

Functional integral formulations for classical fluids

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Various functional integral formalisms of classical monatomic fluids are considered with their applicabilities and limitations compared. For length scales large compared to the particle size, the density field theory, in which the action of the functional integral is simply given by the mean field free energy functional expression, is shown to be a well-defined and rigorous formulation. For short range properties of dense fluids, a different version of the functional integral method is developed by explicitly separating out the hard core part of the interaction. The resulting functional integral is seen to require correlation functions of the hard sphere fluid as the input. The generalized van der Waals equation and the random phase approximation of the cluster diagrammatic methods are recovered simply as the stationary-phase approximation and its Gaussian correction to the functional integral, respectively. © 2001 American Institute of Physics. [DOI: 10.1063/1.1353553]

I. INTRODUCTION

The nature of short range correlations in dense fluids near the triple point is known to be dominated by the effect of hard core repulsion, with the attractive tail merely providing uniform backgrounds holding the liquid phase together. Low-order thermodynamic perturbation theories thus provide excellent schemes of calculating structural and thermodynamic properties of dense liquids.^{1,2} As we go away from the triple point, such an approach becomes less and less adequate as the attractive part of the interaction plays increasingly important roles in determining the structure of the fluid. Formalisms based on the diagrammatic expansions of the Mayer cluster series^{1,3,4} have been developed to account for long-range perturbation effects.

In contrast, close to the critical point, conceptual understanding of the critical phenomena of classical fluids is provided by the renormalization group study of the Landau–Ginzburg (LG) free energy functional. A *formal* argument of the relevance of the Ising-type LG functional to the classical fluids can be made for universal properties such as critical exponents,⁵ and is supported *a posteriori* by the close agreement of the exponents with experimental data. Functional integral formulations involved in this context are generally not suitable for studies of short range properties of dense liquids. In the present paper, we explore and compare various different functional integral formulations, with the aim of developing a unified treatment of both the universal and specific properties of the classical simple liquids.

Existing formalisms of reducing the configurational integral to a functional integral expression are based on the analogous reduction of Ising model into LG functional (Sec. II).^{5,6} The average of the field variable of the functional integral is conjugate to the average density, and the interaction part is proportional to the “inverted potential.” The universality of critical phenomena implies that the long range correlations near the critical point giving rise to the second order phase transition in fluids are insensitive to much of the details of interaction potentials. Mathematical subtleties in-

involved in the inversion of the interaction matrix, also encountered in the Ising model case, are thus expected to be irrelevant to studies of critical fluctuations, and any procedure of regularization⁵ justifying the formal manipulation would be rather harmless.

On the other hand, for a formalism potentially aimed at short range correlations in dense liquids, neglect of the effect of highly singular hard core repulsion would be disastrous. An alternative avoiding such difficulties could be provided by *constructing* a functional integral expression on a heuristic physical ground. The action of the field theory is assumed to have the form of the mean field free energy expression, and the average of the field coincides with the physical density.⁷ Although physically more appealing and transparent, a proper justification based on the original configurational integral would be needed.

In Sec. III, it is shown that a mapping from a discrete representation of the configurational integral to a functional integral form naturally leads to such an expression, provided that a coarse-graining procedure to obtain the continuum limit is assumed. We therefore argue that the resulting density field theoretic expression, as opposed to the Ising-type form, is the natural and well-defined platform for studies of long range density fluctuations.

However, the inherent coarse-graining inevitably limits the utility of the functional integral formalism obtained to the structures with length scales larger than the particle size. To address short range correlations, a different approach is explored in Sec. IV, where the hard core part of the interaction is separated out, and the effect of the remaining attractive interaction is treated in the field theoretic methods. The resulting functional integral expression requires the correlation functions of the hard sphere as the inputs, and is shown to include the conventional results such as the random phase approximation of the diagrammatic methods as special cases.

