

$$\begin{aligned}
E_\mu\{\frac{2}{3}t_3 \mid U_2\} &= \begin{bmatrix} \Gamma_\mu(U_2) & 0 & 0 \\ 0 & 0 & [\exp(-i\mathbf{k}\cdot\frac{1}{3}t_3)]\Gamma_\mu(U_2) \\ 0 & [\exp(-i\mathbf{k}\cdot\frac{1}{3}t_3)]\Gamma_\mu(U_2) & 0 \end{bmatrix}, \\
E_\mu\{\frac{2}{3}t_3 \mid C_3^1\} &= \begin{bmatrix} 0 & 0 & [\exp i\mathbf{k}\cdot t_3]\Gamma_\mu(E) \\ \Gamma_\mu(E) & 0 & 0 \\ 0 & [\exp i\mathbf{k}\cdot t_3]\Gamma_\mu(E) & 0 \end{bmatrix}, \\
E_\mu\{\frac{1}{3}t_3 \mid C_3^2\} &= \begin{bmatrix} 0 & [\exp i\mathbf{k}\cdot t_3]\Gamma_\mu(E) & 0 \\ 0 & 0 & \Gamma_\mu(E) \\ \Gamma_\mu(E) & 0 & 0 \end{bmatrix}.
\end{aligned}$$

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Separation of the Interaction Potential into Two Parts in Treating Many-Body Systems. I. General Theory and Applications to Simple Fluids with Short-Range and Long-Range Forces*

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Systematic methods are developed for investigating the correlation functions and thermodynamic properties of a classical system of particles interacting via a pair potential $v(r) = q(r) + w(r)$. The method is then applied to the case in which $w(r)$ is a "Kac potential" $w(r, \gamma) = \gamma^d \varphi(\gamma r)$ (ν the dimensionality of the space) whose range γ^{-1} is very long compared to the range of $q(r)$. Our work is related closely to the work of Kac, Uhlenbeck, and Hemmer. The main new feature of our method is the separation of the correlations, e. g., the two-particle Ursell function $\mathcal{F}(r)$, into a short-range part $\mathcal{F}^s(r, \gamma)$ and a long-range part $\mathcal{F}^L(y, \gamma)$, $y = \gamma r$; r the distance between the particles. The two parts of $\mathcal{F}$ are defined in terms of their representation by graphs with density (or fugacity) vertices and K - and Φ -bonds, $K(r) = e^{-\beta q} - 1$, $\Phi = -\beta w$. A resummation of these graphs then yields a simple graphical representation for the long-range part of the correlation functions in terms of graphs with Φ -bonds and "hypervertices" made up of the short-range part of the correlations. This representation is then used in this paper to make separate expansions of $\mathcal{F}^s(r, \gamma)$ and $\mathcal{F}^L(y, \gamma)$ and through them of the thermodynamic parameters in powers of γ . Explicit calculations of the Helmholtz free energy is carried out to a higher order in γ than done previously by Hemmer and it is shown how to carry out the calculation, in principle, to any order. The general method is further applied (in separate articles) to lattice gases, plasmas, and to the special problem of critical phenomena.

I. INTRODUCTION

THIS paper is the first in a series dealing with classical equilibrium systems. The system discussed in this paper, where the general formalism is developed, is a fluid of point particles interacting

via pair potentials $v(r)$. [Later papers will deal with lattice gases¹ (Ising spin systems), and plasmas.²]

The problem, as usual, is to obtain the thermodynamic properties and low-order correlation functions of the fluid from the properties of the interatomic potential $v(r)$ believed to consist of a very

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¹ S. Baer, J. L. Lebowitz, G. Stell, and W. Theumann (to be published in J. Math. Phys.).

² J. L. Lebowitz and G. Stell, Bull. Am. Phys. Soc. 9, 105 (1964); (article to be published in J. Math. Phys.).

strongly repulsive short-range part and a weaker attractive part of longer range. Of particular interest are the properties of the system at liquid densities and the nature of the ever present phase transition. For these purposes the usual virial expansion is not of much theoretical use. As has been shown recently it is possible for the virial expansion to diverge at a density which is either lower or higher than the density at which a phase transition occurs.³ Also the method often used in the theory of classical fluids, that of approximate integral equations for the radial distribution function, appears to be quite useful for describing the properties of systems interacting via short-range repulsive forces (e.g., hard spheres) but has been less useful for representing the effect of the attractive part of the intermolecular potential,⁴ the part responsible for the existence of the liquid.

This suggests developing a theory, or method, which would use as a reference system, or zero-order term, a system of particles interacting via the short-range repulsive part of the potential only: in contrast to the virial expansion which has the zero density gas as a reference system. One such method that has already been used, successfully, for fluids and spin systems employs a high temperature expansion.⁵ The method we shall consider is somewhat different and consists essentially of an expansion in the ratio of the ranges of the short-range and long-range part of the interatomic potential. The idea of separating the intermolecular potential into a short-range repulsive and long-range attractive part goes back to van der Waals⁶ who used it to derive the famous equation of state bearing his name.

A precise mathematical formulation of van der Waals' idea has been given by Kac⁷ and utilized extensively by Kac, Uhlenbeck, and Hemmer.⁷ They

considered a one-dimensional system with a pair potential $v(r) = q(r) + w(r, \gamma)$,

$$q(r) = \begin{cases} \infty, & r < \delta, \\ 0, & r > \delta, \end{cases}$$

$$w(r, \gamma) = \gamma\varphi(\gamma r) = (\alpha/2)\gamma e^{-\gamma r}, \quad \alpha < 0. \quad (1.1)$$

Kac⁷ first showed that as long as γ is finite, there is no phase transition (this is true in general in one dimension for potentials which fall off reasonably fast with distance). However, in the limit $\gamma \rightarrow 0$, KUH⁷ found the pressure p as a function of density ρ and temperature β^{-1} to be given by the van der Waals equation of state combined with Maxwell's equal area construction,

$$\lim_{\gamma \rightarrow 0} p(\rho, \gamma) = \rho\beta^{-1}/(1 - \rho\delta) + \frac{1}{2}\alpha\rho^2 \quad \text{plus Maxwell's rule.} \quad (1.2)$$

Unfortunately, their actual method of solution depends very much on the exact form of the potential and on it being one dimensional. The main new feature of their potential is the strict separation of $v(r)$ into a short-range part and a *truly long-range* part in the limit $\gamma \rightarrow 0$. It should be emphasized that the limit $\gamma \rightarrow 0$ is taken *after* the size of the system has been made infinite.

The work of Kac, Uhlenbeck, and Hemmer has been extended recently by Lebowitz and Penrose⁸ to higher dimensions and to more general interparticle potentials of the form $v(r) = q(r) + \gamma^v\varphi(\gamma r)$, where v is the dimensionality of the space. In this work, which is also related to recent work by van Kampen,⁹ it is proven rigorously for a wide class of q 's and φ 's that in the "van der Waals limit", $\gamma \rightarrow 0$, the equation of state assumes the form

$$\lim_{\gamma \rightarrow 0} p(\rho, \gamma) = p^0(\rho) + \frac{1}{2}\alpha\rho^2 \quad \text{plus Maxwell's rule,}$$

where $p^0(\rho)$ is the pressure in the reference system, $w(r) = 0$, and $\alpha \equiv \int \varphi(y)dy$.

In actual physical systems the potential does not, of course, have infinite range in the above sense. The separation of the potential should still be useful though whenever many particles can fit in within the range of one particle's attractive potential. This was, in fact, the central idea behind the earlier work of Brout for lattice systems which was further

³ J. L. Lebowitz and O. Penrose, J. Math. Phys. 5, 841 (1964); O. Penrose, *ibid.* 4, 1312 (1963).

⁴ A major obstacle has been the difficulty in obtaining the solutions of these equations in a tractable enough form to be sure just what they predict about liquids, especially in transition and critical regions. Furthermore even where these equations have been solved numerically it is difficult to assess their worth because of uncertainty of the exact form of intermolecular potentials of real systems and lack of molecular dynamical or Monte Carlo results comparable in accuracy to corresponding hard-sphere results.

⁵ R. W. Zwanzig, J. Chem. Phys. 22, 1420 (1954); E. B. Smith and B. Alder, *ibid.* 30, 1190 (1959); H. L. Frisch, E. Praestgaard, and J. L. Lebowitz, Bull. Am. Phys. Soc. 9, (1964); C. Domb, Advan. Phys. Soc. 9, No. 34, 35 (1960); M. E. Fisher, J. Math. Phys. 4, 278 (1963).

⁶ J. D. van der Waals, Dissertation, Leiden (1873); L. S. Ornstein, dissertation, Leiden (1908).

⁷ M. Kac, Phys. Fluids, 2, 8 (1959). M. Kac, G. Uhlenbeck, and P. C. Hemmer, (abbreviated KUH), J. Math. Phys. 4, 216, (1963); UHK, *ibid.* p. 229; HKU, *ibid.* 5, 60 (1964). "KUH" will refer in the text to all four of these articles.

⁸ J. L. Lebowitz and O. Penrose, A Rigorous Treatment of the van der Waals-Maxwell Theory of the Liquid-Vapour Transition (to be published in J. Math. Phys.).

⁹ N. van Kampen, Phys. Rev. 135, 362 (1964).

developed and generalized by Horwitz and Callen, Englert, and Coopersmith and Brout.¹⁰

Following the work of KUH, Lebowitz and Percus¹¹ investigated the asymptotic form of the radial distribution function in a fluid with particular reference to systems whose interparticle potential has a weak long-range part. Their results, though not rigorous, applied to more general systems (e.g., plasmas) and agreed with the results of KUH.

It is the purpose of our work to exploit further the idea of separating the potential into a short-range and a long-range part. To this end we develop general systematic methods for expanding the correlation functions (and through them the thermodynamic functions) about their values in a reference system whose particles interact only via the short-range part of the potential. Our method utilizes the language of graphs¹² and is related closely to the work of Hemmer.¹³ When applied to the lattice systems it also turns out to be related closely to the work of Horwitz and Callen, Englert,¹⁰ and Stillinger,¹⁴ although we have used the usual Mayer cluster expansions as a starting point, rather than introduce separate formalisms as those authors did. We believe our method clarifies the relations between the expansions they developed and the cluster series commonly used to treat continuum fluids. Our work also makes contact with several other recent treatments of systems with long-range forces¹⁴ and we shall discuss these in the appropriate place.

In Sec. II, we develop a general graphical formalism for a system whose interparticle potential is separated, essentially arbitrarily, into a sum of two terms, $v(r) = q(r) + w(r)$. This analysis is entirely formal and its usefulness only becomes apparent in Sec. III where w is specified to have the form $\gamma^r \varphi(\gamma r)$. The ordering of graphs introduced in Sec. II is then given meaning in terms of an ordering in the param-

eter γ . An expansion of the two body Ursell function, the direct correlation function, and of the thermodynamic functions in powers of γ is carried out in Secs. IV, V, and VI. In Sec. V, is also introduced a new auxiliary function W which is more convenient for some purposes than the direct correlation function. In Sec. VII we discuss briefly some of the uses of our general formalism for lattice gases as well as the limitation of the γ -expansion to regions of density and temperature in which the system is in a single phase. In the Appendices we prove a lemma that we use in obtaining our graphical formalism, and carry its development further.

II. GENERAL FORMALISM

We consider a system of particles interacting via a pair potential $v(r)$ having the form

$$v(r) = q(r) + w(r). \quad (2.1)$$

The functions $v(r)$ and $q(r)$ are assumed to satisfy the conditions necessary for the existence of a stable thermodynamic system,¹⁵ but are otherwise arbitrary. The particles may also be subject to an external one-body potential $u(r)$. The system is represented by a grand canonical ensemble with a temperature $T = (k\beta)^{-1}$ and fugacity z .

The l -particle distribution function $n_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ is defined as the probability density for finding l distinct particles at positions $\mathbf{r}_1, \dots, \mathbf{r}_l$. We define similarly¹⁶ $\hat{n}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ as the probability density for finding l particles, not necessarily distinct, at positions $\mathbf{r}_1, \dots, \mathbf{r}_l$. Thus,

$$\hat{n}_1(\mathbf{r}) = n_1(\mathbf{r}),$$

$$\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2) + n_1(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2), \dots \quad (2.2)$$

The l -particle Ursell functions $F_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ are defined¹⁶ in terms of the n_i , $i = 1, \dots, l$ in such a way that they vanish whenever their arguments decompose into two or more independent sets

$$F_1(\mathbf{r}_1) = n_1(\mathbf{r}_1),$$

$$F_2(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2) - n_1(\mathbf{r}_1)n_1(\mathbf{r}_2). \quad (2.3)$$

We define $\hat{F}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ to be the same functions of $\hat{n}_i$ as F_l is of the n_i , i.e.,

¹⁵ D. Ruelle, *Helv. Phys. Acta.* **36**, (1963). M. Fisher, "The Free Energy of a Macroscopic System," *Arch. Ratl. Mech. and Analysis* **17**, 377 (1964). These conditions on the potential also guarantee the convergence of the fugacity and virial expansions in a finite domain, cf. Ref. 3. This gives some meaning to our graphical manipulations.

