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Perturbation theory applied to the freezing of classical systems

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We analyze the density-functional perturbation theory for simple classical systems and in particular the application of the perturbation-weighted density approximation to the study of the solid-fluid coexistence. The main assumptions of the approximation are discussed to clarify the dependence of the results with the partition of the intermolecular potential into repulsive and attractive contributions. A simplified version of the theory is presented and the results for the phase diagram of a Lennard-Jones system are compared with other theories and computer simulations.

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I. INTRODUCTION

The development of density-functional approximations has allowed the extensive study of inhomogeneous classical systems [1]. An important part of this effort has been dedicated to the hard-sphere (HS) system. Today we have accurate approximations to predict the structure of a HS fluid against a hard wall and its thermodynamic freezing properties [2], probably two of the hardest tests to be satisfied by any theoretical model of inhomogeneous systems. The common basic idea behind these theories for hard spheres is that the free energy of inhomogeneous systems may be locally mapped into the free energy of homogeneous systems whose density, $\bar{\rho}(\mathbf{r})$, is related in some way to the actual density distribution $\rho(\mathbf{r})$ of the inhomogeneous systems. There are several theoretical models based on different recipes for this thermodynamic mapping [2,3]. However, it has been recently found that some of these theories fail when applied to systems with attractive interactions [4,5]. The failure may be due, at least in part, to the thermodynamic mapping into the condensation density gap where the corresponding homogeneous phase is not defined, so that this deficiency is probably inherent to all these models. An approach to avoid this difficulty is the extension of the well-known perturbation theories for uniform fluids [6] to the case of inhomogeneous systems. Following the standard procedure of perturbation theory, the intermolecular potential is split into a reference part (usually the short-ranged repulsive part) and the perturbation (usually the long-ranged attractive tail). The reference system is then mapped into a HS fluid and the first-order perturbation energy is evaluated with the pair distribution function, $\rho^{(2)}(\mathbf{r},\mathbf{r}')$, of the reference system (essentially the hard sphere system). This perturbation approach was successfully applied to the freezing of a Lennard-Jones system using computer simulation data for the pair-correlation function of the HS system [7,8] and this approach is obviously restricted to the bulk crystal. A density-functional approximation, capable of studying in a consistent way the bulk and interfacial properties, requires a workable approximation for the pair distribution function of inhomogeneous HS systems [9–12]. The usual scheme is to write

$$\rho^{(2)}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})\rho(\mathbf{r}')g(\mathbf{r},\mathbf{r}') , \tag{1}$$

where $g(\mathbf{r},\mathbf{r}')$ is the natural extension of the radial distribution function, $g(|\mathbf{r}-\mathbf{r}'|)$ in homogeneous fluids. The question is whether or not the function $g(\mathbf{r},\mathbf{r}')$ in the inhomogeneous system may be approximated by that of a homogeneous fluid with an "effective density" $\hat{\rho}$, which may depend on $\mathbf{r}$, $\mathbf{r}'$, or some symmetrized combination. In this way we would deal again with the mapping of an inhomogeneous HS system into a homogeneous one, but now this mapping has to include not only the free energy but also the pair distribution function. The idea was easily applied in cases where the inhomogeneity is smooth, like the liquid-vapor interface of a Lennard-Jones fluid far from the triple point [13,14]. Simple choices of the effective density such as $\hat{\rho}(\mathbf{r})=\rho(\mathbf{r})$ or $\hat{\rho}(\mathbf{r},\mathbf{r}')=[\rho(\mathbf{r})+\rho(\mathbf{r}')]/2$, may be justified and have been successfully used in these cases. It is clear that these simple recipes are not valid for strongly inhomogeneous systems, like the solid phase or the fluid against a wall at high bulk densities, because at some points the local density $\rho(\mathbf{r})$ has very large values which would be impossible to reach in homogeneous phases. A possible choice would be to take the hard-sphere "weighted density" $\bar{\rho}(\mathbf{r})$ which results from the free-energy thermodynamic mapping, but it has been recognized that this overestimates the contribution of the perturbation potential [15]. The same applies to any effective density $\hat{\rho}$ of the order of the crystal or the coexistent liquid densities.

