PHYSICAL REVIEW E, VOLUME 64, 062501

Classical density functional theory of freezing in simple fluids: Numerically induced false solutions

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(Received 7 June 2001; published 9 November 2001)

Density functional theory (DFT) has provided many insights into the freezing of simple fluids. Several analytical and numerical solution have shown that the DFT provides an accurate description of freezing of hard spheres and their mixtures. Compared to other techniques, numerical, grid-based algorithms for solving the DFT equations have more variational freedom and are capable of describing subtle behavior, as that seen in mixtures with multipeaked density profiles. However the grid-based approach is sensitive to the coarseness of the mesh employed. Here we summarize how the granularity of the mesh affects the freezing point within the DFT. For coarse meshes, we show that the freezing point is masked by numerically induced false minima of the DFT grand potential. These false minima are removed when a fine enough grid is used to represent properly the density profiles. Our results suggest that others using such grid-based methods have focused on such numerical artifacts that have little to do with real phenomena.

DOI: 10.1103/PhysRevE.64.062501 PACS number(s): 64.60.Cn, 61.66.Dk, 71.20.Be

Recently, we have shown that the additional variational freedom offered by refined grid-based solutions of the liquid-solid freezing point within density functional theory (DFT) for binary hard (or soft) spheres lead to new (multipeaked) density distributions [1]. Our results show that the often used Gaussian or plane-wave densities are an inadequate basis to solve the general freezing problem in mixed sphere systems [1]. Nonetheless, we show here that care also must be taken when using grid-based methods because they can lead to false (numerically induced) minima in the DFT grand potential. Besides revealing the different minima obtained with finer grids than typically used, these calculations show that the separation between adjacent grid points must be smaller than the operative Lindemann parameter to obtain solutions that reflect the continuum limit.

Although the results given here should reflect generic behavior, we show the effect only for a discrete version of the Ramakrishnan and Yussouff density functional theory (RY-DFT) [2]. Within the RY-DFT, the grand potential difference $\Omega-\Omega_0$ between the inhomogeneous and homogeneous fluid [with densities $\rho(r)$ and ρ_0, respectively] is given by

$$\beta(\Omega-\Omega_0)=v_0\sum_i\left[\rho_i\ln\frac{\rho_i}{\rho_0}-(\rho_i-\rho_0)\right]-\frac{v_0^2}{2}\sum_q C_q\Delta\rho_q\Delta\rho_{-q}, \tag{1}$$

where $\Delta\rho=\rho-\rho_0$ and $\beta=(k_BT)^{-1}$ is inverse temperature. We divide the cubic unit cell of volume L^3 into N^3 small subcells of volume a_0^3, with $a_0=L/N$ and $v_0=a_0^3$. In each of these small subcells, denoted by i, we denote the (average) density to be ρ_i. The index in the first sum of Eq. (1) is over all cells, while in the second sum the index refers to all allowed values in reciprocal space, and where $\Delta\rho_q$ is the spatial Fourier transform of $\Delta\rho$. The ideal part of the grand potential energy is most easily expressed as finite sum in real space. The excess grand potential [the last term of Eq. (1)] is also a finite sum, albeit in Fourier space. The last term is handled in this manner due to computational efficiency and, in the case of hard spheres, overcoming the problems brought on by the discontinuity in the direct correlation function (DCF) in real space [1]. The DCF C_q is the value at the midpoint of any small cell in Fourier space where $-\pi N/L<q_x<\pi(N-1)/L$, which is consistent with the finite grid size. Here we are interested in solutions corresponding to the liquid-to-solid transition. Thus, we look for a solution that is periodic and is given by simple unit cells with the usual periodic boundary conditions. A similar method has been used to study crystal-fluid interfaces in hard spheres and Lennard-Jones systems [3] and glassy states in hard spheres [4].

