, \nu_3). \quad (4.5)$$

In general, the k th order in our scheme consist in evaluating the Γ_i^l for $j + l = 2, \dots, k + 1$, as functions of the ν_i , $i = 2, \dots, k + 1$ and then solving k -equations of the form

$$\nu_j(\rho) = f_j(\nu_2, \dots, \nu_{k+1}), \quad j = 2, \dots, k + 1. \quad (4.6)$$

The self-consistency in our scheme refers to the fact that in each order we have $\hat{F}_2(\mathbf{r}_1, \mathbf{r}_1)$ equal to its exact value at the given density ρ . In other words $n_2(\mathbf{r}_1, \mathbf{r}_1) = 0$ in each order, i.e., the average pair density vanishes when the positions of the two particles coincide. In spin language this means that $\langle [\sigma(\mathbf{r}_1)]^2 \rangle = \frac{1}{4}$ in all orders. The discussion following Eq. (2.10) shows that the symmetry properties of \hat{F}_k and ν_k as a function of $\rho - \frac{1}{2} = \langle \sigma \rangle$ remain valid in all orders of our iterative scheme.

A slight modification of this method is to use the auxiliary function \hat{W} (from which \hat{F}_2 may then be determined), Eq. (2.23), in the above iterative scheme. According to (3.16), the l th term in the Γ ordering of \hat{W} , \hat{W}_l will only contain ν_k with $k \leq l + 1$ for $l > 0$, $\hat{W}_0 = \nu_2 \delta(\mathbf{r})$. Thus, in the lowest order, we equate \hat{W} to \hat{W}_0 and obtain the corresponding \hat{F}_2 , (3.20), and again determine ν_2 from (2.9). This leads again to (4.2). In the next order

we retain \hat{W}_0 and \hat{W}_2 in \hat{W} , compute the resulting \hat{F}_2 from (3.21), and determine ν_2 and ν_3 from (4.5) and the equation

$$\nu_2^0(\rho) = \Omega^{-1} \sum_{\mathbf{k}} \{[\nu_2 + \nu_3^2 \tilde{s}(\mathbf{k}; \nu_2)]^{-1} - \tilde{\Phi}(\mathbf{k})\}^{-1} \quad (4.7)$$

$[\tilde{s}]$ defined in (3.12)], which replaces Eq. (4.4). This process may be continued, yielding at each step equations similar to (4.6). The set of graphs contained in \hat{F}_2 obtained from \hat{W} in the n th order is larger than the set $\Gamma_0 + \dots + \Gamma_n$ for $n > 1$. This appears to have advantages for systems where $w(r)$ is not very long range, to which these methods are also applicable.

The results of this iteration scheme will be analyzed in Part III of this series, where it is shown, in particular, that our lowest approximation for the pair-distribution function is identical with that obtained from the mean spherical model of Lewis and Wannier^{10,21} for spin systems which coincide in the thermodynamic limit $\Omega \rightarrow \infty$ with the spherical model of Berlin and Kac.¹¹ This is also similar to the result of Brout.¹⁹

B. Bond Renormalization

We can go a step further in the use of \hat{W} by considering its L -bond expansion instead of its c -bond expansion. For a lattice system the definition of L [Eq. (I-2.19)] is²²

$$L(\mathbf{r}_{12}) = \Phi(\mathbf{r}_{12}) + \sum_{\mathbf{r}_{13}, \mathbf{r}_{14}} \Phi(\mathbf{r}_{13}) \hat{F}_2(\mathbf{r}_{34}) \Phi(\mathbf{r}_{24}). \quad (4.8)$$

In terms of graphs with L -bonds rather than c -bonds, the prescription for \hat{W} following (2.23) includes the added restriction that no graph should contain any *articulation pairs of bonds*, i.e., pairs of bonds which, when cut, cause the graph to separate into two or more parts, one of which contains at least one hypervertex, but no labeled hypervertex. Thus, we have

$$\hat{W}_2(\mathbf{r}_{12}) = \nu_2 + \text{[diagram: a series of graphs connected by plus signs, including a loop, a figure-eight, a diamond, and a more complex loop structure]} + \dots \quad (4.9)$$

(the solid lines now representing L -bonds). Graphs like $\bullet \text{---} \text{---} \text{---} \bullet$ do not appear.

²¹ J. L. Lebowitz and J. K. Percus, Phys. Rev. **144**, 251 (1966).

²² Our L coincides, for lattice gases, with the "renormalized interaction" ν of R. Abe, Ref. 13.

The introduction of the L -bonds may be thought of as a bond renormalization similar in some ways to the introduction of the ν_k 's in place of the μ_k 's, which is a vertex renormalization. One reason for introducing the bond renormalization is that it provides a convenient means of analyzing certain aspects of the critical behavior of $\hat{F}_2(r)$ as well as suggesting a class of approximations that appear to exhibit the kind—although not the precise extent—of deviation from the Ornstein-Zernike¹⁸ theory that is actually found in the behavior of the two-dimensional lattice gas and in real three-dimensional systems. Such approximations can be obtained by applying the same recipe that defines the Γ ordering scheme, described in Sec. III, to the L -bond graphs of \hat{W} . However, we do not pursue the investigation of any such particular approximation here, but instead restrict our remarks to observations that have a more immediate bearing on the behavior of \hat{F}_2 near the critical point.