An alternative is to take the limit $\hat{\rho}=0$, i.e., to describe the radial distribution function by the steplike function given by the Boltzmann factor of the repulsive reference potential. This yields reasonable results for the solid free energy, suggesting that most of the structure in the function $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ in a crystal is already contained in the product of density distributions in (1). However, in a homogeneous fluid $\rho(\mathbf{r})$ is constant and all the structure in the pair correlation is due to the function $g(|\mathbf{r}-\mathbf{r}'|)$.

If this function is approximated by its zero density limit, the contribution of the perturbation potential is grossly underestimated. The phase diagram may be studied using different criteria for the solid and the fluid phases [15], but this is far from being a consistent treatment and it cannot be extended to the study of interfaces. Kyrlidis and Brown [9] have discussed this problem and they propose that instead of mapping $g(\mathbf{r},\mathbf{r}')$ it should be easier to map the full pair distribution function of the crystal. The crystal anisotropy may be avoided by taking the spherical average of $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ and then mapping it into the Percus-Yevick approximation of the metastable isotropic liquid. The contributions of the perturbation potential in this approach are quite reasonable and intermediate between those obtained by using $g(\mathbf{r},\mathbf{r}')\approx g(|\mathbf{r}-\mathbf{r}'|,\hat{\rho})$ with $\hat{\rho}(\mathbf{r})=0$ and with $\hat{\rho}(\mathbf{r})=\bar{\rho}(\mathbf{r})$. Recently [10], we have suggested an approach, the perturbation-weighted density approximation (PWDA), which allows for a consistent treatment of homogeneous and inhomogeneous phases and has competitive accuracy with earlier empirical approximations. However, recent work has indicated some problems, mainly the strong dependence of the results on the partition of the intermolecular potential into reference and perturbation parts. In Sec. II we present a new discussion of the PWDA which clarifies this point and in Sec. III we explore simplified versions of the theory, which drastically reduce the computer calculations, and apply them to study the phase diagram of the Lennard-Jones system. We end with a discussion of the different theoretical results and the comparison with computer simulations.

II. PERTURBATION-WEIGHTED DENSITY APPROXIMATION

Here we summarize the perturbation-weighted density approximation (PWDA), which has been recently proposed [10], and we present a new discussion which clarifies the accuracy of the approximation when applied to a crystal of classical molecules with simple interactions, like the Lennard-Jones (LJ) potential. According to standard perturbation theory, the density functional for the Helmholtz free energy of an inhomogeneous system, $F[\rho(\mathbf{r})]$, may be split in the free energy of an "reference fluid," $F_r[\rho(\mathbf{r})]$, whose molecular interactions match the repulsive part of the intermolecular potential, $\phi_r(r)$, and the perturbation contribution of the attractive potential, $\phi_p(r)$:

$$F[\rho(\mathbf{r})]=F_r[\rho(\mathbf{r})]+U_p[\rho(\mathbf{r})] .$$

The last term, which is also a functional of the density, may be written as

$$U_p[\rho(\mathbf{r})]=\tfrac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})u[\mathbf{r},\rho(\mathbf{r})] , \tag{2}$$

where u is a functional of $\rho(\mathbf{r})$ and a function of $\mathbf{r}$, which represents the average local potential energy acting on a molecule at position $\mathbf{r}$ from all its neighbor molecules:

$$u[\mathbf{r},\rho(\mathbf{r})]=\int d\mathbf{r}'\rho(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\phi_p(|\mathbf{r}-\mathbf{r}'|) , \tag{3}$$

with $g(\mathbf{r},\mathbf{r}')$ defined in (1). We know very little of this function in strongly nonuniform systems, like a crystalline solid described within the density-functional formalism. The main idea in the PWDA is to get some insight in the structure of $g(|\mathbf{r}-\mathbf{r}'|)$ through the exact "local compressibility" equation (see the Appendix of Ref [10]),

$$\int d\mathbf{r}'\rho(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1]=-1+\frac{kT}{\rho(\mathbf{r})}\frac{d\rho(\mathbf{r})}{d\mu} , \tag{4}$$

which generalizes the "local charge neutrality" proposed by Gunnarson, Jonson, and Lundqvist [16] for charged systems. In systems with homogeneous density (4) reduces to the well-known compressibility equation. For the application to dense inhomogeneous systems, like the hard-sphere (HS) fluid acting as reference system in the perturbation analysis, the second term on the right-hand side of (3) may be approximated by

$$\frac{kT}{\rho(\mathbf{r})}\frac{d\rho(\mathbf{r})}{d\mu}=kT\bar{\rho}(\mathbf{r})\chi_T(\bar{\rho}(\mathbf{r})) , \tag{5}$$

