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Perturbation weighted-density approximation: The phase diagram of a Lennard-Jones system

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We present a density-functional approach for the Helmholtz free energy of simple liquids, based on the separation of attractive and repulsive interactions and within the framework of the weighted-density approximations. The approach reduces to the standard perturbation theory of simple fluids for the homogeneous vapor and liquid phases. It gives a good description of the correlation structure in the crystal, based on a *local-compressibility* equation. The phase diagram of a Lennard-Jones system is obtained and compared with a computer simulation.

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Since the work of Ramakrishnan and Yussouff [1], most theoretical studies of solid-fluid phase transitions have been based on the density-functional formalism. The solid is described as a system with periodically modulated density distribution $\rho(\mathbf{r})$ and its free energy is obtained from a density functional $F[\rho]$. The strong modulations of the solid density distribution forbid the use of simple approximations for $F[\rho]$, such as gradient expansions, which have been successfully used for other problems. Thus the study of freezing, besides its intrinsic interest, is a touchstone in the development of new approximations for free-energy density functionals which may be later used in other problems such as interfaces and capillarity [2].

Three main groups of approximations for $F[\rho]$ have been developed in this context, all of them based in the idea that a good description of the thermodynamics properties of inhomogeneous phase can be obtained from the structural properties of a homogeneous phase. The first approximation follows the original approach [1] with the expansion of the free energy around that of a homogeneous system; in practice this expansion is truncated at second or third order. The nonlocal dependence of F on $\rho(\mathbf{r})$ appears through the direct correlation function (related to the second functional derivative of $F[\rho]$) in the homogeneous system [1, 3]. However, the functional expansions may have fundamental problems of convergence [4, 5]. In view of these difficulties two new groups of approximations were open. One, known under the general name of "weighted-density approximation" (WDA) [6–8] is based on the idea of a *local free-energy density* evaluated at a weighted density, $\bar{\rho}(\mathbf{r})$, which is a relatively weakly varying function of the position. The nonlocal dependence of $F[\rho]$ is introduced through the relationship between $\bar{\rho}(\mathbf{r})$ and $\rho(\mathbf{r})$. The last type of approach, the "effective-liquid approximation" (ELA) [9], starts from the free energy obtained by the integration of the direct correlation function, this one being approximated by that of an effective liquid. As in the first case, the nonlocal dependence of F on $\rho(\mathbf{r})$ appears through the direct correlation function of the homogeneous liquid [10]. From another point of view we can distinguish between *global approaches*, in which the inhomogeneous phase maps onto a single homogeneous liquid phase [1, 3–5] and the WDA in which there is a position-depending map. A global version of the WDA, the modified WDA (MWDA), was also developed by Denton and Ashcroft [11]. Although global approaches require lighter computation efforts than WDA they reduce the applicability mainly to macroscopically homogeneous phases; for instance, to describe an interface the two bulk coexisting phases would have to be mapped onto the same homogeneous liquid, which is generally a poor approximation. The global approach based in the free-energy expansion has been generalized in order to describe the solid-fluid interface though with less success than the WDA [3]. A recent review of the subject is given by Baus [12].

Many studies were devoted to the freezing of hard spheres (HS), as the basic reference system in the theory of simple fluids, and it is now clear that a good description of this problem may be obtained with the advanced versions of both the ELA and the WDA approaches. However, it has been recently found by Kuijper *et al.* [13] and Laird and Kroll [14] that theories with global character may fail to predict freezing properties of soft repulsive potentials. Some of them fail even to predict any liquid-solid transition in all cases studied (soft spheres, inverse powers, and truncated Lennard-Jones). The difficulties of the global approach increase when attractive interactions are included: Kyrlidis and Brown have found that for Lennard-Jones potential they cannot give the necessary thermodynamic mapping [15] and the MWDA fails even to predict crystallization of Lennard-Jones systems at low temperatures [13]. Nonglobal approaches have not been applied to these systems but they would probably show the same difficulties. Furthermore all the density-functional approaches discussed above are based in some kind of solid-fluid mapping. For systems with attractive interactions this seems awkward because the free energy as a function of the density is not defined in the large density gaps produced by condensation. A promising approach which avoids all the above difficulties is the separation of repulsive and attractive interactions, following the perturbation scheme successfully used in uniform liquids [16, 17] and generalized for inhomogeneous fluids [18, 19] as the density-functional approximation:

