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

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In a recent numerical study [Phys. Rev. E **64**, 062501 (2001)] of a discretized free-energy functional for the freezing of a hard-sphere fluid, Valera, Pinski, and Johnson (VPJ) found unphysical, spurious free-energy minima. They concluded that free-energy minima obtained in similar previous work on hard spheres using relatively coarse discretization scales were also numerical artifacts. We show here that this conclusion is erroneous: the qualitatively unphysical results found by VPJ do not originate from the coarseness of the mesh but, rather, are themselves artifacts arising from the particular way in which VPJ discretize the direct correlation function. When a more appropriate discretization scheme is used, as in our own earlier work, the results are physical.

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In a recent numerical study [1] of the freezing of a hard-sphere fluid using a discretized form of the Ramakrishnan-Yussouff (RY) free-energy functional [2], Valera, Pinski, and Johnson (VPJ) find certain unphysical, spurious free-energy minima. They attribute the presence of these minima to the coarseness of the mesh size used in the discretization procedure. They then state that the inhomogeneous (crystalline and glassy) free-energy minima obtained in our earlier studies [3] (see also Ref. [4]) using relatively coarse mesh sizes are also "false" and "numerical artifacts that have little to do with real phenomena." In this Comment, we show that the results on which the claim of VPJ is based are themselves artifacts of the way in which they define the discretized direct pair correlation function in the expression for the discretized RY free-energy functional. Our own results [3,4] are derived using a different scheme that is free of the pathologies encountered by VPJ.

The RY theory expresses the grand potential difference $\Delta\Omega$ between an inhomogeneous state, characterized by the time-averaged local density $\rho(\mathbf{r})$, and the uniform liquid of density ρ_0, as a functional of $\rho(\mathbf{r})$. In numerical, grid-based methods [1,3,4] for finding the minima of the RY free energy functional, a cubic computational cell of volume L^3 with periodic boundary conditions is divided into N^3 subcells, each of volume h^3, where $h \equiv L/N$ is the mesh size. In terms of the coarse-grained density variables $\{\rho_i\}$, where $\rho_i \equiv \int_{v_i}\rho(\mathbf{r})d\mathbf{r}$, v_i being the volume contained in the ith subcell, the dimensionless grand potential difference for the discretized system has the form

$$\beta\Delta\Omega = \sum_i \{\rho_i \ln(\rho_i/\rho_\ell) - (\rho_i - \rho_\ell)\} - \frac{1}{2}\sum_i \sum_j C_{ij}(\rho_i - \rho_\ell)(\rho_j - \rho_\ell), \qquad (1)$$

where the sums are over all the subcells of the computational mesh, $\rho_\ell \equiv \rho_0 h^3$, and C_{ij} is a suitably defined discretized form of the direct pair correlation function $C(r)$ [5] of the uniform liquid. For a fluid of hard spheres of diameter σ and dimensionless density $n^* \equiv \rho_0\sigma^3$, an analytic expression for $C(r)$ can be obtained from the Percus-Yevick (PY) approximation [5].

The key point leading to the unphysical results of VPJ is the specific discretization scheme they used for obtaining C_{ij}, not the overall scale h. In the calculations of VPJ, C_{ij} is obtained [1,6] using the "Fourier space" form:

$$C_{ij} = \frac{1}{L^3}\sum_{\mathbf{q}} \tilde{C}(q) e^{i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)}, \qquad (2)$$

where $\tilde{C}(q)$ is the analytically calculated Fourier transform of the continuum PY $C(r)$ [5], and $\mathbf{r}_i$ denotes the location of the ith subcell. The sum over $\mathbf{q}$ in Eq. (2) is restricted to the "first Brillouin zone" of the computational lattice, so that $|q_\mu| \leqslant \pi/h$, $\mu = x,y,z$. This cutoff has an important effect on the results, as will be seen here.