in terms of the isothermal compressibility, χ_T, of a uniform system with the "weighted density," $\bar{\rho}(\mathbf{r})$ used in the thermodynamic mapping of the reference HS fluid. Although, this approximation could be avoided with a self-consistent evaluation of $d\rho(\mathbf{r})/d\mu$, the proposed approximation is a considerable simplification without appreciable deterioration of the results. In fact, in the application to the problem of crystallization, the total contribution of this term is only of order 0.01 to be compared with the term -1, so that any approximation is quite harmless and the second term on the right-hand side of (4) may even be neglected altogether.

In the original presentation of the PWDA it was argued that the function $g(\mathbf{r},\mathbf{r}')$ in a crystal is probably much less structured than the radial distribution function of a dense fluid, because a good part of the structure in the pair distribution function is already included in the product of density distributions in (1). It was then suggested that a possible family of appropriate functions to approximate it could be constructed from the radial distribution function of uniform fluids with low effective density, $\hat{\rho}$,

$$g(\mathbf{r},\mathbf{r}')=g(|\mathbf{r}-\mathbf{r}'|,\hat{\rho}) . \tag{6}$$

If this approximation is included in Eqs. (4) and (5), we get an equation for the local value of $\hat{\rho}(\mathbf{r})$, which may be solved numerically and its solution used in (2), (3), and (6) to obtain the perturbation energy. The results of this approach were promising [10]. The effective density needed to satisfy the local compressibility equation was always much lower than the typical macroscopic density of the crystal, and the function $g(|\mathbf{r}-\mathbf{r}'|,\hat{\rho})$ gave very accurate results for the phase diagram of an LJ system, with the Weeks-Chandler-Andersen (WCA) [6,17] decomposition of the intermolecular potential. However, the same theory applied to the same system but with the potential partition proposed by Barker and Henderson (BH) [6] gives much poorer results (Table I). In both cases the perturbation theory was only carried up to first order and the soft repulsions of the reference fluid were mapped into an equivalent HS diameter with the simple BH criterion dependent of the temperature but not of the densi-

TABLE I. The fluid (ρ_f) and solid (ρ_s) coexisting densities at several temperatures for a Lennard-Jones system (in units of the LJ parameters ϵ and σ). The results of the PWDA with the WCA and the BH partition of the potential are compared with the computer simulations of Ref. [18]. Notice that the triple-point temperature with the BH partition is above $kT/\epsilon=0.75$ so that the coexisting fluid is vapor in that case.

	PWDA (WCA)	PWDA (BH)	MC, Ref. [18]
		$kT/\epsilon=0.75$	
$\rho_f\sigma^3$	0.906	0.003	0.875
$\rho_s\sigma^3$	1.004	0.992	0.973
		$kT/\epsilon=1.15$	
$\rho_f\sigma^3$	0.946	0.836	0.936
$\rho_s\sigma^3$	1.040	0.997	1.024
		$kT/\epsilon=1.35$	
$\rho_f\sigma^3$	0.966	0.873	0.964
$\rho_s\sigma^3$	1.055	1.016	1.053

ty [6]. The difference between the two schemes for dense liquids is small, but the PWDA produces a gross overestimation of the attractive interaction with the BH partition.

To clarify this point, let us reconsider here the assumptions of the PWDA in terms of the "local potential" defined in (3). We may decompose the density distribution $\rho(\mathbf{r})$ in the crystal into the contributions from the unit cell around each lattice vector $\mathbf{R}$,

$$\rho(\mathbf{r}')=\sum_{\mathbf{R}} f(\mathbf{r}'-\mathbf{R}) , \tag{7}$$

so that the function $f(\mathbf{r})$ is a normalized narrow distribution around the origin (usually described by Gaussians). Let us take the position $\mathbf{r}$ in $u[\mathbf{r},\rho]$ within the unit cell associated with $\mathbf{R}=0$. Any sensible approximation for $g(\mathbf{r},\mathbf{r}')$ contains the excluded volume around the origin which avoids the self-interaction of the molecule in each unit cell. This is equivalent to ignoring the term $R=0$ in the sum in (7). Then we split u in a "mean-field" part, without the function $g(\mathbf{r},\mathbf{r}')$, and a correlation part, Δu, which depends on $g(\mathbf{r},\mathbf{r}')-1$:

