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1990 J. Phys.: Condens. Matter 2 SA135

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The generalized effective liquid approximation for the freezing of hard spheres

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Received 9 July 1990

Abstract. The generalized effective liquid approximation (GELA) to the density functional theory of classical non-uniform systems reproduces all the formal properties of the free energy and requires only the direct correlation function of the uniform system as input. In the case of the freezing of hard spheres very accurate free energies, pressures and fluid–solid coexistence data can be obtained from the GELA. The theory predicts, besides the equilibrium FCC solid, metastable BCC and SC phases also.

1. Introduction

The first-principles description of first-order phase transitions is certainly the ultimate goal of equilibrium statistical mechanics. Whereas the phenomenological theory of Landau, based on a series expansion of the free energy in terms of an order parameter, is usually very instructive, it cannot by itself provide a *quantitative* description of the phase transition unless the free energy has been computed by other means. The approximate evaluations of free energies within statistical mechanics can conveniently be divided into three sub-groups. The first main route to the free energy proceeds through the evaluation of the partition function. This route quickly leads to a complicated N -body problem originating from the explicit dependence of the partition function on the system's Hamiltonian. It can thus be followed only when the system is very simple, usually discrete. A second route rests on evaluating first the structural functions from the Born–Green–Yvon hierarchy. Here, continuous systems, with say pairwise interactions, can be treated in principle, but in practice it has turned out to be very difficult to go all the way down from the structural functions corresponding to the given potential to the corresponding free energy, at least for phases that are non-uniform. Finally, in the third route, based on the density functional theory of non-uniform systems, some of these difficulties can be bypassed because this theory provides us directly with an expression for the free energy involving only the one-body density and the two-body direct correlation function.

2. The density functional theory [1]

If we start the description of a classical equilibrium system from the grand potential Ω , viewed as a function of the temperature T and a *functional* of the local chemical potential, $u(\mathbf{r}) = \mu - \varphi(\mathbf{r})$, consisting of the true chemical potential μ and the external potential,

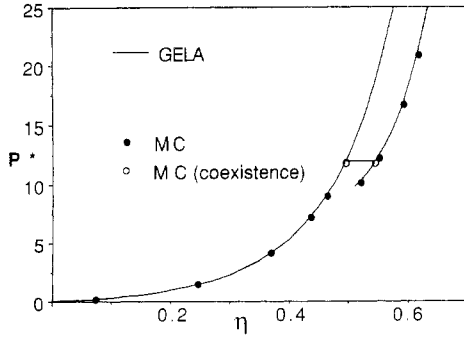


Figure 1. The complete hard-sphere (fluid–FCC) phase diagram in the pressure ($p^* = \beta\rho\sigma^3$)–density ($\eta = (\pi/6)\sigma^3\rho$) plane as obtained from the GELA and compared to the simulation results of [4] (adapted from [3]). Here σ denotes the hard-sphere diameter and β the inverse temperature ($\beta = 1/k_B T$).

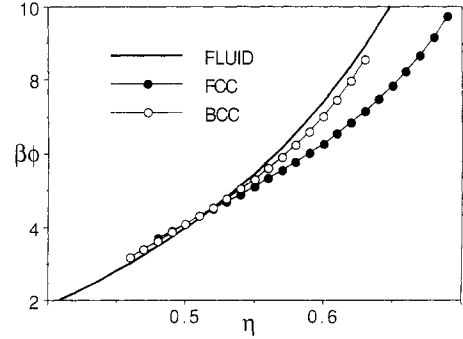


Figure 2. The reduced free energy per particle ($\beta\phi$) versus the packing fraction (η) for the hard-sphere fluid, FCC and BCC solids as obtained from the GELA (adapted from [3]).

$\varphi(\mathbf{r})$ which is specifying the system's boundary conditions (such as its volume, the orientation of the crystal axes, the location of the different phases, and the density profile at the boundaries) and makes any finite system always look formally 'non-uniform', then we may write

$$\Omega = \Omega(T; [u]) \quad (1)$$

where the functional dependence is indicated, as usual, by square brackets. Because there is a unique relation between $u(\mathbf{r})$ and the one-body density, $\rho(\mathbf{r})$, we may eliminate $u(\mathbf{r})$ in favour of $\rho(\mathbf{r})$ by a functional Legendre transformation from the grand potential Ω to the (Helmholtz) free energy F :

$$F(T; [\rho]) = \Omega(T; [u]) + \int d\mathbf{r} u(\mathbf{r}) \frac{\delta\Omega}{\delta u(\mathbf{r})} \quad (2)$$

by using the exact result

$$\delta\Omega/\delta u(\mathbf{r}) = \rho(\mathbf{r}) \quad (3)$$

which implicitly defines $u(\mathbf{r})$ as a functional of $\rho(\mathbf{r})$. The Legendre transformation (2) can then always be inverted as

$$\Omega(T; [u]) = F(T; [\rho]) - \int d\mathbf{r} \rho(\mathbf{r}) \frac{\delta F}{\delta \rho(\mathbf{r})} \quad (4)$$

by using

$$\delta F/\delta \rho(\mathbf{r}) = u(\mathbf{r}) \quad (5)$$

whereas, as for any Legendre transformation, the second-order derivatives are inverses of each other:

$$\int d\mathbf{r}'' \frac{\delta^2 F}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}'')} \frac{\delta^2 \Omega}{\delta u(\mathbf{r}'') \delta u(\mathbf{r}')} = -\delta(\mathbf{r} - \mathbf{r}') \quad (6)$$

which, using the relations ($\beta = 1/k_B T$)

$$(-1/\beta)\delta^2\Omega/\delta u(\mathbf{r}) \delta u(\mathbf{r}') = \rho_2(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') + \delta(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}) \quad (7)$$