For each reference density ρ_0 and each lattice constant L, we minimized the grand potential difference iteratively using the method of steepest descent (see Ref. [1] for details),

$$\rho_i'=\rho_i-\Delta t\,\frac{\partial\beta(\Omega-\Omega_0)}{\partial\rho_i}, \tag{2}$$

where ρ_i' and ρ_i are the new and old values of the site density, respectively. The step size Δt is an arbitrary number chosen to be small enough such that we obtain convergence, yet not too small to be computationally inefficient. With this method, we calculate stable (i.e., $\beta(\Omega-\Omega_0)\leqslant 0$) or metastable structures of the underlying crystal. The minimum where $\beta(\Omega-\Omega_0)=0$ represents the coexistence of the two phases. Thus the locus of such minima determines the phase diagram.

In our iterative procedure, the initial density is chosen close to the equilibrium structures that are expected to form. For example, we expect the fcc solution for hard spheres, and we define the initial density distribution to be a δ function positioned at each site of the fcc lattice. Thus, only the ρ_i at the four sites of the fcc unit cell are set to be nonzero. The grand potential difference is now minimized with respect to the lattice constant L for different liquid densities ρ_0, until we find where the minimum that corresponds to the case $\beta(\Omega-\Omega_0)=0$, the coexistence of the liquid and solid phases. In this way we can obtain the density profile and lattice constant at coexistence.

It is important to note that we are not doing a constrained minimization. We do not impose any relation between the solid density and the lattice constant, so the perfect crystal is not necessarily a minimum of the grand potential. The only constraints in our calculation are those imposed by the periodic boundary conditions and the (cubic) unit cell shape that we use (in general, of course, all of these may be varied beyond what was used here). Previously, we have detailed the importance of having this increased variational freedom in the representation of the density for binary mixtures of hard (or soft) spheres. Specifically, we found significant deviations in the density from Gaussian (or plane-wave) solutions due to the appearance of more stable multipeaked density profiles for the smaller size spheres [1]. This approach produced a rich phase diagram, which included an fcc solid-solution, NaCl and "sublattice melt" phases.

The granularity of the mesh is critical for the results to be meaningful. We found that the separation between adjacent grid points a_0 should be smaller than the spread of the peaks in the density. In the Gaussian method, it would be equivalent to $a_0<\epsilon$, where ϵ is the Gaussian width. By way of example, for $N=64$ and with a lattice constant of $L=1.5\sigma$, the grid size is $a_0\approx 0.02\sigma$, and the spread of the Gaussian is $\epsilon\approx 0.04\sigma$. In such a case, the grid size is small enough for us to be confident in the numerical results.

RESULTS AND DISCUSSION

Our results are summarized in Fig. 1, where we show the effect of the granularity in the calculations for freezing of (single-component) hard spheres. The calculation is performed within a cube of side L with periodic boundary conditions. The iterative procedure is started as described above, and thus L becomes the fcc lattice constant when the appropriate minimum is found. This large cube is broken into small cubes with side L/N defining the mesh. The difference in grand potentials has been explored as a function of lattice constant L for *four* different grids corresponding to values of $N=8$, 16, 32, and 64 at a fixed density. At density of $\rho_0=0.9445$, we show that the curves for $N=32$ and $N=64$ have a common minimum for which $\beta(\Omega-\Omega_0)\approx 0$ and is located at $L=1.5075$. This value of L corresponds to a nearest neighbor distance of $L/\sqrt{2}=1.065\,96$, near which Jones and Mohanty [6] find that hard spheres freeze. Specifically, Jones and Mohanty found a value of $\rho_0=0.9461$ with a nearest neighbor distant of 1.0647 and with a Lindemman parameter of 0.048 σ, which is of the order of (or smaller than) the grid granularity for $N=32$ at the freezing density.

In the figure, we show that the calculated grand potential differences have minima that are strongly dependent upon the granularity of the grid. For particular grids, we find two minima—one being an artifact of the grid size a_0. For the finest grids used, where the large cube is divided into 64^3 (i.e., $N=64$) blocks, two minima are found. The first minima is located at a lattice constant $L\approx 1.51\sigma$; the other at $L\approx 1.43\sigma$. The former corresponds to that found by Jones and Mohanty [6]. The latter is an artifact of the grid used, shifting as N is varied; for $N=32$, the artificial minimum occurs at $L\approx 1.46\sigma$. For $N=8$ and $N=16$, no longer does the grand potential difference exhibit two minima, but only a single, grid-size dependent (nonphysical) minimum.