$$u[\mathbf{r},\rho(\mathbf{r})]=\sum_{\mathbf{R}\neq 0}\int d\mathbf{r}' f(\mathbf{r}-\mathbf{R})\phi_p(\mathbf{r}-\mathbf{r}')+\Delta u[\mathbf{r},\rho(\mathbf{r})] , \tag{8}$$

with

$$\Delta u[\mathbf{r},\rho(\mathbf{r})]=\sum_{\mathbf{R}\neq 0}\int d\mathbf{r}' f(\mathbf{r}'-\mathbf{R})[g(\mathbf{r},\mathbf{r}')-1]\phi_p(|\mathbf{r}-\mathbf{r}'|) . \tag{9}$$

The lattice sites $\mathbf{R}$ far away from the origin $\mathbf{R}=0$ will give small contributions to Δu, because both $g(\mathbf{r},\mathbf{r}')-1$ and $\phi_p(|\mathbf{r}-\mathbf{r}'|)$ decay rapidly with the distance $|\mathbf{r}-\mathbf{r}'|$. The main contribution comes from the nearest-neighbor cell, $|\mathbf{R}|=R_1$ where $|\mathbf{r}'-\mathbf{r}|\approx R$ is within the range of the repulsive potential $\phi_r(r)$. In this region the function $g(\mathbf{r},\mathbf{r}')$ goes briskly from zero to values larger than 1 and its contribution to the perturbation energy is enhanced by being close to the absolute minimum of the intermolecular potential. The accuracy of the PWDA, or of any other similar approach for the thermodynamics of a classical crystal, depends mainly of the capability to describe the correlation contribution from the shell of nearest neighbors, although the lattice sites further away than nearest neighbors may still give a substantial contribution to the mean field part of u.

A parallel line of argument may be followed for the exact local compressibility equation (4). There we may also split the density into the contributions from each lattice site (7). The site at $R=0$ is at the center of the correlation core, and its integral, with $g(\mathbf{r},\mathbf{r}')=0$, cancels exactly the -1 term on the right-hand side of (4). The contributions from lattice cells further away from nearest neighbors are probably small but the sites in the first neighbors shell impose important physical restrictions on the function $g(\mathbf{r},\mathbf{r}')$. By comparing the resulting expressions for Δu and for the local compressibility equation we realize that the information gained with the later may be used in the former by assuming that the perturbation potential is a smooth function of $\mathbf{r}'$, compared with the rapid changes of $f(\mathbf{r}-\mathbf{R})g(\mathbf{r},\mathbf{r}')$ in the region $|\mathbf{r}-\mathbf{r}'|\approx R_1$. A simple analysis based on the Taylor expansion of $\phi_p(\mathbf{r})$ around $r=R_1$ shows that any function $g(\mathbf{r},\mathbf{r}')$ satisfying the local compressibility equation will give the correct leading term for the local effective potential. Obviously, the local compressibility equation is far from fully specifying a unique function $g(\mathbf{r},\mathbf{r}')$ and that is why a solution may be sought within an arbitrary family of functions, like (6). However, the zeroth-order contribution to the perturbation energy in a Taylor expansion of $\phi_p(r)$ is independent of the particular choice.

The difference between the BH and the WCA decompositions of the LJ potential now becomes clear. The WCA partition produces a perturbation potential which is constant and equal to the minimum of the full LJ potential, $\phi(r)$, for $r<r_0$, where r_0 is the position of the minimum of $\phi(r)$. The equivalent HS diameter describing the repulsive reference potential is smaller than r_0, so that $\phi_0(r)$ is flat in the region with the main contribution from the correlation function. The exact zeroth-order term in the Taylor expansion of $\phi_p(r)$, gives most of the correlation contribution to $u[\mathbf{r},\rho(\mathbf{r})]$ independently of

the accuracy of the ansatz (6). Thus the WCA decomposition of the LJ potential seems to be the optimum partition to minimize the error in the perturbation energy with an approximate function $g(\mathbf{r},\mathbf{r}')$ fulfilling the local compressibility equation. On the other hand, the BH decomposition of the LJ potential gives a very steep function $\phi_p(r)$ in the region of the strongly correlated nearest neighbors. The results produced with this partition should depend much more critically on the choice of the particular family of functions.