In Ref. [1], upon minimizing $\beta\Delta\Omega$ as given by Eq. (1) [with C_{ij} given by Eq. (2)] with respect to $\{\rho_i\}$ for different values of L and N, minima corresponding to crystalline fcc states are found if n^* is sufficiently large. For relatively small values of N ($N=8$ and $N=16$), $\beta\Delta\Omega$ for the crystalline state exhibits, as a function of L, a single minimum near $L \approx 1.5\sigma$. For larger N, $\beta\Delta\Omega$ exhibits, in addition to the physical minimum near $L = 1.51\sigma$, a second, "false" minimum at a smaller value of L. The density distribution around

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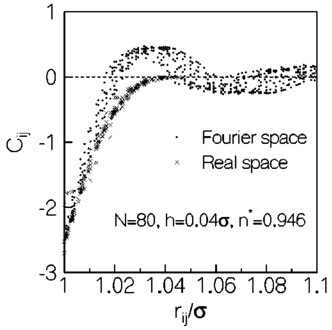

FIG. 1. Plots of C_{ij}, the discrete form of the direct pair correlation function, as a function of r_{ij}, the separation between subcells i and j. Results obtained for $n^*=0.946$, $h=0.04\sigma$, $N=80$, using the real-space prescription (crosses) are compared with those obtained using the Fourier-space prescription (dots). The results represented by the crosses identically vanish beyond $r_{ij}\simeq 1.04\sigma$.

a lattice point of these false minima is almost entirely contained within one subcell. VPJ infer that these spurious minima occur because the mesh size used cannot resolve the density distribution around a lattice point of these minima. Since h is comparable to or larger than the width of the density distribution around a lattice point of the minima found for $N=16$ and $N=8$, they conclude that these minima (and similar minima obtained in our earlier studies using comparable values of h) must also be false.

This conclusion concerning our previous work is in error: in our calculations [3,4], we used a different prescription for calculating the C_{ij} appearing in Eq. (1). We obtained this quantity in coordinate space using the expression

$$C_{ij}=\frac{1}{h^6}\int_{v_i}d\mathbf{r}_1\int_{v_j}d\mathbf{r}_2 C(|\mathbf{r}_1-\mathbf{r}_2|), \qquad (3)$$

where v_i represents the volume contained in the subcell i, and $C(r)$ is the analytical PY expression. In Fig. 1, we compare the C_{ij} calculated from Eq. (2) with that obtained from the real-space prescription, Eq. (3). The data shown are for $n^*=0.946$, $L=3.2\sigma$, and $N=80$ ($h=0.04\sigma$). The scatter of the data points arises because C_{ij} is not uniquely determined by the separation $r_{ij}\equiv|\mathbf{r}_i-\mathbf{r}_j|$ between subcells i and j. Only the data for $r_{ij}\geqslant\sigma$ are shown because the values of C_{ij} obtained from the two methods are quite similar for smaller values of r_{ij}. C_{ij} remains nonzero for a small region beyond $r_{ij}=\sigma$ because the distance between a point in subcell i and a point in subcell j may be less than σ even if the distance between the centers of the two subcells exceeds σ. The real-space C_{ij} is always less than or equal to zero, correctly reflecting that the exact PY $C(r)$ is bounded from above by zero [5]. On the other hand, the C_{ij} obtained from Eq. (2) exhibits damped oscillations beyond $r_{ij}=\sigma$, taking *positive values* in a region of width $\approx h$. These oscillations arise from the use of a finite number of Fourier components to approximate the PY $C(r)$, which is discontinuous at $r=\sigma$. Since the PY $C(r)$ is strictly nonpositive, the positive values of C_{ij} found in the Fourier-space construction are artifacts of this way of defining C_{ij}.

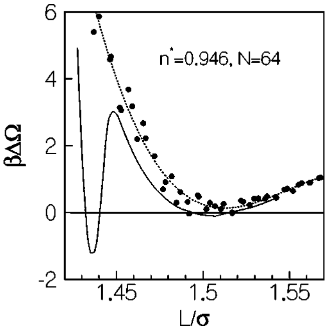

FIG. 2. Plots of the dimensionless grand potential difference $\beta\Delta\Omega$ as a function of L, the size of the cubic unit cell of a fcc crystal. Results obtained for $n^*=0.946$, $N=64$, are shown for both the real-space method (full circles) and the Fourier-space method (solid line) of defining C_{ij}. The dashed line is a polynomial fit to the data obtained using the real-space method.