$$F[\rho] = F_r[\rho] + \tfrac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \; \rho_r^{(2)}(\mathbf{r},\mathbf{r}';[\rho(\mathbf{r})]) \;\; \Phi_p(\mathbf{r}-\mathbf{r}'), \tag{1}$$

where $F_r[\rho]$ is the Helmholtz free-energy density functional for the reference system. The repulsive cores are approximated by a HS system and $F_r[\rho]$ may be obtained from any of the well-tested versions of the WDA. The attractive part of the interaction potential Φ_p is included in the Helmholtz free-energy functional at first order in perturbation theory and $\rho_r^{(2)}(\mathbf{r},\mathbf{r}';[\rho])$ is the pair distribution function in the reference system also as a functional of the density distribution $\rho(\mathbf{r})$. The simplest possible approximation for the pair distribution function is to fully neglect the correlation structure and take $\rho_r^{(2)}(\mathbf{r},\mathbf{r}';[\rho]) \approx \rho(\mathbf{r})\ \rho(\mathbf{r}')$. This is commonly termed a van der Waals theory of nonuniform fluids [2]. For a homogeneous reference fluid of density ρ_0 we have $\rho^{(2)}(\mathbf{r},\mathbf{r}';\rho_0) = \rho_0^2\ g_r(\mid \mathbf{r}-\mathbf{r}' \mid,\rho_0)$, in terms of the radial distribution function, which for HS is well known. This knowledge may be used to go a step further than the van der Waals approximation in the perturbation theory for inhomogeneous fluids taking [18, 19]:

$$\rho_r^{(2)}(\mathbf{r},\mathbf{r}';[\rho]) \approx \rho(\mathbf{r})\rho(\mathbf{r}')g_r(\mid \mathbf{r}-\mathbf{r}' \mid,\hat{\rho}), \tag{2}$$

with the radial distribution function of the reference uniform fluid, $g_r(r,\rho_0)$, at some effective density, $\hat{\rho}$, which may depend on the position and is a functional of the density distribution. The application of the perturbation density functional [(1) and (2)] to systems with smooth density distributions, such as the liquid-vapor interface, produced good results with simple choices for the effective density in (2), such as the local density, $\hat{\rho} = \rho(\mathbf{r})$, or other symmetrized forms such as $\hat{\rho} = [\rho(\mathbf{r}) + \rho(\mathbf{r}')]/2$ or $\hat{\rho} = \rho[(\mathbf{r}+\mathbf{r}')/2]$. However, the application of this approach to a crystal phase was hindered by the difficulty in finding an appropriate effective density.

A perturbation theory has already been pursued by Weis [20] and Ree and co-workers [21] to study the properties of a Lennard-Jones crystal and its solid-fluid transition. These authors proceed with the usual steps of the perturbation theory including the approximation of the reference fluid by a HS one, but contrary to the density-functional approach, in which the free energy (1) is minimized with respect to the density distribution $\rho(\mathbf{r})$, they evaluate the contribution from the attractive perturbation potential with the equilibrium pair distribution function of the reference HS crystal at the same mean density. Both F_r and $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ are obtained from Monte Carlo simulations of the HS crystal and used to get the thermodynamics of the Lennard-Jones system. This is the usual procedure in the perturbation theory for homogeneous fluids, extended to the solid phase as a homogeneous phase at macroscopic level. However, the modern theory of crystallization, based on the description of the solid as a self-structured fluid, requires a perturbation theory within the density-functional formalism. Only in this way may we obtain both the thermodynamics and the structure of a solid phase consistently, through the minimization of the free-energy density functional. Futhermore, in the functional approach the free energy and the radial distribution function of HS are obtained from the theory itself instead of taking them as external inputs from Monte Carlo data.