II. ISING-TYPE FUNCTIONAL INTEGRALS

For completeness and comparison, we briefly reexamine the existing formalism of reducing the grand canonical par-

tion function of a classical fluid to a functional integral expression.^{5,6,8} The configurational integral expression of the grand canonical partition function of a classical fluids with pairwise interaction potential $v(\mathbf{r})$ and external field $u(\mathbf{r})$ can be written as

$$\Xi = \sum_{N=0}^{\infty} \frac{\lambda^N}{N!} \int d^N \mathbf{r}_i \exp \left[-\frac{\beta}{2} \sum_{i \neq j} v(\mathbf{r}_i - \mathbf{r}_j) - \beta \sum_i u(\mathbf{r}_i) \right], \quad (1)$$

where $1/\beta = k_B T$ is the Boltzmann constant times temperature, $\lambda = e^{\beta\mu}/\Lambda^3$ is the fugacity defined in terms of the chemical potential μ , and the thermal de Broglie wavelength Λ . The configurations of the N particles are represented by the set of vectors $\{\mathbf{r}_i\}$. The average of a continuous density field $\rho(\mathbf{r})$ would have to agree with the expectation value of the local density operator,

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (2)$$

To construct a continuous field theory, an auxiliary field ϕ is introduced through the identity,

$$\int \int \mathcal{D}\phi \mathcal{D}\rho \exp \left[i \int d\mathbf{r} \phi(\mathbf{r}) [\rho(\mathbf{r}) - \hat{\rho}(\mathbf{r})] \right] = 1. \quad (3)$$

Inserting Eq. (3) into Eq. (1) and summing over N ,

$$\begin{aligned} \Xi = & \int \int \mathcal{D}\phi \mathcal{D}\rho \exp \left[-\frac{\beta}{2} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \right. \\ & \times [\rho(\mathbf{r})\rho(\mathbf{r}') - \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')] - \beta \int d\mathbf{r} u(\mathbf{r})\rho(\mathbf{r}) \\ & \left. + i \int d\mathbf{r} \phi(\mathbf{r})\rho(\mathbf{r}) + \lambda \int d\mathbf{r} e^{-i\phi(\mathbf{r})} \right]. \quad (4) \end{aligned}$$

Assuming that the interaction potential $v(r)$ has a well-defined inverse, as well as finite $v(0)$, Gaussian integrals over ρ can be done to yield

$$\Xi = \int \mathcal{D}\phi e^{-S[\phi;u]}, \quad (5a)$$

where

$$\begin{aligned} S[\phi;u] = & \frac{1}{2\beta} \int d\mathbf{r} \int d\mathbf{r}' v^{-1}(\mathbf{r} - \mathbf{r}') [\phi(\mathbf{r}) + i\beta u'(\mathbf{r})] \\ & \times [\phi(\mathbf{r}') + i\beta u'(\mathbf{r}')] - \lambda \int d\mathbf{r} e^{-i\phi(\mathbf{r})}, \quad (5b) \end{aligned}$$

and $u'(\mathbf{r}) = u(\mathbf{r}) - v(0)/2$. The stationary-phase approximation to Eqs. (5) leads to

$$\bar{\phi}(\mathbf{r}) = -i\beta u'(\mathbf{r}) - i\lambda \int d\mathbf{r}' \beta v(\mathbf{r} - \mathbf{r}') e^{-i\bar{\phi}(\mathbf{r}')}, \quad (6)$$

and the grand potential $\Omega[u] = -\ln \Xi$ is given by $\Omega = S[\bar{\phi};u]$. Denoting the average density as $\bar{\rho}(\mathbf{r}) = \delta\Omega[u]/\delta\beta u(\mathbf{r})$, we have

$$\bar{\rho}(\mathbf{r}) = \lambda e^{-i\bar{\phi}(\mathbf{r})}. \quad (7)$$

From Eqs. (6) and (7), we identify $i\bar{\phi}(\mathbf{r})$ as the ‘‘mean field’’ at \mathbf{r} produced by the external field and the average density in the neighborhood,

$$i\bar{\phi}(\mathbf{r}) = \beta u'(\mathbf{r}) + \int d\mathbf{r}' \beta v(\mathbf{r} - \mathbf{r}') \bar{\rho}(\mathbf{r}'). \quad (8)$$