When we repeated the calculations of VPJ with the real-space C_{ij}, we found that the "false" minima found by VPJ for $N=32$ and $N=64$ *do not exist* if this form for C_{ij} is used. In Fig. 2, which precisely reflects the figure in Ref. [1], we have shown the results for $\beta\Delta\Omega$ as a function of L for $n^*=0.946$ and $N=64$. Our calculation using the Fourier-space C_{ij} reproduces the results of VPJ, showing a relatively shallow physical minimum with slightly negative $\beta\Delta\Omega$ near $L=1.51\sigma$, and a deeper false minimum near $L=1.435\sigma$. The data points obtained for the real-space C_{ij} show slight irregularities at small scales, because the number of subcells j for which C_{ij} is nonzero for a fixed i varies as L is changed at fixed N. The large-scale behavior of $\beta\Delta\Omega$ as a function of L is, however, quite clear, as shown by the dashed line that represents a smooth polynomial fit to the data points. There is only one minimum, near $L=1.5\sigma$ with $\beta\Delta\Omega$ close to zero. The density distribution at this minimum is very similar to that at the physical minimum obtained using the Fourier-space C_{ij}. The "false" minimum near $L=1.435\sigma$ *is not found in our calculation*. We do not find any crystalline state for $L<1.437\sigma$. Since the conclusion of VPJ about the unphysical nature of the minima obtained for coarse mesh sizes is based entirely on the existence of the "false" minima for $N=32$ and $N=64$, the nonexistence of such minima for our real-space C_{ij} invalidates their argument about the nature of the minima obtained in our earlier work.

Using the real-space C_{ij}, we find qualitatively similar behavior for smaller values of N: for $N=16$, we find a minimum with $\beta\Delta\Omega\simeq-0.5$ near $L=1.51\sigma$, and no crystalline state for $L<1.506\sigma$, and for $L=8$, a minimum with $\beta\Delta\Omega\simeq-1.9$ is found near $L=1.545\sigma$, and no crystalline state is found for $L<1.538\sigma$. Thus, the qualitative results are similar to those at larger N. In some of our calculations [3,4], we used an approximation in which C_{ij} is set to zero if r_{ij} is greater than a cutoff $r_0\geqslant\sigma$. The irregularity in the dependence of $\beta\Delta\Omega$ on L increases when a cutoff $r_0\approx\sigma$ is used. However, we do not find any change in the *qualitative* behavior as N is varied in the range $8\leqslant N\leqslant 64$. These results contradict the conclusion of VPJ about the unphysical nature of the minima obtained for relatively small N.

The results shown in Fig. 1 provide an understanding of the origin of the false minima found by VPJ for $N=64$ and $N=32$. For $N=64$, the spurious minimum occurs near $L=1.435\sigma$, when the spacing between two nearest-neighbor lattice points is $L/\sqrt{2}\simeq 1.0147\sigma$. The observed behavior of the Fourier-space C_{ij} for $r_{ij}\gtrsim\sigma$ suggests that for this system $C_{ij}>0$ if the subcells i and j represent two neighboring lattice points. Indeed, we have found that the value of C_{ij} for such pairs of subcells is close to 1.44 for $L=1.435\sigma$, $N=64$ at $n^*=0.946$. Since the values of ρ_i and ρ_j are close to unity for such subcells, the contribution to the second term in Eq. (1) from such pairs of subcells is negative and relatively large in magnitude. This, we believe, is the reason for the occurrence of the false minima found by VPJ. This is well supported by the absence of spurious minima when the real-space C_{ij}, which is never positive, is used.

Thus, our results show that VPJ's conclusion about the coarseness of the mesh being responsible for the occurrence of the ‘‘false’’ minima is erroneous. Rather, the positive values of C_{ij}, which are artifacts of the Fourier-space method for calculating this quantity, are at the origin of these spurious minima. These artifacts disappear when a more appropriate method, developed in our earlier work, is used to define C_{ij}. We *do not* claim that the results of calculations using coarse mesh sizes are *quantitatively* as accurate as those obtained with finer meshes. Our studies of glassy states were carried out, for practical reasons, using relatively coarse mesh sizes. We believe that the results obtained in these studies are qualitatively correct and physical.

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