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Calculations of free energies in liquid and solid phases: Fundamental measure density-functional approach

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In this paper, a theoretical description of the free energies and correlation functions of hard-sphere (HS) liquid and solid phases is developed using fundamental measure density-functional theory. Within the framework of Weeks-Chandler-Andersen perturbation theory, free energies of liquid and solid phases with many interaction potentials can be obtained from these characteristics of the HS system within a single theoretical description. An application to the Lennard-Jones system yields liquid-solid coexistence results in good agreement with the ones from simulations.

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I. INTRODUCTION

Free energy is an important thermodynamical characteristic of condensed matter systems. If the dependence of free-energy on temperature and the bulk density is known many other thermodynamic quantities of the system, such as chemical potential, pressure, compressibility, can be calculated. It also becomes possible to study phase behaviors, critical temperatures, interfacial properties, and so on.

Calculations of free energies using numerical experiments: Monte Carlo (MC) or molecular dynamics (MD) simulations yield accurate results, but still are time-consuming processes [1]. Perturbation theoretical approaches to the calculations of free energies in fluids [2–8] and solids [9,10] present an attractive alternative. One of the most reliable perturbation theories for free-energy calculations was developed by Weeks, Chandler, and Andersen (WCA) [2,3] for Lennard-Jones (LJ) fluid and was later generalized to fluids near the freezing line [8] and also to solids [9,10]. In the framework of WCA theory the free energy is separated into two contributions: one of them is the free energy of an appropriate reference system whereas the second one is the perturbative part. In general, a hard-sphere (HS) system with an appropriate HS diameter is chosen as the reference system, and the correlation function of that HS system is also utilized in the perturbation calculations. A recent version of WCA theory [10] allows to calculate the free energies both of liquid and of solid phase within a unified framework. It has been successfully applied to the free-energy calculations of liquid and solid phases with different types of intermolecular potentials [10–12]. In those studies properties of the HS reference system were obtained from MC or MD simulation results. For example, HS radial distribution functions of liquid and solid phases are parametrized using simulation data [9,11,13,14], so are the HS free energies of liquid and solid phases [15,16]. Such a strategy is quite successful for a single component system, but the parametrization of multicomponent systems will become extremely demanding and theoretical approaches, such as integral equations [17], do not yield accurate results as the simulations yet. In the present work we developed a unified theoretical approach of calculating the free energies of liquid and solid phases using a fundamental measure density-functional theory. Namely, we can obtain the properties of liquid and solid phases for a HS reference system within a single theoretical framework. At the same time, our approach can be generalized to multicomponent systems since the fundamental measure density-functional theory is known to provide accurate results for mixtures [18,19].

This paper is organized as following. The modified WCA perturbation theory for the free energies of liquid and solid phases is presented in Sec. II to set up the stage for our theoretical development. The fundamental measure density-functional theory is described in Sec. III and applied in Sec. IV to calculate the free energies and correlation functions of HS liquid and solid phases. The results of Sec. IV are used in Sec. V to compute the free energies of Lennard-Jones liquid and solid phases. Some conclusions are given in Sec. VI.

II. PERTURBATION THEORY FOR THE FREE ENERGIES OF LIQUID AND SOLID PHASES

In the framework of WCA perturbation theory, the intermolecular isotropic pair potential $V(r)$ is divided into two parts:

$$V(r) = V_0(r) + V_1(r), \tag{1}$$

where $V_0(r)$ is the short-ranged steeply repulsive part

$$V_0(r) = \begin{cases} V(r) - B(r), & r \leqslant \lambda \\ 0, & r > \lambda \end{cases} \tag{2}$$

and $V_1(r)$ the weaker long-ranged attractive part

$$V_1(r) = \begin{cases} B(r), & r \leqslant \lambda \\ V(r), & r > \lambda. \end{cases} \tag{3}$$

The first one is treated as a reference potential and second one as a perturbation. To treat liquid and solid phases on the same footing, the parameter λ is chosen as [10]

$$\lambda = r^* + s(\rho)(a_c - r^*). \tag{4}$$

Here r^* is the distance where the potential V has a minimum, a_c is the nearest-neighbors distance of the solid lattice and

$$s(\rho)=\begin{cases}0, & \rho\leqslant\rho_1\\ \dfrac{(\rho-\rho_1)^3[6\rho^2-3(5\rho_2-\rho_1)\rho+10\rho_2^2-5\rho_1\rho_2+\rho_1^2]}{(\rho_2-\rho_1)^5}, & \rho_1<\rho\leqslant\rho_2\\ 1, & \rho_2<\rho.\end{cases}\tag{5}$$

In this equation $\rho_1=0.97\rho_c$, $\rho_2=1.01\rho_c$, and ρ_c is the density where $r^*=a_c$. If $\rho\geqslant\rho_2$ (the solids) then Eqs. (4) and (5) give $\lambda=a_c$. If $\rho\leqslant\rho_1$ (the liquid case) this choice reduces to the WCA separation $\lambda=r^*$. At high densities near the freezing line an equilibrium nearest-neighbor separation will lie closer to $r=a_c$ rather than $r=r^*$ due to the strong repulsion of other molecules. Such a choice makes the range of $V_0(r)$ shrink with density. It reduces the corresponding HS diameter and allows to avoid difficulty associated with the metastable HS fluid.

The function $B(r)$ is equal to

$$B(r)=V(\lambda)-\left(\frac{dV(r)}{dr}\right)_{r=\lambda}(\lambda-r).\tag{6}$$

More details of the potential separation can be found in Ref. [10].