¹⁶ J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 1495 (1963). The definitions on the various correlation functions used here as well as their representation as variational derivatives of the grand partition function is given in Sec. II of this reference.

¹⁰ J. Mayer, *J. Chem. Phys.* **18**, 1426 (1950); R. Brout, *Phys. Rev.* **115**, 824 (1959); **118**, 1009 (1960); G. Horwitz and H. B. Callen, *ibid.* **124**, 1757 (1961); F. Englert, *ibid.* **129**, 567, (1963); M. Coopersmith and R. Brout, *ibid.* **130**, 2539 (1963).

¹¹ J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 248 (1963).

¹² An ordering of graphs suitable for long-range potentials was used in a somewhat *ad hoc* fashion in the work of Ref. 10. Its use as a tool in a strict γ -expansion appears to have been first used in Ref. 11. (cf. footnote 11 and 14 in that reference).

¹³ P. C. Hemmer, *J. Math. Phys.* **5**, 75 (1964).

¹⁴ F. H. Stillinger, *Phys. Rev.* **135**, A1646 (1964); A. J. F. Siegert, *Statistical Physics 3, Brandeis Summer Institute 1962* (W. A. Benjamin, Inc., New York, 1963); A. J. F. Siegert, "On the Ising Model with Long-Range Interaction," Northwestern University preprint, 1962; B. Muhlschlegel and H. Zittartz, *Z. Physik* **175**, 553 (1963); G. A. Baker, Jr., *Phys. Rev.* **126**, 2072 (1962); E. Helfand, *J. Math. Phys.* **5**, 127 (1964); J. Percus and G. Yeveick, *Phys. Rev.* **136**, B290 (1964); C. Bloch and J. Langer, *J. Math. Phys.* **6**, 554 (1965).

$$\begin{aligned}\hat{F}_1(\mathbf{r}_1) &= \hat{n}_1(\mathbf{r}_1), \\ \hat{F}_2(\mathbf{r}_1, \mathbf{r}_2) &= \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) - \hat{n}_1(\mathbf{r}_1)\hat{n}_1(\mathbf{r}_2) \\ &= F_2(\mathbf{r}_1, \mathbf{r}_2) + n_1(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2).\end{aligned}\quad (2.4)$$

The representation of the n 's and F 's by means of graphs with Mayer f -bonds and either fugacity vertices $z_1(\mathbf{r}) = z \exp [-\beta u(\mathbf{r})]$ or density vertices $n_1(\mathbf{r})$ is well known.^{17,18} For the purposes of our analysis we shall break up each f -bond into "short-range" K -bonds and "long-range" Φ -bonds,¹³

$$\begin{aligned}f(r_{ij}) &= e^{-\beta u(r_{ij})} - 1 \\ &= K(r_{ij}) \left[\sum_{m=0}^{\infty} \frac{1}{m!} \Phi^m(r_{ij}) \right] \\ &\quad + \sum_{m=1}^{\infty} \frac{1}{m!} \Phi^m(r_{ij}),\end{aligned}\quad (2.5)$$

where

$$K(r) = e^{-\beta u(r)} - 1, \quad \Phi(r) = -\beta w(r).$$

Pictorially the K -bonds will be represented by dotted lines and the Φ -bonds by solid lines. Our graphs will then consist of points or vertices representing the functions $z_1(\mathbf{r})$ or $n_1(\mathbf{r})$ and K - and Φ -bonds. Between any pair of vertices there can be zero or one K -bond and any number (including zero) of Φ -bonds.¹³ We shall call these graphs *composite* graphs. In conformity with the usual graphical notation, vertices colored black represent unlabeled *field points* over which integrations are performed while white vertices represent labeled points (*root points*). Each graph is associated with its corresponding integral (over the field points) divided by $\sigma \prod (t_{ij}!)$, where σ is the symmetry of the graph, t_{ij} is the number of Φ -bonds between the points i and j . The product of t_{ij} 's is taken over all pairs of vertices. As an illustration, we have, for example

$$\begin{aligned}1 \text{---} 2 &= \frac{1}{2!} \int w_1(\mathbf{r}_1) K(\mathbf{r}_1 - \mathbf{x}) \\ &\quad \times \Phi(\mathbf{r}_1 - \mathbf{x}) w_1(\mathbf{x}) [\Phi(\mathbf{x} - \mathbf{r}_2)]^2 w_1(\mathbf{r}_2) d\mathbf{x},\end{aligned}\quad (2.6)$$

where $w_1(\mathbf{r})$ stands for either $z_1(\mathbf{r})$ or $n_1(\mathbf{r})$.

In terms of the usual graph language we then have^{13,17}

$F_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ = the sum of all composite irreducible (or connected) graphs with

$n_1(\mathbf{x})$ -vertices [or $z_1(\mathbf{x})$ -vertices] having l white vertices labeled by 1, 2, $\dots$, l , respectively. (2.7)

By irreducible we mean both connected and free of *articulation vertices*, i.e., vertices whose removal would separate the graph into two or more parts, one of which is free of white vertices. The delta-functions that arise in the relationship between the F_i and the $\hat{F}_i$ can be represented by letting any subset of k white vertices coalesce to form a single white vertex labeled with k numbers. Such a vertex represents the function w_1 times the product of delta functions in the differences of the k arguments, e.g.,

$$\begin{aligned}1 \text{---} 2 \text{---} 3 \text{---} 4 &= w_1(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &\quad \times \delta(\mathbf{r}_1 - \mathbf{r}_3) \Phi(r_{14}) w_1(\mathbf{r}_4).\end{aligned}\quad (2.8)$$

We thus have, when $l \geq 2$,

$\hat{F}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ = the sum of all composite irreducible (or connected) graphs with $n_1(\mathbf{x})$ -vertices (or $z_1(\mathbf{x})$ -vertices) having $m \leq l$ white vertices, each labeled by a subset of the set of numbers $\{1, \dots, l\}$. The subsets are disjoint and exhaust the set $\{1, \dots, l\}$. When $l = 1$ this characterization is still true for the connected graphs with $z_1(\mathbf{x})$ -vertices. (2.9)

The characterization given in (2.7) lends itself immediately to an expansion of the F 's in powers of the density or powers of the fugacity. This is however not what we are interested in. We desire (for reasons indicated in the introduction and elucidated later) a representation of the F 's, and $\hat{F}$'s, in terms of graphs which contain only Φ -bonds. In order to accomplish this we shall consider graphs consisting of Φ -bonds and *hypervertices*. A hypervertex, which represents a function $w_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$, can be pictured as a *large* circle, along the circumference of which are attached k vertices (or points). We shall call k the *order* of the hypervertex. The small vertices can be either black or white and correspond, respectively, to *field points* over which integrations are performed and to labeled points (*root points*),

e.g., . 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 integral (over the field points) divided by $\sigma \prod (t_{ij}!)$ defined previously, (treating each hypervertex as a

¹⁷ G. Stell in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz, (W. A. Benjamin Company, Inc., 1964).

¹⁸ G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics* edited by J. de Boer and G. E. Uhlenbeck, (North-Holland Publishing Company, Inc., Amsterdam, 1962).

point for the purpose of counting). As an illustration



$$= \frac{1}{2!3!} \int w_3(\mathbf{r}_1, \mathbf{x}_2, \mathbf{x}_3) \Phi(\mathbf{x}_2, \mathbf{x}_4) \Phi(\mathbf{x}_3, \mathbf{x}_5) \\ \times w_5(\mathbf{x}_4, \mathbf{x}_5, \mathbf{x}_6, \mathbf{x}_7, \mathbf{x}_8) \Phi(\mathbf{x}_6, \mathbf{x}_9) \Phi(\mathbf{x}_7, \mathbf{x}_{10}) \\ \times \Phi(\mathbf{x}_8, \mathbf{x}_{11}) w_4(\mathbf{x}_9, \mathbf{x}_{10}, \mathbf{x}_{11}, \mathbf{r}_2) d\mathbf{x}. \quad (2.10)$$

The usual graph theory, with its point vertices, may be recovered from our formalism by setting $w_k(\mathbf{r}_1, \dots, \mathbf{r}_k) = w_1(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_3) \dots \delta(\mathbf{r}_1 - \mathbf{r}_k)$.

We shall now divide each of the F_i 's and $\hat{F}_i$'s into two parts F_i^s and F_i^L . This division is defined in terms of their graphical representation given in (2.7), i.e., $F_i^s(\mathbf{r}_1, \dots, \mathbf{r}_i)$, (F_i short range), is the subset of all composite graphs in $F_i(\mathbf{r}_1, \dots, \mathbf{r}_i)$ in which there is a path, consisting of K -bonds alone, connecting the labeled points $\mathbf{r}_1, \dots, \mathbf{r}_i$. Then

$$F_i(\mathbf{r}_1, \dots, \mathbf{r}_i) = F_i^s(\mathbf{r}_1, \dots, \mathbf{r}_i) + F_i^L(\mathbf{r}_1, \dots, \mathbf{r}_i). \quad (2.11)$$

The second term in (2.11) will be called the long-range part of F_i . A similar definition applies to $\hat{F}_i$,

$$\hat{F}_i = \hat{F}_i^s + \hat{F}_i^L \quad (2.12)$$

with labeled points replaced by *distinct* labeled points in the above characterization, i.e., the graph $1,2 = \delta(\mathbf{r}_1 - \mathbf{r}_2)$ belongs to $\hat{F}_2^s$ clearly

$$F_1^s(\mathbf{r}) = \hat{F}_1^s(\mathbf{r}) = n_1(\mathbf{r}). \quad (2.13)$$

The definition of F_i^s and F_i^L is clearly independent of whether composite graphs with $n_1(\mathbf{x})$ or $z_1(\mathbf{x})$ vertices are used.

The F_i^s may themselves be divided into a subset F_i^{s0} containing those graphs with $z_1(\mathbf{x})$ -vertices in which there is a path consisting of K -bonds alone, connecting all the vertices and a remainder $F_i^{s'}$. Thus,

$$F_i^s(\mathbf{r}_1, \dots, \mathbf{r}_i) = F_i^{s0}(\mathbf{r}_1, \dots, \mathbf{r}_i) + F_i^{s'}(\mathbf{r}_1, \dots, \mathbf{r}_i) \quad (2.14)$$

and similarly for the $\hat{F}_i^s$. Finally F_i^{s0} will contain a subset of graphs F_i^{s00} in which there are no Φ -bonds. This F_i^{s00} is just the value of F_i considered as a functional of $z_1(x)$ and φ when $\varphi = 0$.

A little thought (see Appendix A for details) now shows that a resummation of the graphs in (2.9) yields the following prescription for the $\hat{F}_i$,

$$\hat{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_i) = \text{the sum of all irreducible (connected) graphs with } \Phi\text{-bonds and } \hat{F}_k^s(\mathbf{x}_1, \dots, \mathbf{x}_k)\text{-hypervertices}$$

hypervertices), having l white vertices labeled by $1, 2, \dots, l$, respectively. (2.15)

In considering the connectedness or irreducibility of a graph each hypervertex is to be thought of as a single point. The simplest graph in (2.15) consists of a single hyper-vertex. In the case where $q(r)$ vanishes, $K(r) = 0$, then both the F_i^s and F_i^L vanish for $l > 1$, and

$$\hat{F}_i^s(\mathbf{x}_1, \dots, \mathbf{x}_i) = n_1(\mathbf{x}_1) \delta(\mathbf{x}_1 - \mathbf{x}_2) \dots \delta(\mathbf{x}_1 - \mathbf{x}_i), \quad (2.16)$$

$$\hat{F}_i^L(\mathbf{x}_1, \dots, \mathbf{x}_i) = z_1(\mathbf{x}_1) \delta(\mathbf{x}_1 - \mathbf{x}_2) \dots \delta(\mathbf{x}_1 - \mathbf{x}_i),$$

and (2.15) reduces to the usual expansion in Φ -bonds and density (fugacity) vertices for systems with interparticle potential $w(r)$. Equation (2.15) may thus be considered a generalization of these expansions to the case where there is an extra term $q(r)$ in the interparticle potential, i.e., the reference system is no longer one in which the potential is zero but one in which the potential is q .