The ‘‘density functional’’ $\Omega[\bar{\rho}]$, defined as the the Legendre transform

$$\Omega[\bar{\rho}] = \Omega[u] - \int d\mathbf{r} \bar{\rho}(\mathbf{r}) \beta u(\mathbf{r}), \quad (9)$$

is obtained under the stationary-phase approximation as

$$\begin{aligned} \Omega[\bar{\rho}] = & \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \beta v(\mathbf{r} - \mathbf{r}') [\bar{\rho}(\mathbf{r})\bar{\rho}(\mathbf{r}') \\ & - \bar{\rho}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')] - \beta \mu \int d\mathbf{r} \bar{\rho}(\mathbf{r}) + \int d\mathbf{r} \bar{\rho}(\mathbf{r}) \\ & \times [\ln \bar{\rho}(\mathbf{r}) \Lambda^3 - 1]. \quad (10) \end{aligned}$$

The functional integral expression given by Eqs. (5) is a complete analogue of the corresponding result for the Ising model obtained by the Hubbard–Stratonovich transformation. A LG-type functional can be derived by making functional expansions with respect to the field $\phi(\mathbf{r})$ in Eq. (5).

III. DENSITY-FIELD THEORY

For any realistic interaction potential possessing a hard core repulsion part, the inversion of the potential involved in Eqs. (5) is not well-defined. As far as one is interested only in the critical properties of the liquid–gas transition, however, Eqs. (5) can be quite adequately justified by noting that the long range correlations observed in the critical region is dominated by the attractive part of the interaction, and therefore the nonessential effect of the repulsive interaction can be absorbed into the wave vector cutoff of the field theory. In this viewpoint, the interaction potential $v(r)$ in Eqs. (5) should be interpreted as a coarse-grained attractive part of the original interaction. The microscopic length scale associated with the wave vector cutoff would necessarily be required to be larger than the particle size.

An alternative formulation which does not require the inversion of potential could be considered on a heuristic physical argument. The physical significance of the mean field density functional expression (10), consisting of the mean energy and the ideal entropy associated with the continuous density field $\rho(\mathbf{r})$, obviously transcends the apparent limitations imposed by the current derivation. Therefore, one might construct a density field theoretic expression,

$$\Xi = \int \mathcal{D}\rho e^{-S[\rho]}, \quad (11a)$$

where

$$\begin{aligned}
 S[\rho] = & \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \beta v(\mathbf{r}-\mathbf{r}') [\rho(\mathbf{r})\rho(\mathbf{r}') \\
 & - \rho(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')] - \beta\mu \int d\mathbf{r}\rho(\mathbf{r}) \\
 & + \int d\mathbf{r}\beta u(\mathbf{r})\rho(\mathbf{r}) + \int d\mathbf{r}\rho(\mathbf{r})[\ln \rho(\mathbf{r})\Lambda^3 - 1].
 \end{aligned}
 \tag{11b}$$

In contrast to the formulation described in Sec. II, the density field itself instead of the field $\phi(\mathbf{r})$ serves as the variable in the functional integral, and the nonlinearity of the field theory, renormalizing the interaction $v(r)$, is seen to arise from the entropy term in the action. In fact, the density field theoretic expression (11) can be *derived* from the original configurational integral. One abandons the Gaussian integration over the density field $\rho(\mathbf{r})$ in Eq. (4), which is, although formally exact, ill-defined. Applying the stationary-phase approximation to the auxiliary field $\phi(\mathbf{r})$ with fixed $\rho(\mathbf{r})$ immediately yields Eqs. (11).⁹

Physically more transparent and free of inverted potential, Eqs. (11) are expected to be a more advantageous functional integral representation of the classical fluids compared to the Ising-type form (5). However, due to the stationary-phase approximation used in its derivation, it is not clear what its range of applicability and limitations are. In this section, we explore a rigorous reformulation of the functional integral form (11) from the original configurational integral without using the stationary-phase approximation.