The free energy can be exactly expressed as [20]

$$F[\rho(\vec{r})]=F_0[\rho(\vec{r})]+\frac{1}{2}\int_0^1 d\alpha\int d\vec{r}_1 d\vec{r}_2 V_1(r_{12})\rho^{(2)}(\vec{r}_1,\vec{r}_2,\alpha).\tag{7}$$

$F_0[\rho(\vec{r})]$ is the free energy of the reference system ($\alpha=0$), and α is the coupling parameter for the interaction potential $V(r;\alpha)=V_0(r)+\alpha V_1(r)$. $\rho^{(2)}(\vec{r}_1,\vec{r}_2;\alpha)$ is the pair distribution function when the potential is $V(r_{12};\alpha)$ but the density is $\rho(\vec{r})$. To lowest order approximation, Eq. (7) yields

$$F[\rho(\vec{r})]=F_0[\rho(\vec{r})]+\frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 V_1(r_{12})\rho_0^{(2)}(\vec{r}_1,\vec{r}_2),\tag{8}$$

which can be also written as [21]

$$F[\rho(\vec{r})]/N=F_0[\rho(\vec{r})]/N+\frac{1}{2}\rho\int d\vec{r}V_1(r)\tilde{g}_0(r),\tag{9}$$

where N is the number of particles and $\tilde{g}_0(r_{12})$ the angle-averaged correlation function in the reference system

$$\tilde{g}_0(r_{12})=\frac{1}{4\pi V\rho^2}\int d\Omega\int d\vec{r}_1\rho_0^{(2)}(\vec{r}_1,\vec{r}_2).\tag{10}$$

In the WCA framework, the reference system is further approximated by a hard-sphere system with the intermolecular pair potential

$$V_{HS}(r)=\begin{cases}+\infty, & r\leqslant d\\ 0, & r>d,\end{cases}\tag{11}$$

where d is a temperature dependent hard-sphere diameter since a lot of information about the HS system was collected from theoretical treatments and numerical experiments [17].

To approximate the reference system with the intermolecular potential $V_0(r)$ by a HS system, the hard-sphere diameter d is chosen to satisfy the equation (2)

$$\int d\vec{r}(e^{-\beta V_0(r)}-e^{-\beta V_{HS}(r)})y_{HS}(r/d)=0,\tag{12}$$

where $\beta=1/k_BT$ (k_B is the Boltzmann constant, T temperature), y_{HS} is the cavity function [11,22] of the HS system. With such a choice of HS diameter, the reference system F_0 and $\tilde{g}_0$ are related to the ones of the HS system as: $F_0=F_{HS}+O(\delta^2)$ and $\tilde{g}_0=\tilde{g}_{HS}+O(\delta)$. The small parameter δ is equal to

$$\delta=\int_0^\lambda dr\left(\frac{r}{d_B}-1\right)^2\frac{d}{dr}e^{-\beta V_0(r)},\tag{13}$$

and

$$d_B=\int_0^\lambda dr(1-e^{-\beta V_0(r)})\tag{14}$$

is the Barker-Henderson diameter [4].

Instead of Eq. (12) we will use a fast and accurate but approximate way of solving for d with help of the formula (13),

$$d=d_B\left(1+\frac{\sigma_1}{2\sigma_0}\delta\right),\tag{15}$$

where

$$\sigma_0=y_{HS}(r=d),\tag{16}$$

$$\sigma_1=2\sigma_0+[dy_{HS}/dx]|_{x=r/d=1}\tag{17}$$

[Eq. (15) is obtained from Eq. (12) as an expansion on the small parameter δ [13] by neglecting the extremely small high-order term of $\int_0^\lambda dr(r/d_B-1)^3 de^{-\beta V_0(r)}/dr$; for example, for Lennard-Jones system with temperatures $T^*=0.75, 2.74$ this term is 10^{-7} *and* 10^{-5} respectively].

Using the above equations, we finally have

$$F[\rho(\vec{r})]/N=F_{HS}[\rho(\vec{r})]/N+\frac{1}{2}\rho\int d\vec{r}V_1(r)\tilde{g}_{HS}(r/d).\tag{18}$$

To yield accurate results of the free energy in Eq. (18), the HS free energy F_{HS} and correlation function $\tilde{g}_{HS}$ for liquid and solid phases are obtained from simulations. In this work we will get the properties of the HS reference system by using a theoretical approach rather than numerical simulations. Namely, we will use fundamental measure density functional to calculate the free energies and correlation functions of both liquid and solid phases within a single framework.

III. FUNDAMENTAL MEASURE DENSITY-FUNCTIONAL THEORY

The density-functional theory (DFT) is a powerful tool for studying the properties of fluids and solids (see review of Evans [20]). In the framework of DFT, the hard-sphere free energy F_{HS} is considered as a functional of number density profile $\rho(\vec{r})$. It consists of two parts: an ideal-gas contribution $F_{id}[\rho]$ and the excess free energy $F_{ex}[\rho]$ over the ideal-gas part

$$F_{HS}[\rho(\vec{r})] = F_{id}[\rho(\vec{r})] + F_{ex}[\rho(\vec{r})], \tag{19}$$

where

$$F_{id}[\rho(\vec{r})] = k_B T \int dV \rho(\vec{r})(\ln[\rho(\vec{r})] - 1). \tag{20}$$

[In this work, the $k_B TN \ln(\Lambda^3)$ and $k_B T \ln(\Lambda^3)$ contribution to the free energy and chemical potential respectively are neglected since they do not affect our results besides a temperature dependent constant. Λ is the thermal de Broglie wavelength.]

The grand canonical potential functional Ω_{HS} can also be constructed

$$\Omega_{HS}[\rho(\vec{r})] = F_{HS}[\rho(\vec{r})] - \int d\vec{r}[\mu\rho(\vec{r}) - U(\vec{r})], \tag{21}$$

where μ is chemical potential, $U(\vec{r})$ is the external potential. The variational principle

$$\left.\frac{\delta\Omega_{HS}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right|_{\mu} = 0 \tag{22}$$

determines the equation for the equilibrium density profile in an external potential.

Various approximations to the density functional have been proposed [23–27] to construct the excess free energy F_{ex} for the HS system. In our study we will apply the fundamental measure (FM) density functional proposed by Rosenfeld [28] and extended by many others [19,29–31]. Below we list the main equations of FMT for one-component HS system used in this work.