The density-functional perturbation theory proposed here is based on the same scheme [(1) and (2)] used for the liquid-vapor interface but with a better choice for the effective density $\hat{\rho}$ in (2). It is obvious that in a crystal we cannot use any recipe based on the local density, $\rho(\mathbf{r})$, which may be a hundred times larger than the maximum mean density in homogeneous HS systems. A more promising choice could be to identify $\hat{\rho}$ with the mean density of the solid or the local weighted density $\bar{\rho}(\mathbf{r})$ used in the WDA. However, any of these choices produces a gross overestimation of the first-order contribution from the attractive interactions in the solid. The reason is that in the crystal, as described in the density-functional formalism, most of the structure in $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is already included in $\rho(\mathbf{r})$ while in the homogeneous fluid all the structure is in the function $g(|\mathbf{r}-\mathbf{r}'|,\rho_0)$. As a limiting case, in a classical crystal at zero temperature $\rho(\mathbf{r})$ is a sum of δ functions at the lattice sites and the pair distribution function $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is the sum of δ function products at any pair of different sites. Thus the correlation is only the exclusion of double occupancy of a lattice site, which may be described by a steplike function or by the limit $\hat{\rho} = 0$ in (2). Therefore the use of a perturbation scheme for the attractive interactions in the solid requires a prescription for the correlation function in the HS crystal very different from that of a dense fluid. This was included in an empirical way in the early work by one of us [6], through the use of different effective interactions in the solid and in the fluid phases. In a more elaborated theory, Curtin and Ashcroft [22] get excellent results for freezing of a Lennard-Jones fluid, with an empirical expression for the direct correlation function in the solid. Besides their partially *ad hoc* choice, the main drawback of their approach is that it goes back to the "global character" by including the difference between the solid and the fluid density distributions as the expansion variable. Thus the approach becomes a workable and accurate theory of freezing but it does not provide a general density functional for a system with attractive and repulsive interactions. The reader should be aware that what is reported as $g(r)$, from Monte Carlo simulations for HS, by Weis [20] and Ree and co-workers [21] corresponds to the angular average of $\rho(\mathbf{r})g(r)/\rho_0$ in our notation (ρ_0 being the mean density of the solid).

Our proposal here is free of *ad hoc* approximations and it gives a good representation of the pair distribution function in a crystal. The idea is a generalization of the WDA first proposed by Gunnarsson, Jonson, and Lundqvist [23] for the electron fluid. It takes the form (2) to approximate $\rho_r^{(2)}(\mathbf{r},\mathbf{r}')$, with a position-dependent

$\hat{\rho}(\mathbf{r})$ determined by the exact "local-compressibility" relation (see the Appendix), which generalizes that of "local charge neutrality" [23]:

$$\int d\mathbf{r}'\rho(\mathbf{r}')[g_r(\,|\,\mathbf{r}-\mathbf{r}'|,\hat{\rho}(\mathbf{r}))-1]=-1+\frac{k_BT}{\rho(\mathbf{r})}\ \frac{d\rho(\mathbf{r})}{d\mu}\ , \tag{3}$$

where μ is the chemical potential. Although the choice of $\hat{\rho}$ as a function of $\mathbf{r}$ violates the exact symmetry $g(\mathbf{r},\mathbf{r}')=g(\mathbf{r}',\mathbf{r})$, this is a reasonable simplification very common both in classical fluids and in the electron gas theories. Equation (3) reduces to the well-known compressibility equation [16] for uniform systems, with the isothermal bulk compressibility $\chi_T=\rho^{-2}\ d\rho/d\mu$. If the reference fluid free energy F_r in (1) is described with any version of the WDA, we may approximate the right-hand side of (3) by its "local thermodynamics" value:

$$\frac{1}{\rho(\mathbf{r})}\ \frac{d\rho(\mathbf{r})}{d\mu}\approx\bar{\rho}(\mathbf{r})\ \chi_T(\bar{\rho}(\mathbf{r})), \tag{4}$$

with the same weighted density $\bar{\rho}(\mathbf{r})$ used to evaluate the free-energy density in F_r. This completes our proposed perturbation WDA (PWDA) for the contribution of the attractive interactions to the free energy of a simple fluid. Notice that (3) comes from an exact equation for $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ and, as commented below, (4) does not appreciably affect the results. The main approximation is to represent $\rho_r^{(2)}(\mathbf{r},\mathbf{r}')$ by (2), in terms of the isotropic radial distribution function of a fluid, and the crucial point in the PWDA is that the effective density, $\hat{\rho}(\mathbf{r})$, which satisfies [(3) and (4)] includes the effect described above: the weak structure of the pair correlation in the crystal, compared with that of a dense fluid.

We apply the PWDA to obtain the phase diagram of a Lennard-Jones (LJ) system. The interaction potential is split as in the Andersen-Chandler-Weeks perturbation theory [17]. The function $g_r(r,\rho)$ is obtained from the Verlet-Weis [24] approximation for HS and the Boltzmann factor of the soft repulsive potential, as usual in perturbation theory of simple liquids [16, 17]. To simplify calculations the reference system is approximated by a HS fluid with the Barker-Henderson criterium [16] to determine the diameter (as in Ref. [22]). This criterium only depends on the interaction potential and the temperature. Thus in the minimization of the free energy at each temperature the HS diameter is constant, otherwise it would entangle the numerical calculations. An effort to improve the determination of the HS diameter is in progress. We take F_r in (1) as that of HS with the WDA version developed in [8] (other versions, with their relative merits and disadvantages, might also be used within our general scheme).