It is convenient to start with a discrete version of the configurational integral (1),

$$\Xi = \sum_{N=0}^{\infty} \frac{\bar{\lambda}^N}{N!} \sum_{\{\mathbf{r}_i\}} \exp \left[-\frac{\beta}{2} \sum_{i \neq j} v_{\mathbf{r}_i, \mathbf{r}_j} - \beta \sum_{i=1}^N u_{\mathbf{r}_i} \right], \tag{12}$$

where $\bar{\lambda} = a^3\lambda$ is the reduced fugacity, and $v_{\mathbf{r}, \mathbf{r}'}$, $u_{\mathbf{r}}$ are the discrete counterparts of the interaction potential and the external field. The lattice spacing a is yet arbitrary, so that continuum limit could be taken later after suitable manipulations. The set of lattice vectors $\{\mathbf{r}_i\}$ specifying the center of particles, represent each configuration. We define a microscopic occupation number operator $\hat{n}_{\mathbf{r}}$ as

$$\hat{n}_{\mathbf{r}} = \sum_{i=1}^N \delta_{\mathbf{r}, \mathbf{r}_i}, \tag{13}$$

where $\delta_{\mathbf{r}, \mathbf{r}'}$ is the Kronecker delta. The continuum counterpart, Eq. (2), can be obtained by $a \rightarrow 0$ with $\hat{n}_{\mathbf{r}}/a^3 \rightarrow \hat{\rho}(\mathbf{r})$.

Field theoretic expression is constructed by utilizing the identity,

$$\prod_{\mathbf{r}} \left(\sum_{n_{\mathbf{r}}=0}^{\infty} \int_{-\pi}^{\pi} \frac{d\phi_{\mathbf{r}}}{2\pi} \right) \exp \left[i \sum_{\mathbf{r}} \phi_{\mathbf{r}} (n_{\mathbf{r}} - \hat{n}_{\mathbf{r}}) \right] = 1. \tag{14}$$

Inserting Eq. (14) into Eq. (12), we get

$$\begin{aligned}
 \Xi = & \sum_{\{n_{\mathbf{r}}\}} \prod_{\mathbf{r}} P(n_{\mathbf{r}}) \\
 & \times \exp \left[\frac{-\beta}{2} \sum_{\mathbf{r}} \sum_{\mathbf{r}'} [n_{\mathbf{r}}n_{\mathbf{r}'} - n_{\mathbf{r}}\delta_{\mathbf{r}, \mathbf{r}'}] v_{\mathbf{r}, \mathbf{r}'} - \beta \sum_{\mathbf{r}} n_{\mathbf{r}}u_{\mathbf{r}} \right],
 \end{aligned}
 \tag{15}$$

where

$$P(n_{\mathbf{r}}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\phi \exp(i\phi n_{\mathbf{r}} + \bar{\lambda} e^{-i\phi}). \tag{16}$$

The integral (16) can be done [$P(n) = \bar{\lambda}^n/n!$] (Ref. 10) to yield

$$\Xi = \sum_{\{n_{\mathbf{r}}\}} e^{-\beta H[n_{\mathbf{r}}]}, \tag{17a}$$

where

$$\begin{aligned}
 \beta H[n_{\mathbf{r}}] = & \beta \sum_{\mathbf{r}} \sum_{\mathbf{r}'} [n_{\mathbf{r}}n_{\mathbf{r}'} - n_{\mathbf{r}}\delta_{\mathbf{r}, \mathbf{r}'}] v_{\mathbf{r}, \mathbf{r}'} + \frac{\beta}{2} \sum_{\mathbf{r}} n_{\mathbf{r}}u_{\mathbf{r}} \\
 & + \sum_{\mathbf{r}} \ln n_{\mathbf{r}}! - [\beta\mu + \ln(a^3/\Lambda^3)] \sum_{\mathbf{r}} n_{\mathbf{r}}.
 \end{aligned}
 \tag{17b}$$