First of all a set of weighted densities is defined

$$n_\alpha(\vec{r}) = \int d\vec{r}\,'\rho(\vec{r}\,')\omega_\alpha(\vec{r} - \vec{r}\,') \tag{23}$$

with the density-independent weight functions ω_α given by

$$\omega_2(y) = \delta\left(\frac{d}{2} - y\right), \tag{24}$$

$$\omega_3(y) = \Theta\left(\frac{d}{2} - y\right), \tag{25}$$

$$\vec{\omega}_{v_2}(\vec{y}) = \vec{e}_y\delta\left(\frac{d}{2} - y\right), \tag{26}$$

$$\hat{\omega}(\vec{y}) = \vec{e}_y\vec{e}_y\delta\left(\frac{d}{2} - y\right). \tag{27}$$

Here, $\vec{e}_y$ is a unit vector along the $\vec{y}$ direction, $\Theta(r)$ the Heaviside step function, $\delta(r)$ the Dirac delta function, and $\vec{\omega}_{v_2}$ and $\hat{\omega}$ are the vector and tensor weighted densities, respectively.

The excess part of the free energy can be written in the following form:

$$\beta F_{ex} = \sum_{i=1}^{3} \int d\vec{r}\Phi_i\{n_\alpha(\vec{r})\}, \tag{28}$$

where

$$\Phi_1 = \frac{n_2}{\pi d^2}\ln(1 - n_3), \tag{29}$$

$$\Phi_2 = \frac{n_2^2 - n_{v_2}^2}{2\pi d(1 - n_3)}, \tag{30}$$

and

$$\Phi_3 = f_3\phi_3(n_3). \tag{31}$$

Various approximations of FMT employed different functions f_3 and ϕ_3 in Eq. (31).

The first approximation of f_3 and ϕ_3 was given by Rosenfeld [28]:

$$f_3^{(V1)} = \frac{n_2^3 - 3n_2 n_{v_2}^2}{24\pi} \tag{32}$$

and

$$\phi_3^{(PY)} = \frac{1}{(1 - n_3)^2}, \tag{33}$$

and we will denote this version of the theory as $V1PY$.

In the homogeneous limit the functional Eqs. (28)–(33) recover the Percus-Yevick excess free-energy density. Functional derivative of the F_{ex} in the homogeneous limit yields the PY pair distribution function. In the 1D limit (hard rods) it reproduced the exact density functional of 1D system. Although the functional is successful for the description of liquids it completely failed to describe liquid-solid coexistence. The problem was overcome partially in Ref. [29] with the introduction

$$f_3^{(V2)} = \frac{(n_2^2 - n_{v_2}^2)^3}{24\pi n_2^3} \tag{34}$$

(denoted as $V2PY$). A systematic way to improve the Rosenfeld functional lies in the fact that in the $0D$ limit (a spherical cavity holds no more than one particle) the excess free-energy functional should satisfy exactly known solution, which is crucial to describe solids. Using this dimensional crossover argument, a new version (denoted as $T1PY$) [30] using

$$f_3^{(T1)} = \frac{9}{16\pi}\det\hat{n}, \tag{35}$$

and a variation (denoted as $T2PY$) [31] with

$$f_3^{(T2)} = \frac{3}{16\pi}[\vec{n}_{v_2}\hat{n}\vec{n}_{v_2} - n_2\vec{n}_{v_2}^2 - tr(\hat{n}^3) + n_2 tr(\hat{n}^2)] \tag{36}$$

can be used to describe many properties of HS solids. For example, the version with $\Phi_3 = f_3^{(T2)}\phi_3^{(PY)}$ ($T2PY$) yields correct asymptotics for the HS fcc lattice near close packing density and even can be used to describe the metastable HS bcc lattice [31].

The Φ_3 contribution can also be improved to describe the fluid phase better, namely, in the limit of bulk density the Carnahan-Starling (CS) equation of fluid state should be reproduced rather than the PY equation of state. Recently [19,32,33] this has been achieved by the introduction of

$$\phi_3^{(CS)} = \frac{2}{3} \times \frac{1}{n_3^2}\left(\frac{n_3}{(1-n_3)^2} + \ln(1-n_3)\right). \tag{37}$$

A combination of this function with $f_3^{(T2)}$ yields a new version of functional, $\Phi_3 = f_3^{(T2)}\phi_3^{(CS)}$ (denoted as $T2CS$) was discussed in detail [19,33]. For instance $T2CS$ version of FMT gave the best values of the coexisting HS liquid and solid densities. This is the version that we will use to compute properties of HS liquid and solid phases. Some details of calculations of the weighted densities $\{n_\alpha\}$ can be found in Appendix A.

IV. PROPERTIES OF LIQUID AND SOLID PHASES OF THE HARD-SPHERE SYSTEM

A. Free energies and correlation functions of HS solids

In a solid the density profile can be approximated as a sum of identical Gaussian peaks centered at the lattice sites $\vec{R}_i$,

$$\rho(\vec{r}) = \sum_i \rho_\Delta(\vec{r} - \vec{R}_i) = \left(\frac{\alpha}{\pi}\right)^{3/2}\sum_i e^{-\alpha(\vec{r}-\vec{R}_i)^2}. \tag{38}$$

Given the weighted functions in Sec. III the weighted density can be written as

$$n_\alpha(\vec{r}) = \sum_i n_\Delta^{(\alpha)}(\vec{r} - \vec{R}_i). \tag{39}$$

Moreover, the scalar, vector, and tensor weighted densities $n_\Delta^{(\alpha)}(\vec{r})$ can be found in analytical forms (see Appendix B).

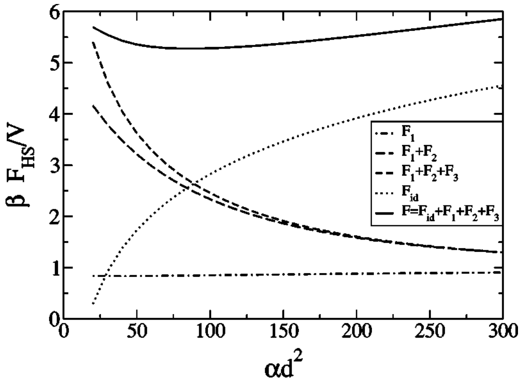

FIG. 1. Contributions of different terms in the free-energy functional to the free-energy density $\beta F_{HS}/V$ at $\rho d^3 = 1.05$ using $T2CS$.