The relation (2.15) expressing $\hat{F}_i^L$ in terms of graphs with Φ -bonds and $\hat{F}_i^s$ hypervertices may be supplemented by an explicit formal expression for $\hat{F}_i^L$. To accomplish this we introduce the notion of the *very long-range* part of F_i , $F_i^{L'}$; where

$$F_i^{L'}(\mathbf{r}_1, \dots, \mathbf{r}_i) = \text{the subset of } F_i^L \text{ consisting of all these graphs in which there is no path consisting of } K\text{-bonds alone connecting any pair of labeled points } \mathbf{r}_1, \dots, \mathbf{r}_i. \quad (2.17)$$

We then have

$$\hat{F}_i^L(\mathbf{r}_1, \dots, \mathbf{r}_i) = \mathfrak{N} \left\{ \exp \left[\sum_{k=2}^i (1/k!) \int d\mathbf{x}_1 \dots d\mathbf{x}_k \right. \right. \\ \times F_k^{L'}(\mathbf{x}_1, \dots, \mathbf{x}_k) \delta^k / \prod_{i=1}^i \delta n_1(\mathbf{x}_i) \left. \left. \right] \right\} \\ \times \hat{F}_i^s(\mathbf{r}_1, \dots, \mathbf{r}_i; [n_1(\mathbf{x})]), \quad (2.18)$$

where $\delta/\delta n_1(\mathbf{y})$ means, as usual, the variational derivative with respect to $n_1(\mathbf{y})$ and $\hat{F}_i^s$ is the value of F_i considered as a functional of the density $n_1(\mathbf{x})$ and Φ when $\Phi = 0$. The script $\mathfrak{N}$ indicates a normal order in which all variational derivatives go to the right before evaluation. Equation (2.18) can be most easily obtained by noting the relationship between functional differentiation and a graphical operation¹⁷, since graphically it is a simple identity.

In the case of the ordinary cluster series it was found profitable by a number of workers¹⁷ to con-

sider a resummation of the $n_1(\mathbf{x})$ -vertex $f(\mathbf{x}_1, \mathbf{x}_2)$ -bond graphical expansions which yields $n_1(\mathbf{x})$ -vertex and $[F_2(\mathbf{x}_1, \mathbf{x}_2)/n_1(\mathbf{x}_1)n_1(\mathbf{x}_2)]$ -bond expansions. This resummation yields expansions in terms of graphs that are characterized by the absence of articulation pairs of points as well as articulation points. (An articulation pair is a pair of vertices whose removal will disconnect the graph into two or more pieces such that one of the pieces contains at least one unlabeled vertex but no labeled vertices.) It is natural to ask if there is any analogous resummation that we can perform on our graphs with $\hat{F}^*$ -hypervertices and Φ -bonds and if such a resummation has any use. The answer to the first question is yes; we shall indicate in a later article why the answer to the second question may also be yes. The new graphs we shall consider will have L -bonds where

$$L(\mathbf{r}_1, \mathbf{r}_2) = \Phi(\mathbf{r}_{12}) + \int d\mathbf{r}_3 d\mathbf{r}_4 \Phi(\mathbf{r}_{13}) \hat{F}_2(\mathbf{r}_3, \mathbf{r}_4) \Phi(\mathbf{r}_{42}). \quad (2.19)$$

If we use L -bonds instead of Φ -bonds, then instead of (2.15), we find, when $l \geq 2$

$$\hat{F}_l(\mathbf{r}_1, \dots, \mathbf{r}_l) = \text{the sum of all irreducible graphs with } L\text{-bonds and } \hat{F}_k^*(\mathbf{x}_1, \dots, \mathbf{x}_k)\text{-hypervertices such that } l \text{ white vertices are labeled by } 1, 2, \dots, l, \text{ respectively, and the graphs are free of articulation pairs of vertices. (Note that this last requirement is quite different from the restriction that the graphs be free of articulation pairs of } \textit{hyper}\text{-vertices.}) \quad (2.20)$$

Equation (2.20) is obtained from (2.15) on the basis of exactly the same reasoning that yields the $n_1(\mathbf{x})$ -vertex, (F_2/n_1n_1) -bond expansion for F_l , $l \geq 3$, from its n_1 -vertex, f -bond expansion.¹⁷

III. SHORT- AND LONG-RANGE FORCES

In the last section the division of the potential into two parts q and w was entirely arbitrary. We now specialize to the case where q and w are truly short range and long range. For this purpose we follow Kac⁷ and introduce a parameter γ into w such that γ^{-1} measures the range of w ,

$$w(r, \gamma) = \gamma^3 \varphi(\gamma r). \quad (3.1)$$

[More generally $\gamma^\nu \varphi(\gamma r)$, where ν is the dimensionality of the space.] The functions q and φ are assumed to have the property that a system of particles interacting via a pair potential $q(r)$ or $v(r)$ has a stable thermodynamic limit¹⁸ for any $\gamma > 0$. [This requires, in particular,¹⁸ that there exists some δ , such that

$|q(r)| \leq D/e^{3+\epsilon}$ for $r > \delta$.] We shall require in addition that

$$(a) \quad \int w(r, \gamma) dr = \int \varphi(y) dy = \alpha < \infty, \quad (3.2)$$

$$(b) \quad |q(r)| < Ae^{-\lambda r} \quad \text{for } r > \delta; A, \lambda \geq 0, \quad (3.3)$$

$$(c) \quad \varphi(y) \text{ is piecewise analytic and bounded for all } y \geq 0. \text{ We have in mind here a } \varphi(y) \text{ of the type}$$

$$\varphi(y) = (\alpha/8\pi)e^{-y} \quad \text{or} \quad \varphi(y) = \bar{\alpha}(\pi)^{-3/2}e^{-y^2}. \quad (3.4)$$

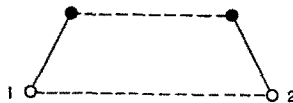
Condition (a) is essential for the existence of the van der Waals limit⁸ $\gamma \rightarrow 0$. Conditions (b) and (c) are only necessary for the existence (formally at least) of a power-series expansion in γ , [cf. Eqs. (3.6) and (3.7)], which we now discuss. The reason for introducing the parameter γ is to be able to consider the case in which $\gamma \ll \delta^{-1}$ i.e. $\varphi(\gamma r)$ is very long range. Our interest now is to obtain an expansion in ascending orders of γ for thermodynamic quantities and distribution functions of the system, and in particular for the two-particle Ursell function $F_2(\mathbf{r}_1, \mathbf{r}_2)$ or $\hat{F}_2(\mathbf{r}_1, \mathbf{r}_2)$.

In order to carry out this expansion we shall first go to the thermodynamic limit, i.e., let the size of the system become infinite. Assuming for simplicity the absence of any external potential, $u(\mathbf{r}) = 0$, the one-particle density is constant, $n_1(\mathbf{r}) = \rho$, and $F_2(\mathbf{r}_1, \mathbf{r}_2) = F_2(r_{12})$ where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Now in order for an expansion of $F_2(r, \gamma)$, in powers of γ , to be useful it must have the property that truncation of the expansion after a finite number of terms yield reasonable approximations for those properties of the system which are of physical interest, e.g., x-ray scattering cross sections, equation of state, etc. For this to be the case it is essential that each term in the expansion approach zero as $r \rightarrow \infty$, as does $F_2(r)$ itself. On the other hand, consider the value of $F_2(r, \gamma)$ at very low densities ρ^2 (exp. $\{-\beta[q(r) + \gamma^3 \varphi(\gamma r)] - 1\}$). On expansion in γ this would give terms proportional to r^n . What is clearly necessary is to treat the short- and long-range parts of $F_2(r)$, F_2^s and F_2^L , on a different footing. We thus write

$$F_2(r, \gamma) = F_2^s(r, \gamma) + F_2^L(y, \gamma), \quad y \equiv \gamma r \quad (3.5)$$

and expand them separately as functions of r and y , in powers of γ .

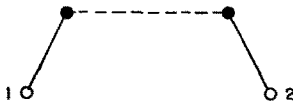
In order to illustrate the difference in treatment of F_2^s and F_2^L we consider two graphs of (2.7) with ρ -vertices, the first belonging to $F_2^s(r_{12}, \gamma)$ and the second to $F_2^L(y_{12}, \gamma)$. Thus, after some change of variables,



$$= \rho^4 \beta^2 K(r_{12}) \gamma^3 \iint \varphi(\mathbf{x}_1 + \gamma \mathbf{r}_{12}) \varphi(\mathbf{x}_1 + \gamma \mathbf{x}_2) K(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$= \gamma^3 \beta^2 \rho^4 K(r_{12}) \left\{ \iint K(\mathbf{x}_2) [\varphi(\mathbf{x}_1)]^2 d\mathbf{x}_1 d\mathbf{x}_2 + \gamma \iint K(\mathbf{x}_2) \varphi(\mathbf{x}_1) [\mathbf{r}_{12} + \mathbf{x}_2] \cdot \nabla \varphi(\mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}_2 + O(\gamma^2) \right\}, \quad (3.6)$$

while



$$= \gamma^3 \beta^2 \rho^4 \iint \varphi(\mathbf{y}_{12} + \mathbf{x}_1) K(\mathbf{x}_2) \varphi(\mathbf{x}_1 + \gamma \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$= \gamma^3 \beta^2 \rho^4 \left\{ \int d\mathbf{x}_2 K(\mathbf{x}_2) \int \varphi(\mathbf{y}_{12} + \mathbf{x}_1) [\varphi(\mathbf{x}_1) + \gamma \mathbf{x}_2 \cdot \nabla \varphi(\mathbf{x}_1)] d\mathbf{x}_1 + O(\gamma^2) \right\}. \quad (3.7)$$

In either case the graph is of $O(\gamma^3)$, but in one case the coefficient of γ^3 is a function of r_{12} , and in the other case it is a function of $y_{12} = \gamma r_{12}$. To obtain the general order of a graph appearing in (2.7) or (2.9) we note first that the integrand of a graph containing t Φ -bonds in $O(\gamma^{3t})$. On the other hand, each "free integration", i.e., one not tied down by a K -bond,¹³ brings in a factor γ^{-3} . The number of free integrations m is obtained by erasing all the Φ -bonds and counting the number of remaining disjoint components in the K -graph not containing any root point. The graph is then $O[(\gamma^3)^{t-m}]$.

This suggests ordering the composite graphs, with density vertices appearing in $\hat{F}_t$, according to the value of $t - m$. For $\hat{F}_t^*$ $m = 0, 1, \dots$, and $t \geq m$, while for $\hat{F}_t^L$ $m = 0, 1, \dots$, and $t \geq m + 1$. Thus

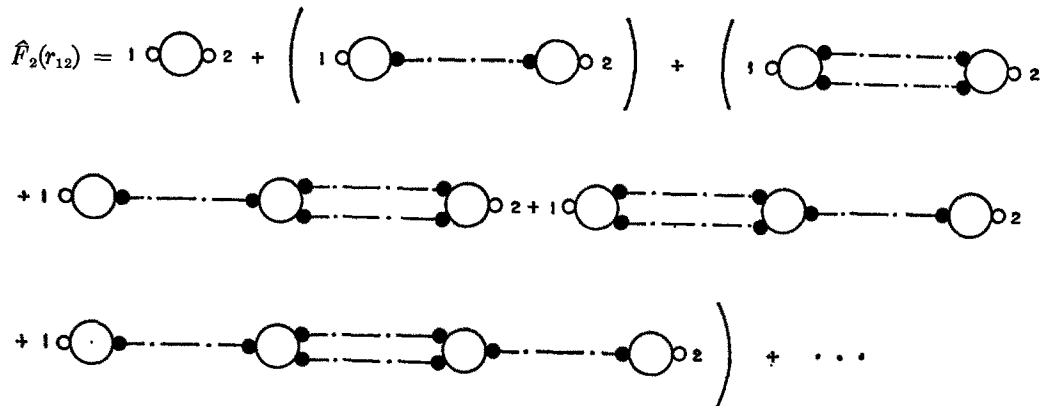
$$\begin{aligned} \hat{F}_t^* &= \hat{F}_{t|0}^* + \hat{F}_{t|1}^* + \dots, \\ \hat{F}_t^L &= \hat{F}_{t|1}^L + \hat{F}_{t|2}^L + \dots, \end{aligned} \quad (3.8)$$

where for each k , $\hat{F}_{t|k}$ is the sum of all graphs for which $t - m = k$ in the expansion of F_t , (short or long range). An analysis similar to that given in (3.6) and (3.7) shows that $\hat{F}_{t|k}$ can be expanded in a power series in γ , starting with γ^{3m} ,

$$\hat{F}_{t|k}(\gamma) = \sum_{j=3m}^{\infty} \gamma^j \hat{F}_{t|k|j}. \quad (3.9)$$

In particular $\hat{F}_{t|0}^*$ is the value of $\hat{F}_t$ considered as a functional of ρ and φ when $\varphi = 0$. We shall call this ordering of the graphs in (2.7) γ -ordering.