The L -bond expansion seems better suited to examining critical behavior of \hat{F}_2 than the expansions we have previously considered, because one already has the defining relation (2.23) for \hat{W} in terms of \hat{F}_2 and any sufficiently simple second relationship between \hat{W} and L —and hence between \hat{W} and \hat{F}_2 through Eq. (4.8)—immediately provides a convenient means of determining the spatially asymptotic behavior of \hat{F}_2 at the critical point where we assume¹³

$$1 - \tilde{\Phi}(0)\bar{W}(0) = 0. \quad (4.10)$$

We start by assuming that when (4.10) is satisfied, \hat{F}_2 behaves like some inverse power of r for large r , and we use the kind of analysis initiated by Green²³ and generalized by Stillinger and Frisch,²⁴ Fisher,²⁵ and Stillinger.²⁶ We find, then, that (2.23), (4.10), and the assumptions that

$$\bar{W}(r) \sim A[L(r)]^m, \quad \text{for } r \rightarrow \infty \quad (4.11)$$

and

$$\hat{F}_2(r) \sim B/r^n, \quad \text{for } r \rightarrow \infty \quad (4.12)$$

²³ M. S. Green, J. Chem. Phys. **33**, 1403 (1960).

²⁴ F. H. Stillinger, Jr., and H. L. Frisch, Physica **27**, 751 (1961).

²⁵ M. E. Fisher, J. Math. Phys. **5**, 944 (1964).

²⁶ F. H. Stillinger, Jr. (private communication). Stillinger has made a detailed examination of consequences of assuming more general forms than (4.11), including such possibilities as an addition $(\ln r)^c$ term in the denominator and the replacement of the constant by some reasonable angular dependent quantity. He has concluded that such modifications will not change the relationship among constants such as our n , ν , and m .

imply that²⁷

$$n = 2\nu/(1 + m), \quad (4.13)$$

where we have also assumed that $\Phi(r)$ is short-ranged enough so that, for large r , $L(r)$ as well as $\hat{F}_2(r)$ is given by (4.12). Here, ν is the dimensionality of the space. Instead of (4.11) and (4.12), we now consider the more general possibility [imposed upon us by the form of (4.17)]:

$$\hat{W}(r) \sim A[L(r)]^m f_a(r), \quad \text{for } r \rightarrow \infty \quad (4.14)$$

and

$$\hat{F}_2(r) \sim B f_b(r)/r^n, \quad \text{for } r \rightarrow \infty, \quad (4.15)$$

where f_a and f_b are functions of order less than any positive power and greater than any negative power of r . (When the letter f appears hereafter in this section it always denotes such a function.)

The same arguments that are used to obtain (4.13) from (4.11) and (4.12) suggest that (4.14) and (4.15) also yield (4.13), supplemented by a relation between f_a and f_b . Although a general demonstration for arbitrary f_a or f_b has not been given, and is not attempted here, these remarks can be made more precise²⁸ for an important class of particular f_a and f_b . For example, in the simple but representative case of $f_a = (\log r)^t$ and $f_b = (\log r)^{-t}$, we obtain (4.13) and the relation

$$l = \epsilon(1 + m). \quad (4.16)$$

Furthermore, as Green²³ and Abe¹³ have pointed out, simple dimensional arguments can be applied to graphs of the sort that appear in the L -bond expansion of $\hat{W}(r)$. These arguments indicate that any graph in the L -bond expansion of $\hat{W}(r)$ consisting of b -bonds and k -hypervertices will behave like

$$r^{-[bn - \nu k + 2\nu]} f_c(r) = f_d(r)[L(r)]^m, \quad \text{for } r \rightarrow \infty, \quad (4.17)$$

where $L(r)$ is assumed to go asymptotically as $f(r)/r^n$. Such dimensional considerations are somewhat crude but they probably give a reasonable picture of the relative dominance of the various graphs at large r , and we now consider their implications. Equation (4.17) yields

$$\hat{W}(r) \sim \sum_i A_i r^{-[b_i n - \nu k_i + 2\nu]} f_i(r), \quad \text{for } r \rightarrow \infty, \quad (4.18)$$

where the sum is over all graphs in \hat{W} , and A_i , b_i , k_i , and f_i are associated with the i th graph. At the

²⁷ The argument leading to (4.13) from (2.23), (4.11), (4.12), and the assumption that $1 - \Phi(0) \hat{W}(0) = 0$ is identical to the one used by Fisher (Ref. 25) in discussing the hypernetted-chain equation, and we refer the interested reader to that reference for details.