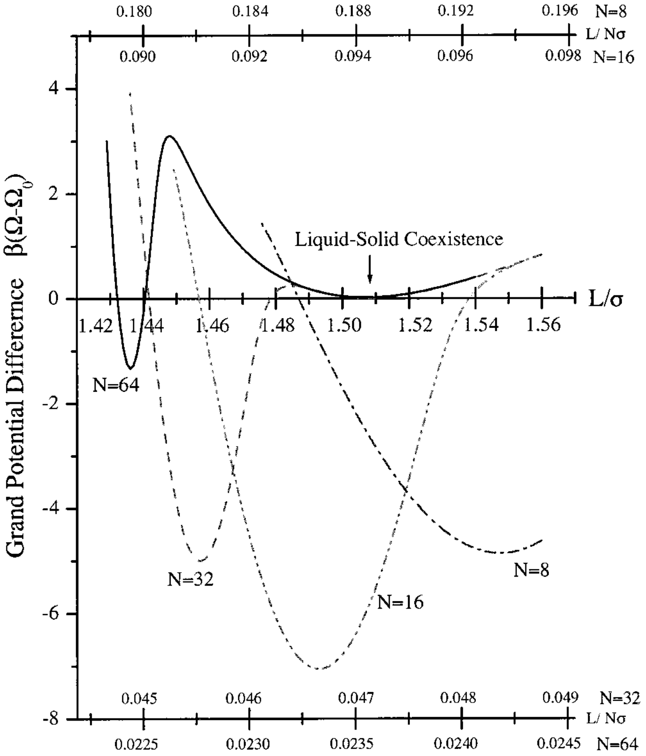

FIG. 1. Difference in the grand potential $\beta(\Omega-\Omega_0)$ plotted as a function of the fcc lattice constant L for different mesh granularities, i.e., for $N=8$, 16, 32, and 64. Also shown, for each N, are the separations between adjacent grid points, $a_0=L/N\sigma$ in units of the hard sphere diameter σ.

What is the origin of these false minima? If one looks closely at the densities that correspond to the "false" minima, one finds that the peaks in the density have no spread (for all N) and are contained within a single mesh point. Typically, a Gaussian representation of the density is thought to be reasonable for single-component spheres. At these false minima, the grid size a_0 is larger than the Gaussian width (or Lindemann parameter)—the discrete method fails to represent accurately the density. In particular, we find that a relatively fine mesh is necessary; values of $N=8$ (with $a_0\approx 0.19\sigma$) or $N=16$ (with $a_0\approx 0.09\sigma$) are insufficient as adjacent grid points are separated by distances larger than the expected Lindemann parameter (or Gaussian width) 0.04 σ. We note that in other cases (e.g., mixtures [1]) the Gaussian representation may also fail to describe the density. Thus, in all cases, the grid-based approach can accurately and reliably describe the density profiles (including multiple peaks) and physical minima if care is taken in the choice of the grid granularity.

In the past, Dasgupta [4], and Dasgupta and Valls [5] have exploited grid-based methods to study the formation of glasses and the grand potential landscape in single-component hard spheres. However, they used grids such that peaks in the densities were contained within a single mesh point. The results shown in this paper cast doubt on their results. Their solutions found for amorphous solids (given by a minimum in the grand potential) may be simply artifacts of the coarseness of the mesh used, and the resulting poor representation of the density.

To summarize, in this paper we have explored the numerics of grid-based DFT solutions describing freezing in single-component systems, and have uncovered artifacts and unphysical behavior that have affected works of others. We have shown that unbiased numerical solution of the Ramakrishnan and Yussouff density functional theory [2] for freezing can provide accurate solutions, but care must be taken to test the grid granularity needed for a sufficient representation of the densities. Any structure of the density should extend over several grid elements (i.e., the Lindemman parameter must be greater than the separation of adacent points on the grid).

This research was supported by the National Science Foundation Grant No. DMR-9531223 (M.V. and F.J.P.), the U.S. Department of Energy Grant Nos. DE-FG02-96ER45439 with Frederick Seitz Materials Research Laboratory and by DE-AC04-94AL85000 with Sandia (D.D.J.).

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