For the fcc solid phase of a HS system, using the symmetry of the crystal the volume of integration can be reduced to a simplex corresponding to $1/48$ of the unit cell [34]. The contributions from all 13 sites of the unit cell (for fcc lattice) to the total weighted densities can be calculated. For a given bulk density the functional dependence of the solid free energy on the Gaussian parameter α of density distribution [Eq. (38)] was plotted in Fig. 1. The minimum of this function gives the equilibrium values of free energy and parameter α. Figure 1 illustrates the different contributions from the dependence of $\beta F_{HS}/V$ on α for $\rho d^3 = 1.05$ (where $F_i = \int d\vec{r}\Phi_i$, $i = 1, 2, 3$). For all versions of FMT except $V1PY$, Fig. 1 is qualitatively the same.

The dependence of equilibrium free energy $\beta F_{HS}/N$ on the densities ρd^3 is shown in Fig. 2. The calculated results are in excellent agreement with MC simulations [16].

The correlation function can be calculated using the approach of Rascon *et al.* [35,36]. In contrast to liquid phase, the structural properties of a solid phase is mainly determined by one particle density $\rho(\vec{r})$. Let $\rho(\vec{r}_2)$ be the density probability of finding a particle at $\vec{r}_2$ without fixing any other particles. The probability density of finding a second particle at $\vec{r}_2$ provided the first particle is already fixed at $\vec{r}_1$ is equal to $\rho^{(2)}(\vec{r}_1, \vec{r}_2)/\rho(\vec{r}_1)$. Thus, two angular average probability densities can be defined

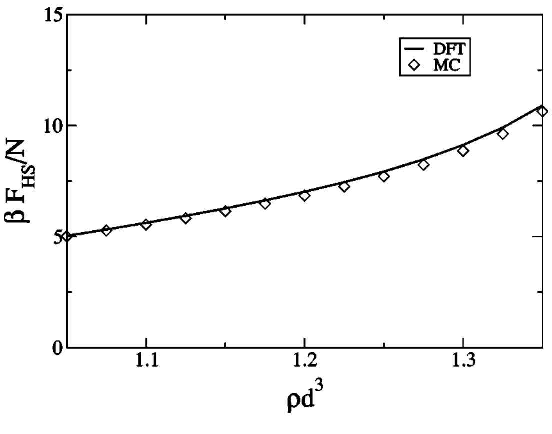

FIG. 2. Dependence of the free-energy density $\beta F_{HS}/N$ on ρd^3. Results of the present theory ($T2CS$) are plotted as a solid line, MC simulation results [16] as diamonds.

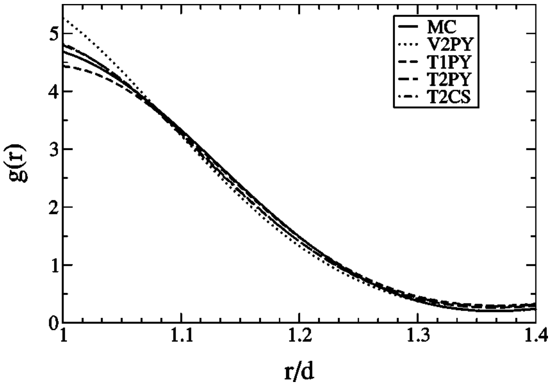

FIG. 3. Details of the first peak of the pair distribution function $\tilde{g}(r)$ for the solid at $\rho d^3 = 1.04$ for MC simulation results [11] and different versions of the fundamental measure density-functional theory (DFT).

$$\tilde{g}^{(0)}(r) = \frac{1}{4\pi V\rho^2}\int d\vec{r}_1 d\Omega \rho(\vec{r}_1)\rho(\vec{r}_1+\vec{r}), \qquad (40)$$

and

$$\tilde{g}(r) = \frac{1}{4\pi V\rho^2}\int d\vec{r}_1 d\Omega \rho^{(2)}(\vec{r}_1,\vec{r}_1+\vec{r}), \qquad (41)$$

where $\tilde{g}^{(0)}(r)$ is the correlation function when the particle at the origin is not fixed and $\tilde{g}(r)$ is the correlation function, which describes the structure of solid in the "external" field of the particle fixed at the origin. It can be shown that the function $\tilde{g}(r)$ should be used for the perturbation calculations of the free energy in Eq. (18) [21].

Putting Eq. (38) into Eq. (40), the correlation function $\tilde{g}^{(0)}$ can be reduced to the sum of contributions $\tilde{g}_i^{(0)}$ from the successive peaks of lattice sites [35]

$$\tilde{g}_i^{(0)}(r) = \frac{n_i}{4\pi\rho R_i}\left(\frac{\alpha}{2\pi}\right)^{1/2}\frac{e^{-\alpha(r-R_i)^2/2}+e^{-\alpha(r+R_i)^2/2}}{r} \qquad (i>0), \qquad (42)$$

where n_i is the coordination number of shell i and R_i being the corresponding radius. Rascon *et al.* [35,36] showed that for small value of compressibility $\chi_T = (\partial\rho/\partial(\beta P))_T$ (which is the case for HS solids) the successive peaks of $\tilde{g}(r)$ differ negligibly from the ones of $\tilde{g}^{(0)}(r)$ except the first peak with $i=1$, thus,

$$\tilde{g}(r) = \tilde{g}_1(r) + \sum_{i\geqslant 2}\tilde{g}_i^{(0)}(r). \qquad (43)$$

The first peak of $\tilde{g}(r)$ (denoted as $\tilde{g}_1$) is due to the nearest neighbors which bear the most important part of the short-range correlations and can be parametrized as [35]

$$\tilde{g}_1(r) = A\frac{e^{-\alpha_1(r-r_1)^2/2}}{r}, \qquad (44)$$

where the parameters A, α_1, and r_1 can be found from the sum rules conditions given below.