The approximation (6) does not reproduce all the features of $g(\mathbf{r},\mathbf{r}')$ observed in the computer simulation data (see Fig. 7 in Ref. [9]), but it may be regarded as a convenient functional family which satisfies two basic requirements: all the functions have the correlation hole around the origin, as needed to avoid the self-interaction of the molecules, and the effective density $\hat{\rho}$ is a smooth parameter to tune the local compressibility with the strongly structured density distributions typical of a crystal. Moreover, it becomes exact in the limit of homogeneous fluids, which is an important requirement in the study of solid-fluid interfaces. The PWDA, together with the WCA partition of the intermolecular potential, provide a workable and accurate density functional which may be applied to the study of systems with arbitrary inhomogeneity.

III. SIMPLIFIED PERTURBATION-WEIGHTED DENSITY APPROXIMATION

If we focus our attention on systems which are macroscopically homogeneous, such as a bulk crystalline solid, the perturbation energy (2) is proportional to the number of molecules, N and using (7)–(9) we get

$$\frac{U_p}{N}=\frac{1}{2}\int d\mathbf{r}\, f(\mathbf{r})\, u[\mathbf{r},\rho(\mathbf{r})] ,$$

which may again be decomposed into "mean-field" and "correlation" contributions:

$$\frac{U_p}{N}=\frac{1}{2}\sum_{\mathbf{R}\neq 0}\int d\mathbf{r}\int d\mathbf{r}'\, f(\mathbf{r})\, f(\mathbf{r}'-\mathbf{R})\,\phi_p(|\mathbf{r}-\mathbf{r}'|) + \frac{\Delta U_p[\rho(\mathbf{r})]}{N} . \tag{10}$$

where, as before, the exclusion of the $\mathbf{R}=0$ in the mean-field part avoids the self-interaction of the molecule in each unit cell. The correlation contribution is now

$$\frac{\Delta U_p}{N}=\frac{1}{2}\sum_{\mathbf{R}\neq 0}\int d\mathbf{r}'\, f(\mathbf{r})\, f(\mathbf{r}'-\mathbf{R})[g(\mathbf{r},\mathbf{r}')-1]\phi_p(|\mathbf{r}-\mathbf{r}'|) . \tag{11}$$

As in the previous discussion, the main contribution to this energy comes from the shell of nearest neighbors, $|\mathbf{R}|=R_1$, where the function $g(\mathbf{r},\mathbf{r}')$ presents a strong dependence on $|\mathbf{r}-\mathbf{r}'|$. If we use the WCA partition of the LJ potential, $\phi_p(r)$ is smooth function and we may expand it around $r=R_1$. The leading (zeroth-order) contribution is proportional to

$$\int d\mathbf{r}\int d\mathbf{r}'\, f(\mathbf{r})\, f(\mathbf{r}'-\mathbf{R}_1)[g(\mathbf{r},\mathbf{r}')-1] , \tag{12}$$

where R_1 is any lattice vector in the first correlation shell. Double integrals like (12) appear in a "global compressibility" equation obtained by integration in a unit cell of the exact "local compressibility" equation (4) multiplied by the local cell density $f(\mathbf{r})$:

$$\begin{aligned}\int d\mathbf{r}\, f(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1] &=\sum_{\mathbf{R}}\int d\mathbf{r}\int d\mathbf{r}'\, f(\mathbf{r})\, f(\mathbf{r}'-\mathbf{R})[g(\mathbf{r}-\mathbf{r}')-1]\\ &=-1+\int d\mathbf{r}\, f(\mathbf{r})\frac{kT}{\rho(\mathbf{r})}\frac{d\rho(\mathbf{r})}{d\mu} .\end{aligned} \tag{13}$$

As far as $g(\mathbf{r},\mathbf{r}')$ contains the exclusion hole around $\mathbf{r}-\mathbf{r}'=0$, the restriction to normalized unit cell densities cancels out the -1, in the last term of (13), with the contribution from the lattice vector $\mathbf{R}=0$. The contribution for the remaining sites is again dominated by the shell of nearest neighbors so that any function $g(\mathbf{r},\mathbf{r}')$ fulfilling the global compressibility equation (13), would give an excellent estimate of the integral (12) and hence a good approximation to the correlation energy (11) for the WCA perturbation potential, for the same reasons discussed in the previous paragraph.