critical point, $\rho = \frac{1}{2}$ and any graph containing a ν_k with odd k vanishes [thus, among the graphs actually drawn in (4.9) only the last one remains]. Among the graphs that are left, the ones whose hypervertices are all ν_k 's are the ones with the fewest bonds for a given number of hypervertices ($b+1=2k$). We might expect these to be the dominant graphs for large r , and according to (4.18) this expectation is fulfilled as long as

$$\sum_{\{b_i+1=2k_i\}} A_i f_i \neq 0. \quad (4.19)$$

Equations (4.13), (4.17), and (4.19) then yield

$$n = \frac{1}{2}\nu. \quad (4.20)$$

This is the case considered by Abe.¹³ More generally, it follows that

$$n = \nu k_i / (b_i + 1) \quad (4.21)$$

for the pairs $\{k_i, b_i\}$ that correspond to the set of graphs having the longest range (i.e., the single lowest value of $b_i n - \nu k_i + 2\nu$) such that the sum $\sum A_i f_i$ over these pairs is not zero, provided that the series (4.18) is a valid and convergent representation of $\hat{W}(r)$ at the critical point. This latter stipulation, of course, involves not only the validity of (4.17) but also the validity of the L -bond expansion of \hat{W} at the critical point in the first place.

In the case of a nearest-neighbor interaction on square and cubic lattices, the exact \hat{F}_2 at the critical point appears to have the form (4.15) with $n = \frac{1}{4}$ when $\nu = 2$, and $n \simeq \frac{1}{3}$ when $\nu = 3$.²⁸ In order to be in agreement with these figures, we must have $m = 15$ for $\nu = 2$ and $m \simeq \frac{1}{3}$ for $\nu = 3$ ($m = \frac{1}{3}$ would yield $n = \frac{1}{3}$). In light of (4.21), this suggests that either there is wholesale cancellation among graphs or else the series (4.18) does not provide a valid representation of \hat{W} . We further note that the cancellation that would enable us to ignore certain subsums of graphs for $n < \frac{1}{2}\nu$ will necessarily involve cancellation of graphs that are individually divergent [in Eq. (4.18), $b_i n - \nu k_i + 2\nu$ will always be < 0 for some b_i and k_i when $n < \frac{1}{2}\nu$]. This means that, strictly speaking, cancellation is not an alternative to the breakdown of the graphical representation (4.9) but rather a special case of this breakdown.

Percus and one of the authors²⁹ (G.S.) have considered a weakened version of the Ornstein-Zernike theory¹⁴ that does not rest upon the convergence of (4.9). It indicates that the m in Eq. (4.14) may

²⁸ D. S. Gaunt, M. E. Fisher, M. F. Sykes, and J. W. Essam, Phys. Rev. Letters 13, 713 (1964).

²⁹ J. K. Percus and G. Stell (to be published).

be closely connected with the shape of the critical isotherm in the vicinity of the critical point, and further progress in the direction of associating the m and A in Eq. (4.14) with macroscopic features of the lattice system seems likely. The task of obtaining reliable estimates of these quantities directly in terms of Φ and ρ appears much more difficult, however.

The above considerations are not directly applicable to the one-dimensional system with a Kac potential. However, for this case an explicit computation shows that near the critical point [see Eq. (5.9) of Ref. 9] $\mathcal{C} \sim \Lambda^{\frac{1}{2}} e^{-\Lambda r}$ where $\Lambda = s\gamma \sim \gamma^{4/3}$ so that we can use Λ instead of γ as an ordering parameter in \mathcal{C} -bond expansions. It can easily be seen that, in the expansion of F_2^L , the graphs whose labeled hypervertices are ν_2 's and whose unlabeled hypervertices are ν_4 's are all of order $\Lambda^{\frac{1}{2}}$, and that all other graphs are of higher order in Λ . Hence, the sum of these graphs of order $\Lambda^{\frac{1}{2}}$ will yield the

$$\sum_{i \geq 1} a_i \gamma^{\frac{1}{2}} \exp [-b_i \gamma^{4/3} r],$$

which Kac and Helfand have shown to be the dominant term in $F_2^L(r)$ when the critical point is approached. Similarly, in the \mathcal{C} -bond expansion of \hat{W}^L , the graphs whose vertices are all ν_4 's are the dominant ones in the critical region. Hence, in the

L -bond expansion of \hat{W}^L , the graphs whose vertices are all ν_4 's are also the dominant ones in the critical region, since, upon expansion of L in terms of \mathcal{C} , all of the \mathcal{C} -bond graphs with ν_4 vertices come only from the L -bond graphs with ν_4 vertices.

Kac³⁰ has conjectured that, in such graphical representations of F_2 and related functions, the terms that are dominant in the critical region in the one-dimensional case may be the ones that dominate in all dimensions, despite the fact that the degree and even the *kind* of singularities present can be expected to be different in different dimensions. If (4.19) were satisfied, the graph with ν_4 vertices would have a special role in all dimensions and the result would be consistent with Kac's conjecture. However, the confrontation with the known value of n for $\nu = 2$ forces us to either abandon our graphical representation altogether at the critical point or at least conclude that a subtle kind of cancellation among graphs must be occurring so that (4.19) is violated.

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³⁰ Talk presented at Semi-annual Statistical Mechanics Meeting at Belfer Graduate School of Science, Yeshiva University (1964).