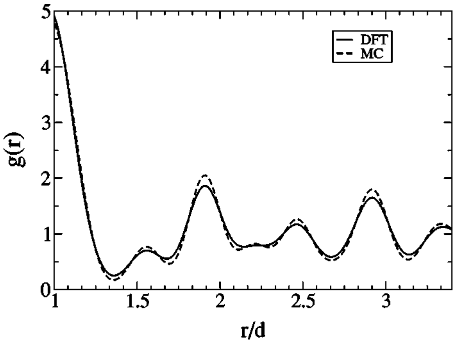

FIG. 4. Pair distribution function $\tilde{g}(r)$ for the solid at $\rho d^3 = 1.05$. The solid line corresponds to the result of the present theory. The dashed line is the Monte Carlo results [11].

(1) Virial theorem:

$$\beta P/\rho = 1 + 4\pi\tilde{g}(d_{HS}). \qquad (45)$$

(2) The normalization of $\tilde{g}_1$ to the nearest-neighbors number:

$$\frac{1}{n_1}\int d\vec{r}\rho\tilde{g}_1(r) = 1. \qquad (46)$$

(3) The mean location of the nearest neighbors $\langle r\rangle$:

$$\langle r\rangle \equiv \frac{1}{n_1}\int d\vec{r}r\rho\tilde{g}_1(r) = \frac{1}{n_1}\int d\vec{r}r\rho\tilde{g}_1^{(0)}(r). \qquad (47)$$

Using the already found dependence of pressure P and α on the density ρ in the equations above all the successive peaks of $\tilde{g}(r)$ can be obtained.

We have calculated the correlation functions using the different versions of the fundamental measure density-functional theory. It is found (see Fig. 3) that the results of the $T2$ versions of the theory gave the best agreement between the contact value of the correlation functions from our calculation and MC simulations [11]. Thus, we are mostly interested in the $T2CS$ version of the theory since it gives the best liquid and solid properties. For this version the resulting correlation functions agree very well with the MC results [11] for the various densities (Figs 4 and 5). (For the low densities the compressibility χ_T gets higher and, thus, the sum rule [Eq. (47)] gets less accurate [36]; as a result near melting density the agreements get a bit worse. There are

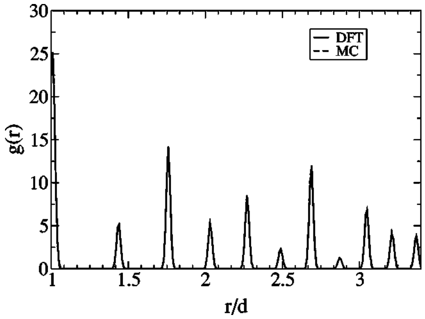

FIG. 5. The same as Fig. 4 except $\rho d^3 = 1.35$.

also no significant differences also if any other DFT approaches are used.) Thus, all of our later calculations will be based upon the *T2CS* version of the DFT theory.

B. Correlation functions in HS liquid

In the homogeneous limit the *T2CS* version of the FM functional reduces to the CS free energy [15],

$$\beta F_{HS}/N = \ln(\rho d^3) - 1 + \frac{\eta(4-3\eta)}{(1-\eta)^2}, \tag{48}$$

where $\eta=(\pi/6)\rho d^3$ is the packing fraction.

To describe the HS liquid structure we note that in a liquid phase the density profile $\rho(\vec{r}_2)$ seen from the origin is just the bulk density ρ. Fixing a test particle at the origin leads to the short-ranged density profile [37] $\rho^{(2)}(\vec{r}_1,\vec{r}_1+\vec{r})/\rho=\rho g(r)$. It can be seen from Eqs. (40) and (41) that in the homogeneous limit the correlation function $\tilde{g}^{(0)}(r)$ and $\tilde{g}(r)$ in solid reduce to 1 and $g(r)$, respectively. Hence the pair distribution function in a liquid $g(r)$ is equal to the density distribution $\rho(r)$ of particles in the external potential created by the test particle fixed at the origin divided by the bulk density ρ [37],

$$g(r) = \rho(r)/\rho. \tag{49}$$

The density distribution $\rho(r)$ can be calculated from the solution of the integral equation obtained from the variational principle for the grand canonical potential Ω_{HS}, Eqs. (19)–(22) and (28)

$$\rho(r) = \exp\{-\delta\beta F^{(ex)}[\rho(\vec{r})]/\delta\rho(\vec{r}) + \beta(\mu - U(r))\} \tag{50}$$

with

$$\beta\mu = \ln(\rho d^3) + \eta\frac{(8-9\eta+3\eta^2)}{(1-\eta)^3} \tag{51}$$

and $U(r)=V_{HS}(r)$.

Note that similar equation as Eq. (50) was used in Ref. [32], but for a different version of the Rosenfeld functional, namely for one with $\Phi_3=f_3^{(V1)}\phi_3^{(CS)}$ (version *V1CS*). The details for the calculation of $\delta\beta F^{(ex)}/\delta\rho(\vec{r})$ in Eq. (50) can be found in Appendix C.

This integral equation (50) can be solved by the iteration method, i.e., at its *i*-step

$$\rho_{in}^{(i+1)} = \rho_{out}^{(i)} = \hat{A}\rho_{in}^{(i)}, \tag{52}$$

where $\hat{A}$ is the integral operator on the right-hand side of Eq. (50). There is a problem for the convergence of the method, namely the weighted function $n_3(r)$ at the small r is higher than 1, a signature that Φ_1 term is an approximation in three dimension. To avoid this we used a mixing scheme,

$$\rho_{in}^{(i+1)} = \kappa\rho_{out}^{(i)} + (1-\kappa)\rho_{in}^{(i)}, \tag{53}$$

with the small mixing parameter κ, which depends on the bulk density. To speed up drastically the convergency of iterations Eqs. (50), (51), and (53), we developed the special optimization method. We have found that the correlation functions $g(r)$ from the *V1CS* and *T2CS* versions of FMT for low densities ρd^3 are almost the same, with the some difference arisen for the high densities. It is also seen from Fig. 6 that for all the densities that the DFT correlation functions are in excellent agreement with the MC results of Verlet-Weis [13] (for the high density $\rho d^3=1.0$ the agreements get a bit worse).