This suggests a simplified version of the PWDA (or SPWDA) based in the approximation (6) for $g(\mathbf{r},\mathbf{r}')$ with a global uniform effective density $\hat{\rho}$ which satisfies Eq. (13), instead of the locally varying $\hat{\rho}(\mathbf{r})$ required to satisfy (4). This simplification provides an important reduction of the numerical calculations and, if our discussion is correct, it should have essentially the same accuracy as the original PWDA (although limited to macroscopically uniform systems). We have checked the SPWDA for the solid-fluid coexistence of the LJ system and the results are compared with the original PWDA [10], with Monte Carlo results [18] and with other theoretical approaches [9,19–21] in Table II. Both the PWDA and the SPWDA use the WCA partition of the LJ potential [17]. The radial distribution functions of the reference system is obtained from the Verlet-Weiss approximation [22] for HS and the Boltzmann factor of the reference potential according with the perturbation theory [6,17]. The soft repulsive potential is represented by hard spheres with a diameter determined with the Barker-Henderson criterion [6], as is also done in the other theories we want to compare with. The use of the more accurate WCA criterion [17], used in perturbation theory of homogeneous liquids together with the WCA partition of the intermolecular potential produces a HS diameter which depends on the density and would be very difficult to treat in non-homogeneous systems. For the reference HS free energy we use the weighted density approximation of Tarazona [15] but any other mapping might be used in our general scheme. The density $\rho(\mathbf{r})$ in the solid phase is parametrized by Gaussians in a fcc lattice and the total free energy in minimized with respect to the Gaussian width [15]. The right-hand side of (13) may be approximated by (5) or, without appreciable effect, we may neglect the compressibility of the solid phase. The results, as presented in Table II are very close to those ob-

TABLE II. Solid-liquid coexistence densities and pressures for the Lennard-Jones system for different temperatures. Comparison of Monte Carlo data (Ref. 18) with those obtained from the PWDA (Ref. [10]), the simplified versions presented here, SPWDA and mean-field (MF), and other theories: Curtin and Achscrof (Ref. [19]), Kyrlidis and Brown, (Ref. [9]), and Choi, Ree, and Ree (Ref. [20]), and Kang *et al.* (Ref. [8]).

	PWDA	SPWDA	MF	MC	Ref. [19]	Ref. [9]	Refs. [8,20]
			$kT/\epsilon=0.75$				
$\rho_l\sigma^3$	0.906	0.898	0.880	0.875	0.855	0.859	0.861
$\rho_s\sigma^3$	1.004	1.001	0.990	0.973	0.970	0.983	0.957
$P\sigma^3/\epsilon$	1.04	0.94	0.60	0.67	0.90	0.65	0.54
			$kT/\epsilon=1.15$				
$\rho_l\sigma^3$	0.946	0.941	0.934	0.936	0.934	0.920	0.950
$\rho_s\sigma^3$	1.040	1.043	1.035	1.024	1.026	1.008	1.027
$P\sigma^3/\epsilon$	5.90	5.78	5.50	5.68	6.40	5.44	6.16
			$kT/\epsilon=1.35$				
$\rho_l\sigma^3$	0.966	0.958	0.953	0.964	0.960	0.943	0.986
$\rho_s\sigma^3$	1.055	1.060	1.054	1.053	1.045	1.024	1.054
$P\sigma^3/\epsilon$	8.65	8.30	8.07	9.00	9.10	8.13	9.60

tained with the PWDA. The overall agreement with the Monte Carlo results and temperature behavior is quite good, even slightly better than our PWDA results at low temperatures, and comparable with the other theoretical results presented in the table.

At this stage it is clear that the accuracy of our approaches, either the PWDA or the SPWDA, is mainly due to the use of compressibility equation and the WCA partition of the intermolecular potential, rather than to the validity of the approximation (6) for $g(\mathbf{r},\mathbf{r}')$ in a crystalline solid. As a final check we have explored an even more simplified version of our theory. As we said above, the compressibility contribution in the last term of (13) is negligible, compared with -1, and this later is exactly balanced by the $\mathbf{R}=\mathbf{0}$ contribution over the lattice vectors. Thus, Eq. (13) reduces to

$$\sum_{\mathbf{R}\neq 0}\int d\mathbf{r}\int d\mathbf{r}' f(\mathbf{r})f(\mathbf{r}'-\mathbf{R})[g(\mathbf{r}-\mathbf{r}')-1]\approx 0\ , \qquad (14)$$