To take the continuum limit of Eqs. (17), the nature of the interaction potential $v(\mathbf{r})$ has to be considered carefully. The lattice spacing a underlies any definition of continuous field theory as the microscopic length scale associated with the wave vector cutoff in k -space. If we assume $a > \sigma$, where σ is the characteristic length scale of the repulsive interaction, the hard core part of the interaction potential can effectively be replaced by the wave vector cutoff and the density field fluctuations would be governed by the attractive part of the interaction only. In this case, taking the continuum limit $a^3 \sum_{\mathbf{r}} \rightarrow \int d\mathbf{r}$ and $n_{\mathbf{r}}/a^3 \rightarrow \rho(\mathbf{r})$ with Stirling's approximation to the factorial term in Eq. (17b), we arrive at the density field theoretic expression, Eqs. (11). However, it is also clear that in this case it would be necessary to interpret $v(\mathbf{r})$ in Eq. (11) as the coarse-grained attractive part of the original interaction potential.

Our derivation shows that the approximation involved in the reduction of the configurational integral into the density field theory (11), which is only seen as the mathematical manipulation of the stationary-phase approximation in the continuous representation, can in fact be interpreted as the coarse-graining over the microscopic length scales. Furthermore, for studies of long range density fluctuations in the classical fluid, the representation (11), without any ad hoc features other than the necessary coarse-graining, is now seen as a natural platform as opposed to the Ising-type representation (5).

If we instead assume $a \leq \sigma$, replacement of the total interaction potential with its long range part remains to be a crude approximation of the effect of hard core repulsion, but the configurational summation in Eq. (17a) is now restricted to $n_{\mathbf{r}}=0,1$. In this case, the factorial term in Eq. (17b) is identically zero for any configuration, and Eqs. (17) reduce to the standard lattice gas partition function.

IV. SHORT RANGE CORRELATIONS

The necessary coarse-graining implicit in the density field theoretic expression (11) makes the formalism still inappropriate for studies of short range correlations in dense liquids. In fact, the mean field density obtained by minimizing Eq. (11b),

$$\bar{\rho}(\mathbf{r}) = \frac{e^{\beta\mu}}{\Lambda^3} \exp\left[-\beta \int d\mathbf{r}' v(\mathbf{r}-\mathbf{r}') \bar{\rho}(\mathbf{r}') - \beta u'(\mathbf{r})\right] \quad (18)$$

is unable to support spatially smooth density profile [Eq. (2) is the only form allowed] if the interaction potential $v(\mathbf{r})$ contains the hard core part. Highly singular nature of the hard core interaction makes its treatment within a continuous field theoretic formalism difficult, if not impossible. Instead, the Percus–Yevick solution¹¹ with its empirical correction¹² provides accurate thermodynamic and structural properties of hard sphere fluids. We take the approach of treating hard sphere fluid as the given reference with known properties, and develop field theoretic treatment of the deviations from the hard sphere properties. Such a separation of potential forms the basis of the simple thermodynamic perturbation theories, and the Mayer cluster diagram methods.¹ Parola and Reatto¹³ also have used similar approach to develop a hierarchical theory of integrodifferential equations of classical fluids.