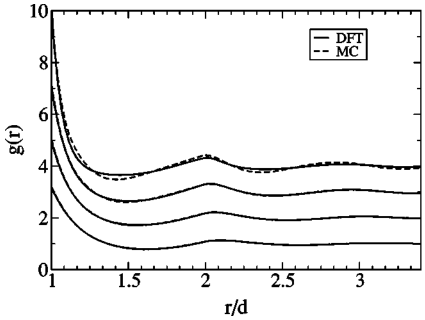

FIG. 6. Pair distribution function $g(r)$ of liquid at densities $\rho d^3=0.7,0.8,0.9,1.0$. The solid line is the result of our theory, the dashed line is the result of MC simulations [13]. For clarity, curves for $\rho d^3=0.8,0.9,1.0$ are shifted upwards by 1,2,3, accordingly.

The pair direct correlation function $c^{(2)}$ in liquids can also be obtained as the second functional derivative of the excess free energy in the homogeneous limit. Since the present functional employs the weight functions of FMT based on one center convolutions it cannot accounts for the decaying tail of $c^{(2)}(r)$ in the region $r>d$. As a result the function $g(r)$ obtained from $c^{(2)}(r)$ via the Ornstein-Zernike equation does not yield results which are in good agrement with the simulations. Possible improvement of the theory requires the inclusion of the two-centers convolutions [19,33].

V. LENNARD-JONES LIQUID AND SOLID COEXISTENCE

In this section we will apply our method to a simple model system with the Lennard-Jones (LJ) intermolecular potential, whose liquid-solid coexistence behaviors are well known from simulations,

$$V_{LJ}(r) = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right), \tag{54}$$

where ϵ and σ are the energy and length parameters of the LJ potential.

Using the correlation functions of the reference HS solid and liquid from the DFT calculations the iterative solution of the equation for the HS diameter d [Eq. (15)] can be found. For some given temperatures $T^*=k_BT/\epsilon=0.75,2.74$ and various liquid and solid densities $\rho^*=\rho\sigma^3$ the free energies $\beta F^{(ex)}/N=\beta F/N-\ln(\rho d^3)+1$ both in liquid and solid phases were obtained with the help of Eq. (18). Some of the results are given in Table I and they are in excellent agreements with the results of MC simulations [8,10].

At the fixed temperature T the coexistence of solid and liquid phases required the equality of the chemical potentials μ and pressures P in the both phases. The coexisting liquid ρ_l^* and solid ρ_s^* densities can be calculated using the Maxwell double-tangent construction, i.e., the condition when

TABLE I. Excess (with respect to an ideal gas at the same temperature and density) free energy per particle $\beta F^{(ex)}/N$ for the Lennard-Jones system obtained from MC simulations [8,10] and the present theory. Values of the HS packing fraction $\eta = (\pi/6\rho d^3)$ obtained in this work are also given.

	$\beta F^{(ex)}/N$ MC simulations	$\beta F^{(ex)}/N$ This work	η
$T^*=0.75$			
Liquid			
0.7	−4.17	−4.15	0.393
0.8	−4.47	−4.45	0.448
0.84	−4.53	−4.50	0.469
Solid			
1.0	−4.48	−4.52	0.566
1.025	−4.41	−4.47	0.574
1.1	−4.17	−4.11	0.595
$T^*=2.74$			
Liquid			
0.2	−0.04	−0.03	0.098
0.4	−0.01	0.005	0.194
0.7	0.38	0.36	0.337
0.8	0.65	0.63	0.384
0.9	1.05	1.02	0.429
1.0	1.58	1.56	0.473
1.1	2.31	2.27	0.504
Solid			
1.2	3.138	3.162	0.541
1.3	4.074	4.052	0.564
1.4	5.31	5.19	0.584
1.6	9.01	9.04	0.620
1.8	14.91	14.95	0.643
2.0	23.74	23.79	0.660
2.4	53.63	53.69	0.684

$\beta F_{solid}/N$ and $\beta F_{liquid}/N$ plotted versus the inverse densities $\rho\sigma^3$ have a common tangent. For $T^*=0.75$ we found that the coexisting densities and the Lindermann ratio are $\rho_s^*=0.959$, $\rho_l^*=0.860$ and 0.13; and for $T^*=2.74$, $\rho_s^*=1.214$, $\rho_l^*=1.155$ and 0.12, which are very close to the results obtained by MC simulations [38] $\rho_s^*=0.973$, $\rho_l^*=0.875$, 0.15 and $\rho_s^*=1.179$, $\rho_l^*=1.113$, 0.14 respectively. If different theories would be applied to compute $\beta F_{liquid}/N$ and $\beta F_{solid}/N$ the differences in the models could affect significantly on the results of coexisting densities. In our present approach the solid and liquid free energies are obtained within a single theoretical framework, thus, such errors are avoided.

VI. CONCLUSIONS

In the present study we have developed a theory to calculate the free energies of liquid and solid phases within a single theoretical framework. To this end the fundamental measure DFT was applied to the theoretical calculations of the free energies and correlation functions in HS liquid and solid phases. These properties of the HS systems were used in the WCA perturbation theory to calculate the free energies both in solid and liquid phases of the Lennard-Jones system. The obtained results are in a good agreement with simulations.

The present study can be extended along several directions. For example, such a approach can be used to compute phase behaviors of simple metallic systems [12] and also of the multicomponent mixture (alloy) systems [39]. Another possible application of this approach is the theoretical description of the solid-melting interface [40,41] of the different substances.

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APPENDIX A: WEIGHTED DENSITIES IN THE LIQUID

At Appendixes A and B we summarize some properties of the weighted densities (part of them was provided already somewhere [29,34]) and also we will give some new details of calculations.