The density distribution in the crystal is parametrized by Gaussian peaks in a fcc lattice and the total free energy is minimized with respect to the Gaussian width parameter [6–8] . To evaluate the contribution of the attractive interactions in (1) we have to solve [(3) and (4)] for $\hat{\rho}(\mathbf{r})$ at each point. Figure 1 shows the values of this effective density, for a typical crystal density, as a function of the distance to a lattice point along several directions. The most important point is that in the neighborhood of the Gaussian peak $\hat{\rho}$ is only about 0.05, to be compared with $\bar{\rho}\simeq0.32$ and the mean density $\rho_s=1.0$ (all in units of the LJ parameter σ). As expected, the results of [(3) and (4)] reflect that most of the pair distribution structure in the crystal is already built in the function $\rho(\mathbf{r})$. The growth of $\hat{\rho}(\mathbf{r})$ when moving away from the Gaussian center is relatively isotropic, which suggests a useful approximation to simplify the numerical calculations: for $\mathbf{r}$ in the Wigner-Seitz cell around the lattice site $\mathbf{R}$ we take

$$\hat{\rho}(\mathbf{r})=\hat{\rho}_0+\tfrac{1}{2}\hat{\rho}_0''\,|\,\mathbf{r}-\mathbf{R}\,|^2\,. \tag{5}$$

We checked that this approximation is good at the typical conditions of the solid phase, and we use it to get the phase diagram. Another numerical simplification, without appreciable change in the results, is to take the right-hand side of (3) to be just -1, neglecting the contribution from the compressibility which is of order 0.01.

Figure 2 shows the phase diagram of the Lennard-Jones system with our theory compared with simulation data [25]. The agreement is good at the temperature range of interest and excellent for the determination of the triple point temperature. The coexisting densities are slightly shifted but the density change at coexistence is very accurate. At high temperatures the transition is dominated by the underlying HS system and it is not very accurate due to our simplified treatment of F_r. The pressure and latent heat results (in Table I) are in reasonable agreement with those of the simulation and show the same behavior with temperature. The results for the Lindemann parameter are very sensitive to the details of the model.

The overall accuracy of the PWDA is clearly better than that obtained with the early "global expansion" treatments [26] and almost comparable to that of Curtin

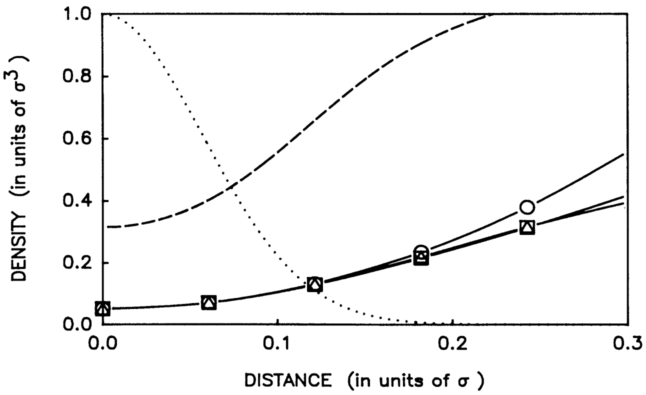

FIG. 1. Effective density $\hat{\rho}$ from [(3) and (4)] in the solid coexisting with liquid at $k_BT=1.0$ (in units of LJ parameter σ^3). The distance r to a lattice site goes along three symmetric directions: cube edge (circles), face diagonal (squares), and cube diagonal (triangles). The dashed line is the angular averaged weighted density, $\bar{\rho}(r)$. The dotted line is a Gaussian function with the same width as those in the variational density distribution (with arbitrary vertical scale), to show the isotropy of $\hat{\rho}(\mathbf{r})$ over the region with not negligible density.