We begin with the discrete representation (17) of the functional integral. Regardless of the feasibility of the direct calculation of hard sphere properties, Eqs. (17) formally contains full information resulting from the original interaction potential, if the lattice spacing a is sufficiently small compared to the particle size. The interaction potential is separated into the repulsive hard core part, $v_{\mathbf{r},\mathbf{r}'}^{(0)}$, and the remaining attraction, $-v_{\mathbf{r},\mathbf{r}'}^{(1)}$,

$$v_{\mathbf{r},\mathbf{r}'} = v_{\mathbf{r},\mathbf{r}'}^{(0)} - v_{\mathbf{r},\mathbf{r}'}^{(1)}. \quad (19)$$

A concrete definition of the two terms can be provided by the Weeks–Chandler–Andersen separation scheme.² We combine the hard core interaction $v_{\mathbf{r},\mathbf{r}'}^{(0)}$, with the remaining terms in Eq. (17b) to define the hard sphere Hamiltonian $H_0[n_{\mathbf{r}}]$, whereupon,

$$\Xi = \sum_{\{n_{\mathbf{r}}\}} \exp\left[-\beta H_0[n_{\mathbf{r}}] + \frac{1}{2} \sum_{\mathbf{r},\mathbf{r}'} \beta v_{\mathbf{r},\mathbf{r}'}^{(1)} n_{\mathbf{r}} n_{\mathbf{r}'}\right]. \quad (20)$$

In Eq. (20), the term proportional to $v_{\mathbf{r},\mathbf{r}'}^{(1)}$ has been absorbed into the chemical potential term in $H_0[n_{\mathbf{r}}]$. With the singular repulsive part separated out, the inverse of the interaction matrix $v_{\mathbf{r},\mathbf{r}'}^{(1)}$ is well-defined, and the Hubbard–Stratonovich transformation can be applied to yield

$$\Xi = \frac{1}{A} \int \mathcal{D}\psi \exp\left[-\frac{1}{2} \sum_{\mathbf{r},\mathbf{r}'} V_{\mathbf{r},\mathbf{r}'} \psi_{\mathbf{r}} \psi_{\mathbf{r}'}\right] \times \sum_{\{n_{\mathbf{r}}\}} \exp\left[-\beta H_0[n_{\mathbf{r}}] + \sum_{\mathbf{r}} \psi_{\mathbf{r}} n_{\mathbf{r}}\right], \quad (21)$$

where $V_{\mathbf{r},\mathbf{r}'}$ is defined by

$$\sum_{\mathbf{r}'} V_{\mathbf{r},\mathbf{r}'} \beta v_{\mathbf{r}',\mathbf{r}''}^{(1)} = \delta_{\mathbf{r},\mathbf{r}''}, \quad (22)$$

and $A = (2\pi)^{M/2} / (\det V)^{1/2}$ is the normalization factor, where M is the number of lattice sites. It is seen that the second factor involving the configurational summation in Eq. (21) has the form of the hard sphere grand canonical partition function with the auxiliary field $\psi(\mathbf{r})$ serving as the “external field.” The continuum limit $a \rightarrow 0$ can now be taken to give

$$\Xi = \frac{1}{A} \int \mathcal{D}\psi \exp\left[-\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' V(\mathbf{r}-\mathbf{r}') \times \psi(\mathbf{r}) \psi(\mathbf{r}') - \Omega_0[\psi]\right], \quad (23)$$

where $\Omega_0[\psi]$ is the grand potential of the hard sphere with the external field $\psi(\mathbf{r})$.

The functional integral expression (23) can be used as a well-defined starting point for a treatment of the short range thermodynamic and structural properties of dense fluids. The equilibrium density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = -\frac{\delta \ln \Xi}{\delta \beta u(\mathbf{r})} = -\left\langle \frac{\delta \Omega_0[\psi]}{\delta \psi(\mathbf{r})} \right\rangle, \quad (24)$$

where the brackets represent the functional integral average. Stationary-phase approximation to Eq. (23) yields

$$\bar{\psi}(\mathbf{r}) = \int d\mathbf{r}' \beta v^{(1)}(\mathbf{r}-\mathbf{r}') \rho(\mathbf{r}'). \quad (25)$$