To transform the expression for the weighted densities [Eq. (23)] the vector $\vec{y}=\vec{r}-\vec{r}'$ can be introduced and $y^2=|\vec{r}-\vec{r}'|^2=r^2+r'^2-2rr'\cos\theta$ (θ is the angle between the vectors $\vec{r}$ and $\vec{r}'$). With the fixed $r=|\vec{r}|$ and $r'=|\vec{r}'|$ it follows that $|r-r'|\leqslant y\leqslant r+r'$ and $r'\sin\theta d\theta=1/r\, ydy$ ($y=|\vec{y}|$). Using this the three-dimensional integral reduces to two one-dimensional integrals

$$n_\alpha(\vec{r})=\frac{2\pi}{r}\int_0^{+\infty} r'dr'\rho(\vec{r}')\int_{|r-r'|}^{r+r'}\omega_\alpha(\vec{y})ydy. \qquad \text{(A1)}$$

Using the Rosenfeld expressions for the scalar, vector, and tensor weight functions [Eqs. (24)–(27)] all the interested weighted densities can be found. Such, the scalar weighted densities n_2 and n_3 reduce to one-dimensional integrals

$$n_2(r)=\frac{\pi d}{r}\int_{|r-d/2|}^{r+d/2} dr'r'\rho(r') \qquad \text{(A2)}$$

and

$$n_3(r)=\frac{\pi}{r}\int_{|r-d/2|}^{r+d/2} dr'r'\left[\frac{d^2}{4}-(r-r')^2\right]\rho(r') + \Theta\left(\frac{d}{2}-r\right)4\pi\int_0^{d/2-r} dr'r'^2\rho(r'). \qquad \text{(A3)}$$

To transform the expressions for vector and tensor densities we write

$$\vec{e}_y = \cos \tilde{\theta} \vec{e}_r + \sin \tilde{\theta} \vec{e}_\perp \tag{A4}$$

($\tilde{\theta}$ is the angle between the vectors $\vec{r}$ and $\vec{y}$; $\vec{e}_r$ and $\vec{e}_\perp$ the unit vectors to be parallel and perpendicular to the $\vec{r}$ direction). Using $r'^2 = |\vec{r}-\vec{y}|^2 = r^2 + y^2 - 2ry \cos\tilde{\theta}$ we find that

$$\cos\tilde{\theta} = \frac{y^2 + r^2 - r'^2}{2ry},$$

$$\sin\tilde{\theta} = \frac{[4r^2r'^2 - (y^2 - r^2 - r'^2)^2]^{1/2}}{2ry}. \tag{A5}$$

Finally, putting Eqs. (26), (27), and (A5) into Eq. (A1) the vector $\vec{n}_{v_2}$ and tensor $\hat{n}$ weighted densities can be found as

$$\vec{n}_{v_2}(\vec{r}) = n_{v_2}(r)\vec{e}_3,$$

$$\hat{n}(\vec{r}) = \sum_{i=1}^{3} \hat{n}_{ii}(\vec{r}) = \sum_{i=1}^{3} n_{ii}(r)\vec{e}_i\vec{e}_i, \tag{A6}$$

where $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ are the unit orthogonal vectors ($\vec{e}_3 = \vec{e}_r$) and

$$n_{v_2}(r) = \frac{\pi}{r^2}\int_{|r-d/2|}^{r+d/2} dr' r' \left(r^2 - r'^2 + \frac{d^2}{4} \right) \rho(r'), \tag{A7}$$

$$n_{11}(r) = n_{22}(r) = \frac{\pi}{2r^3 d}\int_{|r-d/2|}^{r+d/2} dr' r' \times \left[4r^2 r'^2 - \left(\frac{d^2}{4} - r'^2 - r^2 \right)^2 \right] \rho(r'), \tag{A8}$$

$$n_{33}(r) = \frac{\pi}{r^3 d}\int_{|r-d/2|}^{r+d/2} dr' r' \left(\frac{d^2}{4} - r'^2 + r^2 \right)^2 \rho(r'). \tag{A9}$$

From Eqs. (23)–(27) the relations,

$$\vec{n}_{v_2}(\vec{r}) = -\vec{\nabla} n_3(r), \tag{A10}$$

$$tr(\hat{n}(\vec{r})) = n_2(r), \tag{A11}$$

also follow, which are useful to check the results.

In the bulk with $\rho(\vec{r}) = \rho$ the expressions Eqs. (A2), (A3), and (A7)–(A9) reduce just to

$$n_2 = \pi\rho d^2, \quad n_3 = \frac{\pi}{6}\rho d^3, \quad n_{v_2} = 0, \quad n_{ij} = \frac{\pi}{3}\rho d^2 \delta_{ij}. \tag{A12}$$

APPENDIX B: WEIGHTED DENSITIES IN SOLID

When the density $\rho(r)$ is given by the Gaussian distribution around the zero $\rho_\Delta(r) = (\alpha/\pi)^{3/2}\exp(-\alpha r^2)$ the corresponding weighted densities can be found analytically from Eqs. (A2), (A3), and (A6)–(A11),

$$n_\Delta^{(2)}(r) = \frac{d}{2r}\sqrt{\frac{\alpha}{\pi}}\left(e^{-\alpha(d/2-r)^2} - e^{-\alpha(d/2+r)^2}\right), \tag{B1}$$

$$n_\Delta^{(3)}(r) = \frac{1}{2}\left[erf\left[\sqrt{\alpha}\left(\frac{d}{2} + r \right) \right] + erf\left[\sqrt{\alpha}\left(\frac{d}{2} - r \right) \right] + \frac{e^{-\alpha(d/2-r)^2} - e^{-\alpha(d/2+r)^2}}{r\sqrt{\alpha\pi}} \right], \tag{B2}$$

$$n_\Delta^{(v_2)}(r) = \left(\frac{1 + e^{-2\alpha r d}}{1 - e^{-2\alpha r d}} - \frac{1}{\alpha r d} \right) n_\Delta^{(2)}(r), \tag{B3}$$

$$n_\Delta^{(11)}(r) = n_\Delta^{(22)}(r) = \frac{n_\Delta^{(v_2)}(r)}{\alpha d r},$$

$$n_\Delta^{(33)}(r) = n_\Delta^{(2)}(r) - \frac{2n_\Delta^{(v_2)}(r)}{\alpha d r}. \tag{B4}$$

The total scalar, vector, and tensor weighted densities are the sum of the contributions from the different lattice sites [Eq. (39)], moreover, the vector and tensor contributions must be transformed to a common reference frame. To this end we introduce the laboratory-fixed frame $(\vec{e}_x, \vec{e}_y, \vec{e}_z)$ related to the crystal lattice planes. As a result the three position $(\vec{r})$ dependent vectors $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ in Eq. (A6) can be transformed as

$$\vec{e}_i(\vec{r}) = \sum_{\alpha'} a_{i,\alpha'}(r)\vec{e}_{\alpha'} \quad (i = 1,2,3; \alpha' = x,y,z) \tag{B5}$$

with the transformation matrix [42]

$$A = \{a_{i,\alpha'}(r)\} = \begin{pmatrix} -\dfrac{y}{\rho} & \dfrac{x}{\rho} & 0 \\ -\dfrac{xz}{\rho r} & -\dfrac{yz}{\rho r} & \dfrac{\rho}{r} \\ \dfrac{x}{r} & \dfrac{y}{r} & \dfrac{z}{r} \end{pmatrix}, \tag{B6}$$

where $\rho = (x^2 + y^2)^{1/2}$.