$$\beta \delta^2 F/\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')/\rho(\mathbf{r}) - C(\mathbf{r}, \mathbf{r}'; [\rho]) \quad (8)$$

is a statement of the Ornstein–Zernike relation between the pair density, $\rho_2(\mathbf{r}, \mathbf{r}')$, and the direct correlation function (DCF), $C(\mathbf{r}, \mathbf{r}')$. The differential form (8) can also be integrated in density space to yield (Λ being here the cube of the thermal wavelength)

$$\beta F[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) (\ln(\Lambda \rho(\mathbf{r})) - 1) - \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \rho(\mathbf{r}) \rho(\mathbf{r}') C(\mathbf{r}, \mathbf{r}'; [\lambda' \rho]) \quad (9)$$

which is the basic equation of the density functional theory (DFT) relating the free energy F to the structural properties $\rho(\mathbf{r})$ and $C(\mathbf{r}, \mathbf{r}'; [\rho])$.

3. The generalized effective liquid approximation [2, 3]

The first step in an approximate evaluation of the RHS of (9) consists in parametrizing $\rho(\mathbf{r})$ for a given phase. In the present case we will be interested in the liquid–solid transition of a hard-sphere system. In this case it is sufficient to assume that the density of the solid consists of a set of isotropic Gaussian profiles centred on the lattice sites $\{\mathbf{R}\}$:

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \left(\frac{\alpha}{\pi} \right)^{3/2} \exp(-\alpha |\mathbf{r} - \mathbf{R}|^2) \quad (10)$$

so that the freezing transition can be described in terms of a single order parameter α , the inverse width of the Gaussian density profile, with $\alpha > 0$ for the periodic bulk solid and $\alpha = 0$ for the uniform bulk liquid. The major approximation of any DFT concerns then the approximation for $C(\mathbf{r}, \mathbf{r}'; [\rho])$. Since no information about the DCF of a solid is as yet available we will approximate this function by the DCF of an ‘effective’ liquid, $C_0(|\mathbf{r} - \mathbf{r}'|; \hat{\rho})$, of uniform density $\hat{\rho}$. This replacement of an anisotropic DCF by an isotropic DCF is meaningful only under the integral signs of (9), so all angular dependence is averaged out and the correlations in the solid may resemble those of the effective liquid. The remaining point now concerns the determination of the relation between the effective liquid density, $\hat{\rho}$, and the actual density of the solid, $\rho(\mathbf{r})$, which this effective liquid is supposed to describe. This relation will be determined implicitly by imposing self-consistency between the excess free energy per particle of the solid and the excess free energy per particle of the effective liquid. Nowadays it has become customary to write such self-consistency relations in terms of a weighting function, $W(|\mathbf{r}|; [\rho])$, as

$$\hat{\rho}[\rho] = \frac{1}{\rho V} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') W(|\mathbf{r} - \mathbf{r}'|; [\rho]) \quad (11)$$

with ρ the spatial average of $\rho(\mathbf{r})$ over the volume V . The weighting function that characterizes the present generalized effective liquid approximation [3] (GELA) reads then:

$$W(|\mathbf{r}|; [\rho]) = \frac{\int_0^1 d\lambda \int_0^\lambda d\lambda' C_0(|\mathbf{r}|; \hat{\rho}[\lambda' \rho])}{\int_0^1 d\lambda \int_0^\lambda d\lambda' \int d\mathbf{r}' C_0(|\mathbf{r}'|; \lambda' \hat{\rho}[\rho])} \quad (12)$$

where $C_0(|\mathbf{r} - \mathbf{r}'|; \hat{\rho})$ is the DCF of the effective liquid of density $\hat{\rho}$.

Substitution of (12) into (11) yields then the desired self-consistency relation between the effective liquid density $\hat{\rho}$ and the solid density $\rho(\mathbf{r})$ for a given DCF of the liquid. Notice the difference in argument of the DCF in the numerator and in the denominator of (12). This difference, which is implied here by the exact relations of DFT, guarantees then that the formal relations between the approximate free energy of the GELA and the

various DCF remain the same as in the exact DFT and hence also remain exact in the limit of a uniform system ($\rho(\mathbf{r}) \rightarrow \rho$). The somewhat unexpected consequence of this is that the weighting function (12) cannot be normalized, other than for a uniform system, while the self-consistency relation (11) and (12) becomes an integral equation for $\hat{\rho}[\rho]$ instead of a simple transcendental equation. We have found that this integral equation can be solved by expanding $\hat{\rho}[\lambda\rho]$ around either $\lambda = 0$ or $\lambda = 1$ with good convergence properties in both cases.

4. The freezing of hard spheres [3]

The hard-sphere system is a very convenient testing ground for all freezing theories of the above type because, first of all, the temperature scales out and so the only independent thermodynamic variable left over is the density, while the DCF of the fluid, which is required as input, is available in analytic form within the Percus–Yevick approximation which is fairly accurate for hard spheres. When the GELA is worked out for the FCC hard-sphere solid very good agreement with the computer simulations is found (see figure 1). When the Carnahan–Starling equation of state is adopted for the hard-sphere fluid the fluid–solid coexistence data obtained from the GELA are almost indistinguishable from the simulation results (see figure 1). The only exception concerns the Lindemann parameter which is a structural property, while the theory was set out to determine the thermodynamic properties of the solid. Such structural properties are expected to be more sensitive to the parametrization of the density in terms of *isotropic* Gaussians (see (10)) than the thermodynamic properties themselves. Besides its high accuracy, the GELA has also the advantage over other DFT of hard-sphere freezing that it predicts metastable BCC and SC hard-sphere solids (see figure 2). This is important if one wants to set up a hard-sphere perturbation theory of freezing to study softer potentials for which the FCC structure is not the equilibrium structure.

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