The equation of state is given within the stationary-phase approximation by

$$\beta p = \beta p_0 - \frac{1}{2V} \int d\mathbf{r} \int d\mathbf{r}' \beta v^{(1)}(\mathbf{r}-\mathbf{r}') \rho(\mathbf{r}) \rho(\mathbf{r}'), \quad (26)$$

where p and p_0 are the pressures of the total and the hard sphere system, respectively, and V is the total volume. Equation (26) has the usual form of the mean field theory, and the generalized van der Waals-type equation¹⁴ of state is readily obtained for the homogeneous liquid. Corrections to the mean field result are obtained through the functional expansion of the hard sphere grand potential,¹

$$\prod_{m=1}^n \frac{\delta}{\delta \psi(\mathbf{r}_m)} \Omega_0[\psi] = -\rho_c^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n), \quad (27)$$

where $\rho_c^{(n)}$ is the n th order connected correlation function of the hard sphere fluid. Within the second order, correction to the stationary-phase result (26), $\delta(\beta p)$ can be written as

$$e^{\delta(\beta p)V} = \frac{1}{A} \int \mathcal{D}\psi \exp\left[-\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' [V(\mathbf{r}-\mathbf{r}') - \rho_c^{(2)}(\mathbf{r},\mathbf{r}')] \delta\psi(\mathbf{r}) \delta\psi(\mathbf{r}')\right]. \quad (28)$$

The second-order expansion coefficient is given by

$$\rho_c^{(2)}(\mathbf{r},\mathbf{r}') = \rho^{(2)}(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') + \rho\delta(\mathbf{r}), \quad (29)$$

where ρ is the bulk density, and $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ is the two-point correlation function of the hard sphere. For homogeneous liquids, $\rho(\mathbf{r}) = \rho$, and $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r} - \mathbf{r}'|)$, where $g(r)$ is the pair correlation function. In this case, Gaussian integration yields

$$\delta(\beta_p)V = -\frac{1}{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \ln[1 - \rho S(k)\beta\hat{v}^{(1)}(k)], \quad (30)$$

where $\hat{v}^{(1)}(k)$ is the Fourier transform of $v^{(1)}(r)$, and $S(k)$ is the structure factor of the hard sphere fluid. In the random phase approximation within the Mayer cluster diagrammatic formalism, a resummation of the ‘‘ring diagrams’’ yields an expression corresponding to Eq. (30).¹⁵ The dependence of Eq. (30) on $v^{(1)}(r)$ for $r < \sigma$ is an artifact of the approximation. The arbitrary nature of the core part of the attractive interaction can in fact be exploited to enforce the excluded volume constraint on the correlation function.¹⁵

Unlike the cluster diagram methods, however, it is clear within the current functional integral formalism how one could obtain higher order corrections systematically, although such treatments would require correlation functions of the hard sphere fluid beyond the second order. At the same time, it is seen that the random phase approximation exhausts the information given by the two-point correlation of the hard sphere fluid.

V. SUMMARY

Conventional functional integral formalisms of the grand canonical partition function of classical fluids are not suitable for studies of nonuniversal properties of dense liquids, in which the effect of hard core repulsion cannot be ignored. A density-field theory, where the average of the field coincides with the physical density, and the familiar mean field free energy expression itself is taken as the action, is an alternative that avoids the inversion of the singular potential necessary for the Ising-type functional integral formulation.

It was shown that such a density field theory can in fact be regarded as *the correct* platform of studying the density fluctuations on a length scale larger than particle size, as opposed to the conventional Ising-type methods, which is at best formally justifiable.

On the other hand, the coarse-graining over the microscopic length scales, seen to be inherent in such a density-field theory, entails the inevitable loss of any structural information arising from the hard core repulsion in the dense liquid. By separating out the hard core part of the interaction potential and treating the hard sphere reference fluid properties as given by independent methods, a modified version of the density field theory can be constructed. It was seen that the field theory requires correlation functions of the hard sphere fluid as the inputs. The results of the generalized van der Waals-type theory, and the random phase approximation of the Mayer cluster series method are recovered simply as the stationary-phase approximation, and the Gaussian fluctuation corrections.

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