which is satisfied by the trivial solution $g(\mathbf{r},\mathbf{r}')=1$ everywhere except near $|\mathbf{r}-\mathbf{r}'|=0$. This is equivalent to neglecting altogether the correlation contribution to the perturbation energy (11) and keeping only the mean-field part, which still excludes the self-interaction. The results of this mean-field (MF) approximation for the solid-liquid coexistence are also presented in Table II; they are as good as those of the PWDA or the SPWDA and even better at low temperature. However, they are based in a very unphysical assumption, fully neglecting the correlation between nearest-neighbor cells but still keeping the self-exclusion of the molecule in each lattice cell. The function $g(\mathbf{r},\mathbf{r}')$ corresponding to this assumption would be a steplike function going from 0 to 1 but not at a distance $|\mathbf{r}-\mathbf{r}'|$ near the HS diameter, but somewhere around $|\mathbf{r}-\mathbf{r}'|=R_1/2$, in the interstitial region with negligible local density. This unphysical function resembles the empirical correction to the direct correlation function used by Curtin and Ashcroft [19], which also has a step at a distance of half HS diameter: in both cases the functions are built to separate each peak in the crystal $\rho(\mathbf{r})$ from all its neighbors. In the study of crystal phases within the density-functional formalism it is usual to separate the density profile in the individual contributions from each molecule. The results for the HS crystal are better if the minimization of the free energy is restricted to density distributions made of normalized contributions from each molecule as in (7) and the contribution from the attractive interactions is also much easier to approximate if the molecular self-interaction is avoided. This is done by our unphysical $g(\mathbf{r},\mathbf{r}')$ in (14) or by the empirical step in the direct correlation function of Curtin and Ashcroft. It is clear that our good results for the LJ phase diagram cannot be taken in support of this correlation function; the accuracy of the results comes from the cancellation of errors controlled by the compressibility sum rule (13). This should be taken into account when the density functionals developed for the bulk solid are extended to the study of other problems like the wall-fluid interphase or the surface melting, where the separation of $\rho(\mathbf{r})$ into the individual molecular contributions is impossible. The extrapolation to these problems should not include any features associated with the separation of $\rho(\mathbf{r})$ in the contributions of each molecule.

In this respect the PWDA, with the WCA partition of the intermolecular potential and the local compressibility equation solved within the approximation (6), seems to be superior to the other alternatives. Although the radial distribution functions of low density fluids cannot fully match the correlation function in a crystal, they provide important physical features like the presence of the Boltzmann factor with the repulsive reference potential and they are extended in a natural way from the solid to the liquid phase. The accuracy in the evaluation of the WCA perturbation energy is controlled by the local compressibility equation. Now we understand how this sum rule produces good estimates of the crystal free energy and, by the same reason, it should also give accurate results for other inhomogeneous systems: it gives the exact leading contribution for the WCA perturbation potential. If we restrict ourselves to the study of bulk solids, the SPWDA presented here is simple to use and offers a controlled approximation with results comparable to other existing theories, like those of Curtin and Ashcroft [19], Kyrlidis and Brown [9], already mentioned, and the interesting approach of Choi, Ree, and Ree [20] (see also Refs. [7] and [8]). However, the later cannot be compared directly with the functional theories discussed above because it uses the references HS free energy and pair distribution function obtained from Monte Carlo simulations instead of being generated by the theory itself.

Finally we have to remark that our discussion here has been restricted to the perturbation treatment of the attractive interaction. There still remains a relatively weak point in the theoretical treatment: the map of the soft repulsions of the reference fluid into an equivalent hard sphere. In the homogeneous fluid this is done much more accurately by the WCA criterion, with the effective HS diameter which depending on both temperature and density. However, in the crystal the dependence with the density becomes very troublesome and, as in other previous works, we have restricted the map to the simpler BH criterion in which the HS diameter is density independent. This approximation is not very accurate for the free energy, but most the error made in the liquid and in the crystal cancel out, so that the phase diagram may be more accurate than the equation of state of each phase. However, other properties of the crystal, such as the Lindemann ratio, are much more sensitive. The microscopic structures of the density distribution in the LJ crystal should reflect the softness of the core repulsion and the width of the Gaussian peaks are different in a crystal with self-repulsion than in the HS crystal. The equation of state of the crystal at high pressure and the solid fluid phase diagram at high temperature also reflect the problem of the soft repulsive potential which requires further study.

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