A related, and sometimes useful¹, ordering which also has the property that each successive term starts with a higher power of γ may be applied to the graphs appearing in (2.15). These are ordered according to the difference between the number of Φ -bonds and the number of *hypervertices containing no labeled vertices in the graph*. Thus,



$$\begin{aligned} \hat{F}_2(r_{12}) &= 1 \text{ (circle with 1 and 2) } + \left(1 \text{ (circle with 1 and 2) } \cdots \text{ (circle with 1 and 2) } \right) + \left(1 \text{ (circle with 1 and 2) } \cdots \text{ (circle with 1 and 2) } \right) \\ &+ 1 \text{ (circle with 1 and 2) } \cdots \text{ (circle with 1 and 2) } + 1 \text{ (circle with 1 and 2) } \cdots \text{ (circle with 1 and 2) } \\ &+ 1 \text{ (circle with 1 and 2) } \cdots \text{ (circle with 1 and 2) } \left(\right) + \dots \\ &= \Gamma_0(r_{12}, \gamma) + \Gamma_1(y_{12}, \gamma; \{\hat{F}_2^*\}) + \Gamma_2(y_{12}, \gamma; \{\hat{F}_2^*, \hat{F}_3^*\}) + \dots, \end{aligned} \quad (3.10)$$

where the dot-dash line, a $\mathbb{C}$ -bond, introduced here for convenience, is the sum of all chains,

$$\rho^2 \mathcal{C}(y_{12}, \gamma) = 1 \text{---} \bigcirc \text{---} \bigcirc 2 = 1 \text{---} \bigcirc \text{---} \bigcirc 2 + 1 \text{---} \bigcirc \text{---} \bigcirc \text{---} \bigcirc 2 + 1 \text{---} \bigcirc \text{---} \bigcirc \text{---} \bigcirc \text{---} \bigcirc 2 + \dots$$

$$= \rho^2 \left[\Phi(y_{12}) + \iint \Phi(\gamma r_{13}) \hat{F}_2^*(r_{34}, \gamma) \Phi(\gamma r_{41}) dx_3 dx_4 + \dots \right], \quad (3.11)$$

and is evaluated explicitly in the next section [cf. Eq. (4.3)]. In (3.10),

$$\Gamma_n = O(\gamma^{3n}) = \sum_{i=0}^{\infty} \gamma^{3n+i} \Gamma_{n,i}, \quad (3.12)$$

$$\Gamma_0 = \hat{F}_2^*, \quad (3.13)$$

and we indicated explicitly the functional dependence of Γ_n on $\hat{F}_l^*$, for $l \leq n+1$. We shall call this ordering of the graphs Γ -ordering. In this ordering we similarly have

$$\hat{F}_3(r_1, r_2, r_3) = \begin{array}{c} \text{Diagram 1} \\ \text{Diagram 2} \end{array} + \left(\begin{array}{c} \text{Diagram 3} \\ \text{Diagram 4} \end{array} + \dots \text{etc.} \right) \quad (3.14)$$

We note here that the graphical expansion of $\hat{F}_l$ in terms of graphs with $\mathcal{C}$ -bonds is characterized in the same way as its expansion in terms of graphs with Φ -bonds [Eq. (2.15)] with the added restriction that no graphs contain a hypervertex with two black vertices and no white vertices.

IV. EXPANSION OF F_2 IN POWERS OF γ

In this section we shall obtain explicit expressions for the first few terms in the expansion of $\hat{F}_2$ in powers of γ . These will be similar to those obtained by Hemmer¹³ although Hemmer did not make an explicit separation between the short-range and long-range part of the correlations which appears to us essential for clarity. Since the series expansion of $\hat{F}_2^*(r_{12}, \gamma)$ and $\hat{F}_2^L(\gamma r_{12}, \gamma)$ is unique it does not matter when retaining terms up to a certain power in γ , say γ^5 , whether one uses the first two terms in the γ - or Γ -ordering, as these will only differ in terms of higher order in γ . We shall use both orderings interchangeably.

For clarity of notation we shall now replace F_2 by $\mathfrak{F}$ (and make similar replacements for all its superscripted and subscripted versions). The series expansion of $\hat{\mathfrak{F}}^*$ will then have the form, [cf. (3.8), (3.9)]

$$\hat{\mathfrak{F}}^*(r_{12}, \gamma) = \Gamma_0 = \hat{\mathfrak{F}}_0(r_{12}) + \gamma^3 \hat{\mathfrak{F}}_3^*(r_{12}) + \gamma^4 \hat{\mathfrak{F}}_4^*(r_{12}) + \dots, \quad (4.1)$$

where $\hat{\mathfrak{F}}_0(r_{12})$ is the value of $\hat{F}_2$ when $\varphi = 0$, which differs from $\mathfrak{F}_0(r_{12})$ by the terms $\rho \delta(r_{12})$. There are

no $O(\gamma)$ or $O(\gamma^2)$ terms in (4.1) for the type of φ considered here, i.e., satisfying (3.3) and (3.4), [cf. Eq. (6.6)]. The series expansion of $\hat{\mathfrak{F}}^L(y_{12}, \gamma) = \mathfrak{F}^L(y_{12}, \gamma)$ coincides with that of Γ_1 up to $O(\gamma^6)$, [cf. (3.12)],

$$\mathfrak{F}^L(y_{12}, \gamma) = \sum_{i=3}^{\infty} \gamma^i \mathfrak{F}_i^L(y_{12}) = \Gamma_1(y_{12}, \gamma) + O(\gamma^6). \quad (4.2)$$

Utilizing (3.10) and (3.11) we readily find

$$\begin{aligned} \Gamma_1(y, \gamma) &= (2\pi)^{-3} \int e^{i\mathbf{k}\cdot\mathbf{y}} \gamma^3 [\tilde{\Gamma}_0(\gamma k, \gamma)]^2 \mathcal{C}(k, \gamma) d\mathbf{k} \\ &= (2\pi)^{-3} \int e^{i\mathbf{k}\cdot\mathbf{y}} \frac{\gamma^3 [\tilde{\Gamma}_0(\gamma k, \gamma)]^2 \tilde{\Phi}(k)}{1 - \tilde{\Gamma}_0(\gamma k, \gamma) \tilde{\Phi}(k)} d\mathbf{k} \\ &= \left(\frac{\gamma}{2\pi}\right)^3 (\chi^0)^2 \int e^{i\mathbf{k}\cdot\mathbf{y}} \left[\frac{\tilde{\Phi}(k)}{1 - \chi^0 \tilde{\Phi}(k)} \right] d\mathbf{k} + O(\gamma^4), \end{aligned} \quad (4.3)$$

where

$$\tilde{\Gamma}_0(k, \gamma) = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \Gamma_0(r, \gamma) d\mathbf{r}, \quad (4.4)$$

$$\begin{aligned} \tilde{\Phi}(k) &= \gamma^{-3} \int e^{-i\mathbf{k}\cdot\mathbf{y}} \Phi(y) d\mathbf{y} \\ &= -\beta \int e^{-i\mathbf{k}\cdot\mathbf{y}} \varphi(y) d\mathbf{y}, \end{aligned} \quad (4.5)$$

and

$$\chi^0 = \rho / \left(\beta \frac{dp^0}{d\rho} \right) = \int \hat{\mathfrak{F}}_0(r) d\mathbf{r} = \tilde{\Gamma}_{0,0}(0); \quad (4.6)$$

$p^0(\rho, \beta)$ being the pressure and $\beta\chi^0/\rho^2$ the isothermal compressibility in the *absence* of φ . [p^0 differs from $p_0(\rho, \beta)$ which is the van der Waals pressure obtained when γ is set equal to zero *after* the thermodynamic limit has been taken, cf. Eq. (6.2)].

Considering now the next order term in $\hat{\mathfrak{F}}^*$ we note that up to $O(\gamma^6)$ it coincides with $\hat{\mathfrak{F}}_{[1]}^*$ which is given according to (2.18) by

$$\hat{F}_{[1]}^*(\mathbf{r}_{12}, \gamma) = \frac{1}{2} \int \mathfrak{F}_{[3]}^L(\gamma \mathbf{x}_{12}, \gamma) \times \left. \frac{\delta^2 \hat{\mathfrak{F}}_0(\mathbf{x}_1, \mathbf{x}_2; \{n_i(\mathbf{x})\})}{\delta n_1(\mathbf{x}_1) \delta n_1(\mathbf{x}_2)} \right|_{n_i \sim \rho} d\mathbf{x}_1 d\mathbf{x}_2 \quad (4.7)$$

since for the two-particle Ursell function $\mathfrak{F}^L = \mathfrak{F}^{*L}$. Equation (4.7) may be represented graphically in the form

$$\hat{\mathfrak{F}}_{[1]}^* = \text{graphical representation of } \hat{\mathfrak{F}}_{[1]}^* \quad (4.8)$$

with

$$\text{graphical representation of } \hat{\mathfrak{F}}_0(\mathbf{r}_1, \mathbf{r}_2, \{n_i(\mathbf{x})\}) = \text{graphical representation of } \hat{\mathfrak{F}}_0$$

Expanding (4.7) in powers of γ we find

$$\hat{\mathfrak{F}}_{[1]}^* = \frac{1}{2} \gamma^3 \mathfrak{F}_3^L(\gamma r_{12}) \delta^2 \hat{\mathfrak{F}}_0(r_{12}) / \partial \rho^2 + O(\gamma^4) \\ = \frac{1}{2} \gamma^3 \mathfrak{F}_3^L(0) \partial^2 \mathfrak{F}_0(r_{12}) / \partial \rho^2 + O(\gamma^4), \quad (4.9)$$

where use was made in the last equality of the relation [cf. Eq. (2.4)] $\partial^2 \hat{\mathfrak{F}}_0 / \partial \rho^2 = \partial^2 \mathfrak{F}_0 / \partial \rho^2$. The reason for writing out the intermediate equality in (4.9) is that it permits the combining of $\mathfrak{F}_3^*(r_{12})$ with $\mathfrak{F}_3^L(\gamma r_{12})$ to give

$$\mathfrak{F}(r) = \mathfrak{F}_0(r) + \frac{1}{2} \gamma^3 (\partial^2 / \partial \rho^2) [n_2^0(r)] \mathfrak{F}_3^L(\gamma r) + O(\gamma^4), \quad (4.10)$$

where $n_2^0(r)$ is the value of n_2 in the reference system. By combining (4.3) with (4.9) and carrying out explicitly the functional differentiation there we can obtain $\mathfrak{F}$ up to $O(\gamma^6)$ in terms of the properties of the reference system, i.e., one for which $\varphi = 0$. Continuing in this manner it is easy to express $\mathfrak{F}^L$ through $O(\gamma^{11})$ in terms of functions of the reference system. To go beyond this we need to utilize the higher-order terms in (2.18) and the analysis soon gets very complicated.

V. EXPANSION OF THE DIRECT CORRELATION FUNCTION AND A RELATED AUXILIARY FUNCTION

It is convenient for many purposes to introduce the direct correlation function $C(r_{12})$ of Ornstein and Zernike¹⁹, defined by the relation

$$\mathfrak{F}(r_{12}) = \rho^2 C(r_{12}) + \rho \int C(r_{13}) \mathfrak{F}(r_{32}) d\mathbf{r}_3. \quad (5.1)$$

The graphical representation of $\rho^2 C(r_{12})$, in terms of composite graphs with ρ vertices, is similar to that¹⁷ of $\mathfrak{F}(r_{12})$ given in (2.7), with the added restriction that no vertex be a *cutting* or nodal vertex whose removal separates the graph into two or more parts with each of the two white vertices in different parts.

We now divide $C(r_{12})$ like $\mathfrak{F}$, into a short-range and long-range part, (according to whether or not there is a path consisting of short range K -bonds alone connecting the points $\mathbf{r}_1$ and $\mathbf{r}_2$), and write the long-range part as a function of $y = \gamma r$,

$$C(r_{12}) = C^*(r_{12}, \gamma) + C^L(y_{12}, \gamma). \quad (5.2)$$

The relationship between C^* , C^L , and $\mathfrak{F}^*$ is most readily obtained from the graphical interpretation of Eq. (5.1) as representing $\mathfrak{F}$ by the sum of all distinct repeated convolutions involving C^* and C^L

$$\mathfrak{F}(r_{12}) = \text{graphical representation of } \mathfrak{F}(r_{12}) = \text{graphical representation of } \mathfrak{F}(r_{12}) \quad (5.3)$$

where represents C^* , represents C^L .