Finally, in the reference frame the contributions from one lattice site to vector and tensor densities with help of Eqs. (A6) and (B3)–(B6) are given by the expressions

$$\vec{n}_\Delta^{(v_2)}(\vec{r}) = n_\Delta^{(v_2)}(r)\vec{e}_3(\vec{r}) = \sum_{\alpha'} n_\Delta^{(v_2)}(r) a_{3,\alpha'}(r)\vec{e}_{\alpha'}, \tag{B7}$$

$$\hat{n}_\Delta(\vec{r}) = \sum_{i=1}^{3} n_\Delta^{(ii)}(r)\vec{e}_i(\vec{r})\vec{e}_i(\vec{r}) = \sum_{i=1}^{3}\sum_{\alpha',\beta'} n_\Delta^{(ii)}(r) a_{i,\alpha'}(r) a_{i,\beta'}(r)\vec{e}_{\alpha'}\vec{e}_{\beta'}. \tag{B8}$$

APPENDIX C: CALCULATION OF $\delta\beta F^{(ex)}/\delta\rho(\vec{r})$

In this Appendix C we calculate $\delta\beta F^{(ex)}/\delta\rho(\vec{r})$ which arises in Eq. (50). It can be rewritten as

$$\delta\beta F^{(ex)}[\rho(\vec{r}\,)]/\delta\rho(\vec{r}) = \sum_{\alpha} \mathsf{F}_{\alpha}(\vec{r}\,), \tag{C1}$$

where

$$\mathsf{F}_{\alpha}(\vec{r}) = \int d\vec{r}\,' \frac{\delta\Phi}{\delta n_{\alpha}(\vec{r}\,')} \omega_{\alpha}(\vec{r} - \vec{r}\,'). \tag{C2}$$

So, the problem reduces to the calculation of every $\mathsf{F}_{\alpha}(\vec{r}\,)$. To do this, first of all the expression

$$\mathsf{F}_{\alpha}(\vec{r}\,) = \frac{2\pi}{r} \int_{0}^{+\infty} r'dr' \frac{\delta\Phi}{\delta n_{\alpha}(\vec{r}\,')} \int_{|r-r'|}^{r+r'} \omega_{\alpha}(\vec{y}\,) y dy \tag{C3}$$

can be obtained from Eq. (C2) by the same way as Eq. (23) was transformed to Eq. (A1).

For the scalar weight functions with $\alpha = 2,3$ Eqs. (A2) and (A3) can be utilized for $\mathsf{F}_2(r)$, $\mathsf{F}_3(r)$ [in this equations the functions $\delta\Phi/\delta n_2(r')$ or $\delta\Phi/\delta n_3(r')$ should be substituted instead $\rho(r')$].

To calculate the rest of the functions $\mathsf{F}(r)$ we write

$$\frac{\delta\Phi}{\delta\vec{n}_{v_2}(\vec{r}\,')} = \frac{\delta\Phi}{\delta n_{v_2}(r')} \vec{e}\,'_3, \tag{C4}$$

$$\frac{\delta\Phi}{\delta\hat{n}_{ii}(\vec{r}\,')} = \frac{\delta\Phi}{\delta n_{ii}(r')} \vec{e}\,'_i \vec{e}\,'_i \quad (i = 1,2,3), \tag{C5}$$

where $\vec{e}\,'_1$, $\vec{e}\,'_2$, and $\vec{e}\,'_3$ are the unit orthogonal vectors ($\vec{e}\,'_3$ is directed along the vector $\vec{r}\,'$).

Next, as it was done at Eqs. (A4) and (A5) the vector $\vec{e}_y$ can be written as

$$\vec{e}_y = \cos\tilde{\theta}' \vec{e}\,'_3 + \sin\tilde{\theta}' \vec{e}\,'_{\perp} \tag{C6}$$

($\tilde{\theta}'$ is angle between the vectors $\vec{y}$ and $\vec{r}\,'$), and the expressions

$$\cos\hat{\theta}' = \frac{y^2 + r'^2 - r^2}{2r'y},$$

$$\sin\hat{\theta}' = \frac{[4r^2r'^2 - (y^2 - r'^2 - r^2)^2]^{1/2}}{2r'y} \tag{C7}$$

can be found.

Finally, putting Eqs. (26), (27), and (C4)–(C7) into Eq. (C3) we have

$$\mathsf{F}_{v_2}(r) = \frac{\pi}{r} \int_{|r-d/2|}^{r+d/2} dr' \left(\frac{d^2}{4} + r'^2 - r^2\right) \frac{\delta\Phi}{\delta n_{v_2}(r')}, \tag{C8}$$

$$\mathsf{F}_{ii}(r) = \frac{\pi}{2rd} \int_{|r-d/2|}^{r+d/2} dr' \frac{1}{r'} \left[4r^2r'^2 - \left(\frac{d^2}{4} - r'^2 - r^2\right)^2\right] \times \frac{\delta\Phi}{\delta n_{ii}(r')} \quad (i = 1,2) \tag{C9}$$

and

$$\mathsf{F}_{33}(r) = \frac{\pi}{rd} \int_{|r-d/2|}^{r+d/2} dr' \frac{1}{r'} \left(\frac{d^2}{4} + r'^2 - r^2\right)^2 \frac{\delta\Phi}{\delta n_{33}(r')}. \tag{C10}$$

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