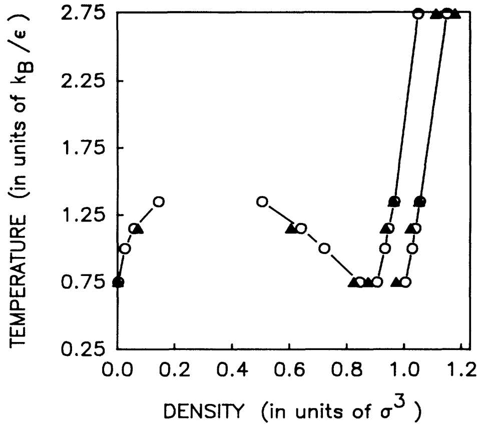

FIG. 2. Phase diagram of the Lennard-Jones system from the PWDA (open circles with the solid line as a guide to the eye) and as found in simulation studies [25] (triangles).

and Ashcroft [22], but the empirical expression for the direct correlation function proposed there has been replaced by an approximation with clear physical interpretation, which yields a good representation of the correlation function in the crystal. The merit of [(3) and (4)] goes beyond being a way to get a low effective density in (2). We have checked that the phase diagram obtained with the empirical approach of taking $\hat{\rho} = 0$ in the solid is quite bad. Even the milder approximation of neglecting the quadratic term in (5) has an appreciable effect in the quality of the results. The local compressibility equations [(3) and (4)] give a fine tuning of the correlation function in the crystal, which is reflected in the accurate results of the PWDA. Moreover, they provide a workable density-functional approximation which may be directly applied to the study of interfaces, including the problem of surface melting. The global expansion around a homogeneous density, as used by Curtin and Ashcroft [22], makes impossible its direct application to the study of the vapor-solid interface without some extra empirical choice for this density expansion, which also changes the bulk phase diagram [27]. Finally, our results provide a hint to the origin of the problems found in the mapping between thermodynamics and structure for fluids with attractive interactions. The description of the free energy of a HS solid requires a dense effective liquid, but its correlation structure may only be described by the radial distribution function of a low density fluid. The contributions to the free energy from the attractive and the repulsive interactions have essentially different maps and they cannot be easily included in the same description.

TABLE I. The liquid (ρ_l) and solid (ρ_s) densities, the pressure (P) , the latent heat ($T\Delta S$) and the Lindemann parameter (L) at coexistence at several temperatures (all in LJ units). The results of the PWDA are compared with computer simulations [25] (in parentheses) and with those of Curtin and Ashcroft [22] (in square brackets).

k_BT	ρ_l	ρ_s	P	$T\Delta S$	L
0.75	0.906	1.004	1.04	0.83	0.075
	(0.875)	(0.973)	(0.67)	(1.31)	(0.145)
	[0.855]	[0.970]	[0.90]	[1.10]	[0.127]
1.15	0.946	1.040	5.90	1.23	0.079
	(0.936)	(1.024)	(5.68)	(1.46)	(0.139)
	[0.934]	[1.026]	[6.40]	[1.50]	[0.126]
1.35	0.966	1.055	8.65	1.37	0.081
	(0.964)	(1.053)	(9.00)	(1.88)	(0.137)
	[0.960]	[1.045]	[9.10]	[1.70]	[0.126]

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APPENDIX

Let μ and $V_{\text{ext}}(\mathbf{r})$ be the chemical potential and an external potential, respectively; then we can define

$$u(\mathbf{r}) \equiv \mu - V_{\text{ext}}(\mathbf{r}). \tag{A1}$$

Then, taking into account the expression of the density-density correlation function

$$G(\mathbf{r},\mathbf{r}') = \rho^{(2)}(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\ \rho(\mathbf{r}') + \rho(\mathbf{r}')\ \delta(\mathbf{r}-\mathbf{r}'), \tag{A2}$$

and its relation with the functional derivative of $\rho(\mathbf{r})$ with respect to $u(\mathbf{r})$ [2]:

$$G(\mathbf{r},\mathbf{r}') = k_BT\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')}, \tag{A3}$$

we have

$$k_BT\frac{\partial\rho(\mathbf{r})}{\partial\mu} = k_BT\int d\mathbf{r}'\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')}\frac{\partial u(\mathbf{r}')}{\partial\mu} = \int d\mathbf{r}'G(\mathbf{r},\mathbf{r}') \tag{A4}$$

$$= \int d\mathbf{r}'[\rho^{(2)}(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')] \tag{A5}$$

$$= \rho(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')[g(\mathbf{r},\mathbf{r}') - 1] + \rho(\mathbf{r}). \tag{A6}$$

Rearranging this equation we find the exact local-compressibility relation:

$$\int d\mathbf{r}'\rho(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1] = -1 + \frac{k_BT}{\rho(\mathbf{r})}\,\frac{d\rho(\mathbf{r})}{d\mu}\,, \tag{A7}$$

and with the approximation (2) we obtain our Eq. (3).

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