¹⁹ L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam, 17, 793 (1914).

represents C^L , and vertices represent ρ . It is now clear that since $\mathfrak{F}^*(r_{12})$ consists of those graphs in $\mathfrak{F}$ in which there is a short-range path from r_1 to r_2 it must be represented by all the convolutions of C^* with itself.

$$\mathfrak{F}^*(r_{12}) = \text{diagram 1} + \text{diagram 2} + \dots, \quad (5.4)$$



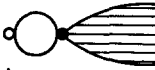
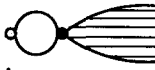
or

$$\mathfrak{F}^*(r_{12}) = \rho^2 C^*(r_{12}) + \rho \int C^*(r_{13}) \mathfrak{F}^*(r_{32}) d\mathbf{r}_3. \quad (5.5)$$

In a similar manner $\mathfrak{F}^L$ will consist of the sum of all graphs containing C^L bonds separated by either a single ρ vertex or by all possible convolutions of C^* with itself, i.e., the C^L bonds will be separated by the hypervertex Γ_0 ,

$$\Gamma_0(r_{12}) = \mathfrak{F}^*(r_{12}) = \mathfrak{F}^*(r_{12}) + \rho \delta(\mathbf{r}_1 - \mathbf{r}_2) = \text{diagram 1}. \quad (5.6)$$


Thus,

$$\begin{aligned} \mathfrak{F}^L(r_{12}) &= \text{diagram 1} + \text{diagram 2} + \dots \\ &= \int \mathfrak{F}^*(r_{13}) C^L(y_{34}) \mathfrak{F}^*(r_{42}) d\mathbf{r}_3 d\mathbf{r}_4 + \int \mathfrak{F}^*(r_{13}) C^L(y_{34}) \mathfrak{F}^L(y_{42}) d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \quad (5.7)$$



Equations (5.5) and (5.7) may be thought of as the generalization of (5.1) from a system whose particles interact *only with the potential* w to a system with interactions $q + w$. Of course when $q = 0$, C^* and $\mathfrak{F}^*$ vanish, $\Gamma_0(r_{12})$ becomes equal to $\rho \delta(\mathbf{r}_1 - \mathbf{r}_2)$, and (5.7) becomes the usual equation for C .

An inspection of the graphs in (5.5) and (5.1) enables us now to obtain simple relations between terms in the γ -ordering of $\mathfrak{F}$ [cf. Eq. (3.9)], and a similar ordering of C , i.e., $C_{[m]}$ is the sum of all those composite graphs appearing in C in which the number of Φ -bonds less the number of free integration is m . Thus,

$$\begin{aligned} \mathfrak{F}_{[m]}^*(r_{12}) &= \rho^2 C_{[m]}^*(r_{12}) \\ &+ \rho \sum_{k=0}^m \int C_{[k]}^*(r_{13}) \mathfrak{F}_{[m-k]}^*(r_{32}) d\mathbf{r}_3 \end{aligned} \quad (5.8)$$

and

$$\begin{aligned} \mathfrak{F}_{[m]}^L(y_{12}) &= \sum_{i+j+k=m} \int \mathfrak{F}_{[i]}^*(r_{13}) C_{[j]}^L(y_{34}) \mathfrak{F}_{[k]}^*(r_{42}) d\mathbf{r}_3 d\mathbf{r}_4 \\ &+ \gamma^{-3} \sum_{i+j+k=m+1} \int \mathfrak{F}_{[i]}^*(r_{13}) C_{[j]}^L(y_{34}) \mathfrak{F}_{[k]}^L(y_{42}) d\mathbf{r}_3 d\mathbf{r}_4, \end{aligned} \quad (5.9)$$

where it should be remembered that in carrying out the convolution of C^L and $\mathfrak{F}^L$ there is introduced an extra free integration. Introducing the Fourier transforms $\tilde{C}$ and $\tilde{\mathfrak{F}}$ we find from (5.5) and (5.8),

$$\begin{aligned} 1 - \rho \tilde{C}^*(k, \gamma) &= [1 + \rho^{-1} \tilde{\mathfrak{F}}^*(k, \gamma)]^{-1} = [1 + \rho^{-1} \tilde{\mathfrak{F}}_0(k)]^{-1} \\ &\times \left[1 + [\rho + \tilde{\mathfrak{F}}_0(k)]^{-1} \sum_{n=1}^{\infty} \tilde{\mathfrak{F}}_{[n]}^*(k, \gamma) \right]^{-1}, \end{aligned} \quad (5.10)$$

which gives, upon equating terms of the same order

$$1 - \rho \tilde{C}_0(k) = [1 + \rho^{-1} \tilde{\mathfrak{F}}_0(k)]^{-1}, \quad (5.11)$$

$$\tilde{C}_{[1]}^*(k, \gamma) = [\rho + \tilde{\mathfrak{F}}_0(k)]^{-2} \tilde{\mathfrak{F}}_{[1]}^*(k, \gamma), \dots \text{etc.}, \quad (5.12)$$

with $\mathfrak{F}_{[1]}^*$ given by (4.8).

In analyzing the long-range parts of C and $\mathfrak{F}$ we must remember, cf. Eq. (4.5), that in any function of $y = \gamma r$, Fourier transformation brings down a factor γ^3 , i.e.,

$$\tilde{C}^L(k, \gamma) = \gamma^{-3} \int e^{-i\mathbf{k}\cdot\mathbf{y}} C^L(y\gamma) d\mathbf{y} \quad (5.13)$$

and similarly for all other functions of y . We then find

$$\begin{aligned} \mathfrak{F}^L(k, \gamma) &= \tilde{C}^L(k, \gamma) [\rho + \tilde{\mathfrak{F}}^*(\gamma k, \gamma)]^2 \{1 - [\rho + \tilde{\mathfrak{F}}^*(\gamma k, \gamma)] \tilde{C}^L(k, \gamma)\}^{-1} \\ &= (\rho + \tilde{\mathfrak{F}}_0)^2 \left[1 + (\rho + \tilde{\mathfrak{F}}_0)^{-1} \sum_{n=1}^{\infty} \tilde{\mathfrak{F}}_{[n]}^* \right]^2 \sum_{n=1}^{\infty} \tilde{C}_{[n]}^L \\ &\times [1 - (\rho + \tilde{\mathfrak{F}}_0) \tilde{C}_{[1]}^L]^{-1} \{1 - [1 - (\rho + \tilde{\mathfrak{F}}_0) \tilde{C}_{[1]}^L]^{-1} \sum_{k+m \geq 1} \tilde{\mathfrak{F}}_{[k]}^* \tilde{C}_{[m+1]}^L\}^{-1}, \end{aligned} \quad (5.14)$$

$$\rho^2 C_{[2]}^L(y_{12}, \gamma) =$$

$$= \frac{\rho^2}{2} \int \cdots \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 d\mathbf{x}_4 \hat{K}_3^0(\mathbf{r}_1, \mathbf{x}_1, \mathbf{x}_2) \mathfrak{F}_{[1]}^L(\gamma | \mathbf{x}_1 - \mathbf{x}_3) \mathfrak{F}_{[1]}^L(\gamma | \mathbf{x}_2 - \mathbf{x}_4) \hat{K}_3^0(\mathbf{x}_3, \mathbf{x}_4, \mathbf{r}_2), \quad (5.19)$$

where the argument of the short-range functions is γk and

$$\mathfrak{F}^L(y, \gamma) = \frac{\gamma^3}{(2\pi)^3} \int e^{i\mathbf{k}\mathbf{y}} \mathfrak{F}^L(k, \gamma) d\mathbf{k}. \quad (5.15)$$

Expanding (5.14) yields

$$\mathfrak{F}_{[1]}^L = (\rho + \mathfrak{F}_0)^2 \tilde{C}_{[1]}^L [1 - (\rho + \mathfrak{F}_0) \tilde{C}_{[1]}^L]^{-1}, \quad (5.16)$$

$$\begin{aligned} \tilde{\mathfrak{F}}_{[2]}^L &= [(\rho + \mathfrak{F}_0)^2 \tilde{C}_{[2]}^L + \gamma^3 \mathfrak{F}_{[1]}^*] \\ &\times [1 - (\rho + \mathfrak{F}_0) \tilde{C}_{[1]}^L]^{-2} - \gamma^3 \mathfrak{F}_{[1]}^*, \text{ etc.} \end{aligned} \quad (5.17)$$

where

$$\begin{aligned} &= \rho^3 \hat{K}_3^0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \rho^3 [K_3^0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \rho^{-2} \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_3)] \\ &= \rho^3 \delta / \delta n_1(\mathbf{r}_3) [C_0(\mathbf{r}_1, \mathbf{r}_2; \{n_1(\mathbf{x})\}) - n_1^{-1}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2)]_{n_1(\mathbf{x})=\rho} \\ &= -\rho^3 \delta^2 \ln z_1^0(\mathbf{r}_1, \{n_1(\mathbf{x})\}) / \delta n_1(\mathbf{r}_2) \delta n_1(\mathbf{r}_3) |_{n_1(\mathbf{x})=\rho}. \end{aligned} \quad (5.20)$$

$\rho^3 K_3^0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is the sum of all diagrams, with ρ vertices and K -bonds, having three distinct labeled vertices and no vertices, black or white, whose removal would separate the graph into two or more parts. K_3 is the "natural" generalization of the direct correlation function C , the superscript zero indicating as usual that it is to be evaluated in the reference system $\varphi = 0$. The second equality follows from the definition of the direct correlation function as a variational derivative,¹¹

$$\begin{aligned} C(\mathbf{r}_1, \mathbf{r}_2; \{n_1(\mathbf{x})\}) \\ = \delta \ln [n_1(\mathbf{r}_1)/z_1(\mathbf{r}_1, \{n_1(\mathbf{x})\})] / \delta n_1(\mathbf{r}_2), \end{aligned} \quad (5.21)$$

with $z_1(\mathbf{r}_1) = ze^{-\beta u(\mathbf{r}_1)}$ (u the external potential) considered as a functional of the nonuniform density $n_1(\mathbf{x})$, while z_1^0 is again this functional in the absence of φ . Substituting (5.20) into (5.19) and carrying through an analysis similar to that done in Eq. (4.8) we find that the lowest-order term in $C_{[2]}^L$, $C_{[2],\delta}^L$ is given by

The only graph contributing to $C_{[1]}^L$ is one consisting of a single Φ -bond,

$$C_{[1]}^L(y, \gamma) = \Phi(y, \gamma) = -\beta \gamma^3 \varphi(y), \quad (5.18)$$

so that to this order C^L is equal to $-\beta$ times the long-range potential.¹¹ Combining (5.18) with (5.16) yields, of course, the same result (except for a factor ρ^2) as the first integrand in (4.3) when Γ_0 there is replaced by $\mathfrak{F}_0$.

The evaluation of $C_{[2]}^L$ is also straightforward. Graphically,

$$\begin{aligned} C_{[2],\delta}^L(y_{12}) &= \frac{1}{2} [\mathfrak{F}_3^L(y_{12})]^2 \\ &\times \left[\iint \delta^2 \ln z_1^0(\mathbf{r}_1) / \delta n_1(\mathbf{x}_1) \delta n_1(\mathbf{x}_2) |_{n_1=\rho} d\mathbf{x}_1, d\mathbf{x}_2 \right]^2 \\ &= \frac{1}{2} [\mathfrak{F}_3^L(y_{12})]^2 [\partial^2 \beta \mu^0 / \partial \rho^2]^2, \end{aligned} \quad (5.22)$$

where $\mu^0(\rho, \beta)$ is the value of the chemical potential in the reference system, $\rho \partial \mu^0 / \partial \rho = \partial p^0 / \partial \rho$. By substituting (5.22) into (5.17) and utilizing previously obtained results we may obtain an explicit expression for $\mathfrak{F}_{[2],\delta}^L$.

Note added in proof: In terms of the Γ -ordering given at the end of Sec. III we have simply¹

$$\mathfrak{F}^L(\mathbf{k}, \gamma) = \tilde{\Gamma}_1(\mathbf{k}, \gamma) + \tilde{\Gamma}_2(\mathbf{k}, \gamma) + O(\gamma^4)$$

and

$$\tilde{\Gamma}_2(\mathbf{k}, \gamma) = \frac{1}{2} \left(\frac{\partial^2 \beta \mu^0}{\partial \rho^2} \right)^{-2} [1 - x^0 \Phi(\mathbf{k})] \tilde{T}(k) + O(\gamma^4)$$

where $\tilde{T}(k)$ is the Fourier transform of $\mathfrak{C}^2(y)$.

Equation (5.22) is of some interest for its own

sake since in terms of our ordering it makes more precise the popular notion that $C(r) - \Phi(r)$ should be short ranged compared to $\mathfrak{F}(r)$. To second order in the γ -ordering, $C(r) - \Phi(r)$ has "one-half" the range of $\mathfrak{F}(r)$ when the coefficient $(\partial^2 \beta \mu^0 / \partial \rho^2)$ is not zero. However, the coefficient will be zero for some important special cases—for example, for a field-free Ising model (or lattice gas at $\rho = \frac{1}{2}$)—and in such cases $C - \Phi$ vanishes to second order in the γ ordering.

The function $C(r)$ is introduced in considering fluids as a convenient auxiliary function. The fact that $C(r)$ itself cannot be characterized as a sum of graphs with $\hat{F}_n^*$ -hypervertices and Φ -bonds robs it of some of its convenience for our purposes. For this reason we introduce another auxiliary function by subtracting $\Phi(r)$ from $C(r)$ and repeatedly convoluting the result with itself. The sum of $C(r) - \Phi(r)$ and all such convolutions we shall denote by $W(r)$.

$$W(r_{12}) = C(r_{12}) - \Phi(r_{12}) + \int d\mathbf{r}_3 [C(r_{13}) - \Phi(r_{13})] \rho [C(r_{32}) - \Phi(r_{32})] + \dots, \quad (5.23)$$

or in terms of Fourier transforms with respect to r (rather than γr)

$$\tilde{W}(k) = [\tilde{C}(k) - \tilde{\Phi}(k)] / \{1 - \rho[\tilde{C}(k) - \tilde{\Phi}(k)]\}. \quad (5.24)$$

Alternatively, we could define $\tilde{W}(k)$ directly in terms of $\tilde{\mathfrak{F}}(k)$:

$$\begin{aligned} \tilde{\mathfrak{F}}(k) &= \rho^2 \left[\frac{\tilde{W}(k) + \tilde{\Phi}(k)[1 + \rho\tilde{W}(k)]}{1 - \rho\tilde{\Phi}(k)[1 + \rho\tilde{W}(k)]} \right] \\ &= -\rho + \frac{\rho[1 + \rho\tilde{W}(k)]}{1 - \rho\tilde{\Phi}(k)[1 + \rho\tilde{W}(k)]}. \end{aligned} \quad (5.25)$$

It is easy to verify that separating W in the usual way into short- and long-range parts we have $W = W^* + W^L$ where $W^*(r, \gamma)\rho^2 = \mathfrak{F}^*(r, \gamma)$

$\rho^2 W^L(y_{12}, \gamma)$ = the sum of all irreducible graphs with Φ -bonds and $\hat{F}_n^*$ -hypervertices such that each graph contains two white vertices labeled by 1 and 2, respectively, and there are no *cutting bonds*, i.e., bonds whose removal separates the graph into two parts, each of which contains a white vertex. (5.26)

In terms of L -bonds rather than Φ -bonds, we have the same representation, except that we must add the restriction that the graphs contain no articulation pairs of vertices. The resulting series is a natural generalization of an expansion that Stil-

linger¹⁴ has introduced to treat lattice systems and reduces to his expansion for such systems.

VI. EXPANSION OF THERMODYNAMIC FUNCTIONS

In order to obtain the thermodynamic functions as an expansion in powers of γ it is possible either to start directly with a graphical representation¹³ of the Helmholtz free energy (or some related function, cf. App. C) or to use one of the several methods which connect thermodynamic properties with integrals over the two-body distribution functions which we have already investigated. We shall begin here by mentioning two commonly used relations of the latter type: the virial theorem and the fluctuation theorem. Both of these methods permit, utilizing our previous results on $\mathfrak{F}$, calculation of the equations of state through $O(\gamma^5)$, a result already obtained by Hemmer.¹³ We shall then develop a new method which will utilize our previous results to yield the Helmholtz free energy (and the equation of state) through $O(\gamma^8)$, (or more generally through $O(\gamma^{3\nu-1})$ where ν is the dimensionality of the space.)

The virial theorem may be written in the following form:

$$\begin{aligned} p &= \rho kT - \frac{2}{3} \pi \int_0^\infty q'(r) [\rho^2 + \mathfrak{F}(r)] r^3 dr \\ &\quad + 2\pi \rho^2 \int_0^\infty \varphi(y) y^2 dy \\ &\quad - \frac{2}{3} \pi \int_0^\infty \varphi'(y) \mathfrak{F}^L(y) y^3 dy \\ &\quad - \gamma^4 \frac{2}{3} \pi \int_0^\infty \varphi'(\gamma r) \mathfrak{F}^*(r) r^3 dr, \end{aligned} \quad (6.1)$$

where q' and φ' are the derivatives of $q(r)$ and $\varphi(y)$ with respect to r and y and we have put the term $\rho^2 + \mathfrak{F}(r) = n_2(r)$, together in the term containing $q'(r)$ to enable us to use the proper limiting procedure in case $q(r)$ has discontinuities (e.g., hard core, square well). Equation (6.1) yields to zero order in γ , the "van der Waals" equation of state,⁹

$$\begin{aligned} p &= \left\{ \rho kT - \frac{2}{3} \pi \int q'(r) [\rho^2 + \mathfrak{F}_0(r)] r^3 dr \right\} \\ &\quad + \frac{1}{2} \rho^2 \int \varphi(y) dy + O(\gamma^3) = p^0 + \frac{1}{2} \rho^2 \alpha \\ &\quad + O(\gamma^3) = p_0 + O(\gamma^3). \end{aligned} \quad (6.2)$$

To obtain the $O(\gamma^n)$ corrections to p_0 from (6.1) we need to know both $\mathfrak{F}_i^*$ and $\mathfrak{F}_i^L$ to the same order. Our previous calculations of $\mathfrak{F}_{11}^*$ and $\mathfrak{F}_{11}^L$ thus enable us, at least in principle, to obtain p through $O(\gamma^5)$ from the properties of the reference system; to go to

higher order we must use $\mathfrak{F}_0^*$ which can be obtained in principle from (2.18).

We next consider the fluctuation theorem [cf. Eq. (4.6)]. This is best expressed in terms of the direct correlation function and may be written in the form¹¹

$$\beta \frac{dp}{d\rho} = 1 - \rho \int C^*(r, \gamma) d\mathbf{r} - \gamma^{-3} \rho \int C^L(y, \gamma) dy \\ = 1 - \rho \tilde{C}^*(0, \gamma) - \rho \tilde{C}^L(0, \gamma). \quad (6.3)$$

While (6.3) is simpler in structure than (6.1) it requires knowledge of C^L to order $n+3$ to obtain p to $O(\gamma^n)$. To zeroth order we, of course, have again as in (6.2)

$$\beta \frac{dp_0}{d\rho} = 1 - \rho \int C_0(r) d\mathbf{r} \\ + \beta \rho \int \varphi(y) dy = \beta \frac{dp^0}{d\rho} + \beta \rho \alpha. \quad (6.4)$$

The next-order term in p may now be obtained from (5.12), (4.9), and (5.22). Again we cannot go higher than $O(\gamma^5)$ with the available information on $\mathfrak{F}$ and C .

In order to make further progress we now utilize the functional relation between the Helmholtz free energy and the two particle distribution function n_2 . We have, for a uniform system,

$$n_2(r_{12}) = 2\rho \delta A(\rho, \{v\}) / \delta v(r_{12}), \quad (6.5)$$

where A is the nonideal-gas part of Helmholtz free energy per particle [the ideal-gas part making no contribution to (6.5) anyway] considered as a functional of the interparticle potential $v(r)$ and the density. Equation (6.5) is a special case of the more general relation holding also for a nonuniform system,

$$\int n_2(\mathbf{r}_{12}, \mathbf{r}_2) d\mathbf{r}_2 = 2\delta \mathcal{Q}(\{n_1(\mathbf{x})\}, \{v\}) / \delta v(r_{12}) \quad (6.6)$$

where $\mathcal{Q}$ is the Helmholtz free energy (non-ideal part) of the whole system. Equation (6.6) may be derived either from the graphical representation¹⁷ of $\mathcal{Q}$ or more directly from the definition of $-\beta\mathcal{Q}$, for a system with a fixed number of particles, as the logarithm of the canonical partition function.

We may now rewrite (6.5) in the form

$$\mathfrak{F}(r_{12}) = -2\beta\rho \frac{\delta[A - \frac{1}{2}\rho\alpha]}{\delta\Phi(r_{12})}, \quad (6.7)$$

since $v = q - \beta^{-1}\Phi$. "Inversion" of (6.7) then yields

$$\beta A = \beta A_0 - \frac{1}{2}\beta\gamma^3\varphi(0) + \rho^{-1} \frac{1}{2} \left(\frac{\gamma}{2\pi} \right)^3 \int d\mathbf{k} \ln [1 - \mathfrak{F}_0(\gamma k) \tilde{\Phi}(k)] \\ - \frac{1}{4}\rho^{-1}(\gamma/2\pi)^6 \iint d\mathbf{k} d\mathbf{k}' \left[\frac{1}{3} \frac{1}{\chi^0} \left(\frac{\partial \chi^0}{\partial \rho} \right)^2 \frac{\chi^0 \tilde{\Phi}(k') \chi^0 \tilde{\Phi}(|\mathbf{k} - \mathbf{k}'|) \chi^0 \tilde{\Phi}(k)}{[1 - \chi^0 \tilde{\Phi}(k)][1 - \chi^0 \tilde{\Phi}(k')][1 - \chi^0 \tilde{\Phi}(|\mathbf{k} - \mathbf{k}'|)]} \right. \\ \left. + \frac{1}{2} \frac{\partial^2 \chi^0}{\partial \rho^2} \frac{\chi^0 \tilde{\Phi}(k) \chi^0 \tilde{\Phi}(k')}{[1 - \chi^0 \tilde{\Phi}(k)][1 - \chi^0 \tilde{\Phi}(k')]} \right] + O(\gamma^7). \quad (6.14)$$

²⁰ Hemmer's (Ref. 13) expression for A through $O(\gamma^5)$ does not contain the term $-\frac{1}{2}\beta\gamma^3\varphi(0)$. This term makes no contribution to the pressure, cf. (6.16).

$$A = A^0 + \frac{1}{2}\rho\alpha - \frac{1}{2\beta\rho} \int d\mathbf{r} \int \mathfrak{F}(r, \rho, \{\Phi\}) \delta\Phi, \quad (6.8)$$

where $A^0(\beta, \rho)$ is the free energy per particle (non-ideal part) in the reference system $\varphi = 0$, and we have indicated explicitly the functional dependence of $\mathfrak{F}$ on Φ . In order to carry out the functional integration indicated in (6.8) we consider a process in which Φ is "turned on" from zero to its final value⁴ via a parameter λ . We write

$$\Phi(r, \lambda) = \lambda\Phi(r) = -\lambda\beta\gamma^3\varphi(\gamma r). \quad (6.9)$$

For $\lambda = 0$, the system is in its reference state and for $\lambda = 1$ the system is in its final state. Equation (6.8) may now be written in the form

$$A = A^0 + \frac{1}{2}\rho\alpha - \frac{1}{2\beta\rho} \int d\mathbf{r} \int_0^1 \mathfrak{F}(r, \rho, \lambda) \Phi(r) d\lambda \\ = A^0 + \int_0^1 d\lambda \left\{ \frac{1}{2} \rho^{-1} \int n_2(r, \lambda) \gamma^3 \varphi(\gamma r) d\mathbf{r} \right\}. \quad (6.10)$$

We note that in the case where $q(r)$ is a simple hard-core potential, $q(r) = \infty$, for $r < \delta$, and vanishes for $r > \delta$, (including the case $\delta = 0$, or $q = 0$), the term in the bracket in the second equality in (6.10) is just the average potential energy per particle E while the parameter λ enters only in the combination $\lambda\beta$. Equation (6.10) becomes in this case

$$A = A^0 + \beta^{-1} \int_0^{\beta} E(\rho, \beta) d\beta, \quad (6.11)$$

which is usual thermodynamic relations between A and E .

Returning now to the general case we may write (6.10) in the form

$$A = A_0 + \frac{1}{2}\rho^{-1}\gamma^3 \int d\mathbf{r} \varphi(\gamma r) \int_0^1 \mathfrak{F}'(r, \gamma, \lambda) d\lambda \\ + \frac{1}{2}\rho^{-1} \int d\mathbf{y} \varphi(y) \int_0^1 \mathfrak{F}^L(y, \gamma, \lambda) d\lambda, \quad (6.12)$$

where

$$A_0 = A^0 + \frac{1}{2}\rho\alpha \quad (6.13)$$

is the van der Waals form of the Helmholtz free energy. We see now that our knowledge of $\mathfrak{F}^*$ to $O(\gamma^5)$ and $\mathfrak{F}^L$ to $O(\gamma^8)$ permits us to compute A to $O(\gamma^8)$. The calculation to $O(\gamma^6)$ is straightforward and gives²⁰

Equation (6.14) may be evaluated explicitly for the one-dimensional system investigated by Kac, Uhlenbeck, and Hemmer, cf. Eq. (1.1), to yield

$$\begin{aligned} \beta A = & \ln \rho / (1 - \delta \rho) + \frac{1}{2} \rho \alpha \beta - \frac{1}{4} \gamma \alpha \beta \\ & - \frac{1}{2} \gamma \rho^{-1} \{1 - [1 + \alpha \beta \rho (1 - \delta \rho)]^{\frac{1}{2}}\} \\ & + \frac{1}{4} \gamma^2 \frac{\alpha^2 \beta^2 \rho (1 - \delta \rho)^4}{36(1 + \alpha \beta \rho (1 - \delta \rho))^2} [9\delta(2 - 3\delta\rho) \\ & + \alpha \beta (1 - \delta \rho)^2 (1 + 12\delta\rho - 18\delta^2 \rho^2)] + O(\gamma^3). \end{aligned} \quad (6.15)$$

The pressure, internal energy, specific heat and other thermodynamic functions may be obtained directly from (6.14). The specific heat per particle is thus given (in units of Boltzmann's constant) by

$$\begin{aligned} C = C_0 - \left(\frac{\gamma}{2\pi}\right)' \frac{1}{2\rho} \int \frac{\beta^{-2} \frac{\partial^2 \chi^0}{\partial (\beta^{-1})^2} \tilde{\Phi}(\mathbf{k})}{1 - \chi^0 \tilde{\Phi}(\mathbf{k})} d\mathbf{k} \\ + \left(\frac{\gamma}{2\pi}\right)' \frac{1}{2\rho} \int \frac{\left[\frac{\partial}{\partial \beta} (\beta \chi^0) \tilde{\Phi}(\mathbf{k})\right]^2}{(1 - \chi^0 \tilde{\Phi}(\mathbf{k}))^2} d\mathbf{k} + O(\gamma'^{+1}), \end{aligned} \quad (6.16)$$

where C_0 is the specific heat of the van der Waal's system which coincides with that of the reference system, C^0 , in the *uniform* state. It should be noted here though that as we approach the van der Waal's coexistence curve⁸, which coincides with $[1 - \chi^0 \tilde{\Phi}(0)] = 0$, the coefficient of (γ') in C will become infinite, with the nature of the singularity depending on the number of dimensions ν . Similar singularities will occur in the expansion of all other thermodynamic functions and will get worse for higher terms in the expansion. This expansion therefore breaks down completely near the critical point^{7,11,13}: the zero-order term however remaining exact⁸, (cf. Sec. VII).

VII. DISCUSSION

In Sec. II, and parts of Sec. V, of this paper we have set up a general formalism, utilizing graphs, for systems whose interparticle potential consists of two parts $v(r) = q(r) + w(r)$. This formalism uses a system with interparticle potential $q(r)$ as a reference system. We then obtained the first few terms in a γ -expansion of the two-particle correlations, and of the free energy, for the case where w is a Kac type long-range potential of the form $\gamma^\nu \varphi(\gamma r)$, (ν the dimensionality of the space). It thus serves as a natural extension of Ref. 8 where only the limit $\gamma \rightarrow 0$ is considered. In obtaining these few terms in the γ -expansion, the general formalism was, however, utilized only to a limited extent and is almost unnecessary (cf. Hemmer, Ref. 13). The main prac-

tical value of the general formalism lies (for us) in lending itself readily to approximations that are not simply the result of considering successively higher powers of γ . Thus in the case of a lattice gas discussed in the next paper¹ we use the Γ -ordering of the graphs and evaluate the hypervertices by requiring that the various Ursell functions obtained successively in this ordering, satisfy certain conditions. The results, even in the lowest order, are an improvement over the mean-field and spherical-model approximations. Also investigation of the behavior of fluids and lattice gases with long (but not infinite) range forces near the critical point appears to be facilitated by approximations for C and W suggested by our Γ -ordering. To make the connection between our expansions and the lattice-system expansions of Brout, Horwitz and Callen, Englert, and Stillinger, we can let $q(r)$ express that impossibility of multiple particle-occupancy of sites and $w(r)$ describe the rest of the interparticle interaction. (For convenience, we use lattice-gas language here rather than spin-system language.) Thus $q(\mathbf{r}_{ij}) = \infty$ when $r_{ij} = 0$, i.e., when i and j refer to the same site, and $q(\mathbf{r}_{ij}) = 0$ otherwise. The functions $w(\mathbf{r}_{ij})$ can be set equal to zero for $r_{ij} = 0$. For this lattice system, some of the expressions we have derived reduce to expressions already obtained by the authors cited. For example, our $\hat{F}'_k$ and $\hat{F}''_k$ reduce to Englert's semi-invariants M_k^0 and renormalized semi-invariants M_k , respectively.¹⁰ When $\rho = \frac{1}{2}$ the system corresponds to the field-free spin system considered by Stillinger¹⁴ and our $W(\mathbf{r}_{ij})$ reduces to his $W(\mathbf{r}_{ij})$ (for $\mathbf{r}_{ij} \neq 0$). We defer further examination of these correspondences until our next paper.

We now discuss briefly the possible range of validity of our expressions in γ . We distinguish here the case $\alpha < 0$ and $\alpha > 0$. The van der Waals free energy per particle A obtained formally by letting $\gamma \rightarrow 0$, (after taking the thermodynamic limit), considered as a function of the volume per particle ρ^{-1} has the form⁸

$$A_0(\rho^{-1}) = A^0(\rho^{-1}) + \frac{1}{2} \alpha \rho^{-1}. \quad (7.1)$$

For $\alpha = 0$, A_0 coincides with A^0 while for $\alpha > 0$, $A^0(\rho^{-1})$ will be a monotonically decreasing concave function⁸ of ρ^{-1} . This follows from our assumption that the reference system has a thermodynamic limit so that $A^0(\rho^{-1})$ is a monotonically decreasing non-convex function¹⁵ of ρ^{-1} . Hence the system characterized by A_0 , the "van der Waals system", will show no first-order phase transition since $A_0(\rho^{-1})$ has no linear region. However if the reference system exists in two phases in the density range $\rho_1 < \rho < \rho_2$,

then $\chi^0(\rho)$ is infinite in this range and our whole expansion scheme breaks down [cf. Eqs. (4.3)–(4.6)]. The expansion in γ can thus be meaningful even for small γ only outside this range of densities.

In the second, physically much more relevant, case where $\alpha < 0$, $A_0(\rho^{-1})$ could be convex for some range of ρ^{-1} (and some range of the temperature T), and there would be a loop in the p vs. ρ^{-1} curve. This nonphysical behavior is caused^{8,9}, by the assumption that $n_1(r)$ is constant [cf. going from (6.6) to (6.7)] while in reality $n_1(r)$ would correspond to the coexistence of two phases since that results in a smaller free energy. In this case the expansion in γ with a uniform density can be meaningful only for those densities for which the van der Waals system have a uniform density. This still leaves open the question of the behavior of the system near the critical point when approached from the gas side, the coefficients of the expansion in γ becoming *infinite* there. KUH⁷ have shown, for their model, that the γ expansion breaks down in the vicinity of the critical point (cf. also Refs. 11 and 13). It appears to us that this breakdown is specifically associated with the non-analytic (in γ) behavior of the *short-range* part of the distribution functions, and that approximations in the critical region can only be adequately made when the effects of the long- and short-range parts of the distribution functions are considered separately. We shall investigate these questions carefully in future installments of this work.

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APPENDIX A. PROOF OF EQ. (2.15)

Equation (2.15) can be obtained by a resummation from Eq. (2.9) in much the same way that the ordinary $n_1(\mathbf{x})$ -vertex, f -bond expansion of F_1 can be obtained by resumming the $z_1(\mathbf{x})$ -vertex, f -bond expansion.¹⁷ In both cases the only problem is to verify that all counting comes out correctly—the topological aspect of the recharacterization is trivial. We prove here a lemma sufficient to establish (2.15); it is a straightforward generalization of a lemma found in Ref. 17 which was used there to establish the usual virial expansion of F_1 , following a method devised by Salpeter and others.¹⁷

As noted in Sec. 2, we can define $\hat{F}_k^*(\mathbf{x}_1, \dots, \mathbf{x}_k)$ [or $\hat{F}'_k(\mathbf{x}_1, \dots, \mathbf{x}_k)$] as a sum of graphs simply by adding to the rhs of (2.9) the stipulation that be-

tween any pair of white vertices (or vertices) there can be found a path consisting of K -bonds if $z_1(r)$ vertices are used. We denote a typical graph in this new sum by $\Gamma_\alpha^i(x_1, \dots, x_i)$ and write

$$\hat{F}_i^*(\mathbf{x}_1, \dots, \mathbf{x}_i) = \sum_{\alpha \geq 1} \Gamma_\alpha^i(\mathbf{x}_1, \dots, \mathbf{x}_i)$$

$$[\text{or } \hat{F}'_i(\mathbf{x}_1, \dots, \mathbf{x}_i) = \sum_{\alpha} \Gamma_\alpha^i(\mathbf{x}_1, \dots, \mathbf{x}_i)]. \quad (\text{A.1})$$

Let G be any graph described on the rhs of (2.15) where *connected* and $\hat{F}_k^*$ (or *irreducible* and $\hat{F}'_k$) are considered, and let T be the set of all distinct graphs $T_1, T_2, \dots$, each of which is obtained by replacing each hypervertex $\hat{F}_i^*$ (or $\hat{F}'_i$) in G by some Γ_α^i . The replacement is to be made in the obvious fashion, i.e., the set of bonds that connects $\hat{F}_i^*$ (or $\hat{F}'_i$) to the rest of G is reattached to the white vertices of Γ_α^i and all of the vertices among these which are replacing black vertices of $\hat{F}_i^*$ (or $\hat{F}'_i$) are then stripped of their labels and blackened. We note that in forming a particular T_1 from G , the same Γ_α^i can be used in replacing several, or all, of the hypervertices $\hat{F}_L^*$ (or $\hat{F}'_L$). We can now prove our Lemma:

$$G = \text{the sum of graphs in } T.$$

Proof. The graph G stands for $1/\sigma_G$ times the integral, where σ_G is the symmetry number of G . We consider the sum of integrals that results when the sum given by (A.1) is substituted for $\hat{F}_i^*$ (or $\hat{F}'_i$) whenever the latter appears in this integral. The result is a product of sums of integrals, which can be rewritten as a single sum if all of the indicated multiplication is done. If the graph G has n black vertices, then a typical term t in this new sum will be some integral $\mathcal{J}$ times $1/\sigma_G \sigma_{\alpha_1} \sigma_{\alpha_2} \dots \sigma_{\alpha_n}$ where σ_{α_i} is the symmetry of $\Gamma_{\alpha_i}^i$ and the integrand of $\mathcal{J}$ is some number—call it N —times a product of n_1 's (or z_1 's), Φ 's, K 's, and factors of the form $\prod (t_{ij}!)$. (See the paragraph above Eq. (2.6) for the definition of t_{ij}). The number N will not necessarily be one, since $\mathcal{J}$ need not correspond to a graph with a symmetry number equal to $\sigma_G \sigma_{\alpha_1} \dots \sigma_{\alpha_n}$. However, there will be other terms in the sum that are indistinguishable from this one in the sense that they are all products of the same factor $1/\sigma_G \sigma_{\alpha_1} \dots \sigma_{\alpha_n}$ times integrals that differ from one another (and $\mathcal{J}$) only by a different labeling of the dummy variables of integration. Suppose that there are a total of s such terms, including t . They can be summed up and written as a single term, $s/\sigma_G \sigma_{\alpha_1} \dots \sigma_{\alpha_n}$ times $\mathcal{J}$. The statement of our lemma amounts to the claim that $\sigma_G \sigma_{\alpha_1} \dots \sigma_{\alpha_n}/s$ is the symmetry number σ_I of the graph corresponding to I . To verify this

claim, we characterize σ_I in terms of a second labeling. We do this by noting that if we consider the graph obtained from G by labeling the hypervertices $1, 2, \dots, n$, then s is the number of distinguishable ways of labeling the hypervertices $1, \dots, n$ with the labels $\alpha_1, \dots, \alpha_n$ (The labels α_i and α_j may be the same for $i \neq j$ i.e. Γ_{α_i} may be the same graph as Γ_{α_j} . If all the Γ_{α_i} 's are different, $s = n!$ If all the Γ_{α_i} 's are the same, $s = 1$.) Now σ_I can be expressed as $\bar{\sigma}\sigma_{\alpha_1} \dots \sigma_{\alpha_n}$ where $\bar{\sigma}$ is the number of permutations among the $\alpha_1, \alpha_2, \dots, \alpha_n$ (or equivalently, among the labels $1, 2, \dots, n$) that leave the doubly labeled graph invariant. But we have also the equation

$$s\bar{\sigma} = \sigma_G. \quad (\text{A2})$$

Equation (A2) is an expression of the fact that the group of permutations among the labels $1, 2, \dots, n$ that leave the doubly labeled graph invariant is a subgroup of the larger group of permutations that leave the singly labeled groups invariant, and the ratio of the orders of the two groups is just the number of distinguished ways that the double labeling can be done. This follows immediately from the appropriate application of Lagrange's theorem relating the order of a group, the order of a subgroup, and the number of cosets induced by the subgroup.

Using Eq. (A2) we can write $\sigma_I = \bar{\sigma}\sigma_{\alpha_1} \dots \sigma_{\alpha_n}$ as $\sigma_G\sigma_{\alpha_1} \dots \sigma_{\alpha_n}/s$ and we are through. Equation (2.15) follows immediately from the lemma.

APPENDIX B. EXPANSION OF $\hat{F}_k$ IN TERMS OF REFERENCE SYSTEM HYPERVERTICES

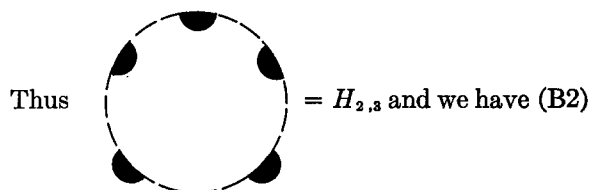
In this Appendix we show more explicitly how Eq. (2.18) can be used to obtain the full expansion for the $\hat{F}_k$ in terms of Φ and functionals of $n_1(x)$ which depend entirely upon the properties of the "unperturbed" system for which $\Phi \equiv 0$.

Combining (2.15) and (2.18), leads to a prescription for $\hat{F}_k$ that can be represented graphically in terms of Φ -bonds and *new* hypervertices which represent the functions

$$\delta^i \hat{F}_k^0 / \delta n_1(\mathbf{x}_{k+1}) \dots \delta n_1(\mathbf{x}_{k+l}) \\ \equiv H_{k,l}(\mathbf{x}_1, \dots, \mathbf{x}_{k+l}). \quad (\text{B1})$$

Here the $H_{k,l}$ -hypervertices must be thought of as having finite extent as we shall consider graphs in which these hypervertices may be connected to each other, as well as to Φ -bonds. In any such connected graph an articulation hypervertex will contain two kinds of vertices—"out" vertices that connect it to the rooted part of a graph and "in" vertices from which are hung pieces that would separate

from all the roots if the hypervertex were deleted. (Any labeled vertex is automatically an "out" vertex, and a hypervertex that is not an articulation hypervertex has only "out" vertices.) The $H_{k,l}$ defined above will be represented pictorially by a hypervertex which has k "out" vertices and l "in" vertices.



Thus $= H_{2,2}$ and we have (B2)

$\hat{F}_m(\mathbf{r}_1, \dots, \mathbf{r}_m)$ = the sum of all distinct connected graphs, rooted at m points, consisting of Φ -bonds and $H_{k,l}$ -hyper-vertices such that there are no articulation vertices (even though there are articulation hypervertices). A vertex belonging to a hypervertex can either have a single bond incident upon it (in which case it must be an "out" vertex) or be shared by another hypervertex (in which case it must be the "out" vertex of one hypervertex and the "in" vertex of the other). Two hypervertices can share at most a single vertex and, as before, a single Φ -bond cannot have both its ends attached to a single hypervertex. (B3)

These expressions involving $H_{k,l}$ are similar to the expressions of Brout¹⁰, and Coopersmith and Brout¹⁰, in the sense that like the vertex functions of those authors, the $H_{k,l}$ are functions of ρ and β and depend only on the unperturbed system for which $\Phi \equiv 0$, (In this respect the expansions of Brout, and Coopersmith and Brout differ from those of Horwitz and Callen and Englert.) However, our expansions are valid for an arbitrary system whereas Coopersmith and Brout were unable to generalize their lattice-system expansions to a continuum fluid without invoking a set of superposition approximations.

APPENDIX C. HYPERVERTEX EXPANSION OF THE THERMODYNAMIC POTENTIALS

Here we supplement the discussion in Sec. VI by considering directly the graphical characterization of the logarithm of Ξ , the grand partition function.

Starting with the standard characterization^{17,18} of $\ln \Xi(\{z_i(\mathbf{x})\})$ as the sum of all unrooted composite connected graphs with K - and Φ -bonds and at least two $z_1(\mathbf{x})$ vertices we first isolate a subset $(\ln \Xi)' \equiv F'_0$

which consists of all those graphs in $\ln \Xi$ for which there is a short-range path between any pair of vertices. $F'_0(\{z_1(x)\})$ serves as a generating functional for the F'_l [defined in (2.14)] in precisely the same manner as $\ln \Xi(\{z_1(x)\})$ does for the F_l ^{16,17},

$$F'_l(\mathbf{r}_1, \dots, \mathbf{r}_m) = \prod_{i=1}^l z_1(x_i) \frac{\delta^l F'_0}{\delta z_1(x_1) \dots \delta z_1(x_l)}. \quad (\text{C1})$$

We can now carry through a functional Taylor expansion of $F'_0(\{z_1(x)\})$ about its value at $z_1 = 0$ to yield

$$F'_0 = \sum_{l=1}^{\infty} \frac{(-1)^{l+1}}{l!} \int F'_l(\mathbf{x}_1, \dots, \mathbf{x}_l) d\mathbf{x}_1 \dots d\mathbf{x}_l. \quad (\text{C2})$$

Equation (C2) remains valid when either the primes are removed from the F_l or when the F'_l are replaced by F_l^0 , the values of the Ursell functions in the reference system. In these cases $F_0 = \ln \Xi(\{z_1(x)\})$ and $F_0^0 = \ln \Xi^0(\{z_1(x)\})$ where $\Xi^0(z_1(x))$ is the value of $\Xi(\{z_1(x)\})$ when $\Phi \equiv 0$. Having isolated F'_0 we now have

$$\ln \Xi(\{z_1(\mathbf{x})\}) = F'_0 + \text{the sum of all unrooted connected graphs composed of } \Phi\text{-bonds and at least two } \hat{F}_k^*\text{-hypervertices.} \quad (\text{C3})$$

To find the $\ln \Xi$ in terms of Φ and functions that depend only on the properties of the unperturbed reference system in which $\Phi \equiv 0$, we use an identity relating the F'_k and the F_k^0 :

$$F'_k(\mathbf{x}_1, \dots, \mathbf{x}_k) = \exp \left\{ \frac{1}{2} \int d\mathbf{y}_1 d\mathbf{y}_2 \left[z_1(\mathbf{y}_1) z_1(\mathbf{y}_2) \times \Phi(\mathbf{y}_1, \mathbf{y}_2) \frac{\delta^2}{\delta z_1(\mathbf{y}_1) \delta z_1(\mathbf{y}_2)} \right] \right\} F_k^0(\mathbf{x}_1, \dots, \mathbf{x}_k). \quad (\text{C4})$$

In order to obtain $\ln \Xi$ from (C3) and (C4) we must be given the fugacity z of the system, since the F_k^0 are functions of z . It is somewhat more convenient to be able to express $\ln \Xi$ in terms of ρ directly. We can do this by working through the $\hat{F}_k^*$ and the functions $G_k(\mathbf{x}_1, \dots, \mathbf{x}_k)$ defined by

$$G_l(\mathbf{y}_1, \dots, \mathbf{y}_l) = \frac{1}{l!} \int \prod_i \Phi(\mathbf{x}_i - \mathbf{y}_i) \times \hat{F}_l(\mathbf{x}_1, \dots, \mathbf{x}_l) d\mathbf{x}_1, \dots, d\mathbf{x}_l. \quad (\text{C5})$$

The $\hat{F}_l^*$, G_l and $\hat{F}_l'$ are related by an expression very similar to (2.18). It is

$$\hat{F}_l'(\mathbf{y}_1, \dots, \mathbf{y}_l) = \mathfrak{N} \left\{ \exp \left[\sum_{k \geq 1} \frac{1}{k!} \int d\mathbf{x}_1 \dots d\mathbf{x}_k \times G_k(\mathbf{x}_1, \dots, \mathbf{x}_k) \frac{\delta}{\Pi \delta \ln z_1(\mathbf{x}_i)} \right] \hat{F}_l'(\mathbf{y}_1, \dots, \mathbf{y}_l) \right\} \quad (\text{C6})$$

where $\mathfrak{N}$ has the meaning of a normal product as in (2.18). For $l > 0$, (C6) is a graphical identity and for $l = 0$ it defines $\hat{F}_0^*$, which can also be obtained by letting $l = 0$ and $\hat{F}_0^* = \{\ln \Xi\}^0$ in (2.18).

We can now use the same combinatorial analysis that has been used by several authors (see Sec. 7 in Ref. 17) to show that $\ln \Xi$ and the excess Helmholtz free energy, α are related by the equation

$$\ln \Xi = \int d\mathbf{x} n_1(\mathbf{x}) - \beta\alpha + \int d\mathbf{x} n_1(\mathbf{x}) \frac{\delta \beta\alpha}{\delta n_1(\mathbf{x})}. \quad (\text{C7})$$

Here $-\beta\alpha$ = the sum of all irreducible simple unrooted graphs with n_1 -vertices and at least one f -bond. This analysis yields in our case the similar-looking equation

$$\ln \Xi = \hat{F}_0^* + S - \sum_{n \geq 1} \int d\mathbf{x}_1, \dots, d\mathbf{x}_n G_n \hat{F}_n^*, \quad (\text{C8})$$

where

$$S = \text{the sum of all irreducible unrooted graphs with } \hat{F}_n^* \text{ hypervertices and at least one } \Phi\text{-bond.} \quad (\text{C9})$$

We note that

$$\delta S / \delta \hat{F}_n^*(\mathbf{x}_1, \dots, \mathbf{x}_n) = G_n(\mathbf{x}_1, \dots, \mathbf{x}_n) \quad \Phi \text{ and } \hat{F}_l^* \text{ for } l \neq n \text{ fixed} \quad (\text{C10})$$

so that (C8) can be rewritten in strict analogy with (C7) as

$$\ln \Xi = \hat{F}_0^* + S - \sum_{n \geq 1} \int d\mathbf{x}_1 \dots d\mathbf{x}_n \hat{F}_n^* \frac{\delta S}{\delta \hat{F}_n^*}.$$

Furthermore, when $q(r) = 0$ so that $v(r) = w(r)$, we have

$$S = -\beta\alpha; \quad \hat{F}_0^* = \int d\mathbf{x} n_1(\mathbf{x}),$$

$$\hat{F}_l^*(\mathbf{x}_1, \dots, \mathbf{x}_l) = n_1(\mathbf{x}_1) \prod_{1 \leq i \leq l} \delta(\mathbf{x}_1 - \mathbf{x}_i) \text{ for } l \geq 2$$

and (C8) reduces to (C7). [When $v(r) = 0$, $S \equiv 0$ and $\hat{F}_0^* = \ln \Xi$.]

Since the $\hat{F}_k^*$ and hence the G_k can be expressed in terms of Φ and the functions $H_{k,l} = \delta^l \hat{F}_k^0 / \Pi \delta n_1(\mathbf{x}_i)$ by using (2.18) as indicated in Appendix B we have succeeded in obtaining $\ln \Xi$ in terms of Φ and functionals of $n_1(x)$ and β that are defined completely in terms of the reference system.

Many of the equations discussed in this Appendix reduce to lattice-system equations derived by Englert, and Bloch and Langer, where $\mathbf{r}$ is restricted to a set of discrete lattice sets. However some of our equations, notably (2.18), are new even for the special case of lattice systems.