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

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Recently we solved, via discrete numerical grids, the Ramakrishna-Yossouff density-functional theory equations for the freezing transition and obtained an intricate phase diagram of hard-sphere mixtures. Even though such methods provide more variational freedom than basis-set methods, we found that the thermodynamic quantities were sensitive to the spacing of numerical grids employed and observed numerically induced false minima. Dasgupta and Valls have commented that these false minima were due to our use of *k*-space methods and, hence, their early works based on a fully *r*-space approach are qualitatively correct, despite also being sensitive to the mesh granularity. Here, we clarify the issues of achieving correct thermodynamic limit from grid-based methods and respond to their Comment, concluding that *r*-space calculations using coarse meshes may provide correct thermodynamic quantities (only by extrapolation) and thus their previous work should be called into question. In general, both methods, *k*-space or *r*-space, suffer from grid-induced problems.

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In our recent paper, Valera, Pinski, and Johnson (VPJ) [1] found solutions to the Ramakrishna-Yossouff (RY) density-functional theory (DFT) equations describing the freezing transition of hard spheres [2]. These solutions were generated using a discrete mesh and parts of the calculations were done using a Fourier transform (i.e., *k* space). Our work included a careful study of the effects due to the granularity of the meshes employed [3]. We found significant shifts in the minima in the grand-potential difference between the liquid and solid phases as a function of this granularity. In addition, for relatively finely spaced meshes, we found numerically induced false minima. The main conclusion in our paper was that the granularity of the mesh influenced the accuracy of calculations of thermodynamic functions. We then added that this mesh sensitivity "casts doubt" on the previous work of Dasgupta and Valls [4,5] who used rather coarse discrete meshes, albeit their calculations were done entirely in real space.

In response, Dasgupta and Valls (DV) have taken issue with our paper and have written a Comment [6] to defend their previous results as being physical even though the meshes employed were rather coarse. Before addressing the DV comments, we make several general and salient points to clarify and delineate the key issues. Afterwards we attempt to enumerate specific items to help resolving the apparent controversy. We conclude that one must understand the effects of the parameters introduced by the numerical method employed and be cautious in extrapolating to the continuum or thermodynamic limit.

The main issue to keep clear is that both the groups are interested in calculating physical properties to describe freezing based on calculations of the same thermodynamic quantities within the same theoretical framework. The key equation to be solved is the classical DFT description of freezing based on RY expansion of the grand potential [2]. The difference in the grand potential $\Delta\Omega$ between the reference homogeneous state with density ρ_o and the inhomogeneous state with density $\rho(\vec{r})$ is approximated by

$$\beta\Delta\Omega=\int d\vec{r}_i\{\rho(\vec{r}_i)\ln[\rho(\vec{r}_i)/\rho_o]-(\rho(\vec{r}_i)-\rho_o)\} -\frac{1}{2}\int\int d\vec{r}_i d\vec{r}_j C(\vec{r}_{ij})(\rho(\vec{r}_i)-\rho_o)(\rho(\vec{r}_j)-\rho_o), \tag{1}$$

where $c(r)$ is the direct correlation function and β is related to the inverse temperature. In particular, the freezing point is defined when an inhomogeneous density is found that gives a vanishing grand-potential difference, such that any density fluctuation produces a positive contribution to this difference, and, in addition, the pressure difference is zero. To solve for this inhomogeneous density a numerical method must be employed, which, by its very nature, is approximate. Both the groups (DV and VPJ) use a mesh-based approach to solve these equations, as compared to basis-set (e.g., Gaussian and plane-wave) methods that have been employed previously. Mesh-based approaches are less restrictive and more robust [1]. However, the continuum limit of discrete numerical solutions may not provide an accurate representation of the thermodynamics as expressed in Eq. (1).

In a broader context, discrete numerical methods for solving many physical and mathematical equations suffer from having different, and potentially incorrect, solutions when compared to the continuum limit. It is well known in lattice gauge theories, for example, that elements of the underlying lattice manifest themselves in nonphysical behavior. Also, notably, the rich structure of the standard logistic map of chaos theory is lost if one considers the differential equation that results by taking the continuum limit of the relevant difference equation.

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For thermodynamic solutions, the continuum limit is required. Solutions of the numerical equations depend upon the coarseness of the grid-meshing employed, as we originally identified [3]. Both DV and VPJ assume that the continuum limit will produce correct thermodynamic solutions of Eq. (1). The expectation is that, with an appropriately fine mesh, convergence will be found for the thermodynamic properties of interest. In other words, the ''correct'' physical solution is identified independent of the artifacts introduced by using a grid. In our paper [3], we identified numerically false solutions for mesh spacings larger than the widths of the physical density profiles (i.e., larger than the Lindemann parameter). Indeed, with fine enough grids, the physical and numerically induced solutions were apparent. The main controversy between DV and VPJ is embedded in the fact that both the groups have solutions that are dependent on the granularity of the mesh, albeit differently. Thus, both groups must ensure that their solutions are independent of this granularity to obtain physical thermodynamic values. VPJ verified the convergence of the thermodynamic results on granularity of the mesh [3] and used such method to investigate the phase diagram of binary mixtures [1].

Methods, based either in *k* space and *r* space, when solved with a discrete mesh have advantages and drawbacks. As stated above, both the approaches provide more variational freedom than basis-set methods. The *k*-space method is intrinsically faster than the *r*-space method if $c(r)$ is spatially extended (due to the use of fast Fourier transforms). In addition, for the *k*-space method, because of the underlying plane-wave basis, the effects from discontinuities arising from a mesh are minimized in the second term of Eq. (1), in contrast to *r* space where some other method for smearing $c(r)$ has to be used. The major drawback of the *k*-space method is that there can be an associated Gibbs' phenomenon for representing the discontinuities in $c(r)$, as pointed out in the Comment of DV.

In many cases, the Percus-Yevick (PY) approximation for $c(r)$ is used. Within this approximation, $c(r)$ is zero for distances beyond the hard-sphere diameter d_{HS} with a discrete step in $c(r)$ at d_{HS}. Dasgupta and Valls' comment attributes the numerically false solutions found in our paper to the overshoot in $c(r)$ caused by the use of a discrete Fourier transform. Such an overshoot is typical of a Gibbs' phenomenon arising from the transform of the steplike functional behavior in $c(r)$. The *r*-space solutions using the PY-based $c(r)$ indeed, as DV have verified, do not show the additional false minimum found, using *k* space, see Fig. 1 of the preceeding paper [6]. Nonetheless, the *r*-space solutions do suffer from the use of discrete grids. The solutions found by DV show sensitivity of thermodynamic functions to grid sizes, as we originally stated in our paper.

Thus we agree with the finding of DV that our use of *k* space produces an effective $c(r)$ that is slightly positive at distances beyond the hard-sphere diameter, contrary to the PY form. We also agree that the false minima we found arise from this representation, but, as we concluded, with fine enough mesh the physical solutions are correctly identified. However, DV then, without further support, conclude that their previously reported *r*-space solutions are not potentially in error, even though those solutions are based on coarse grids.

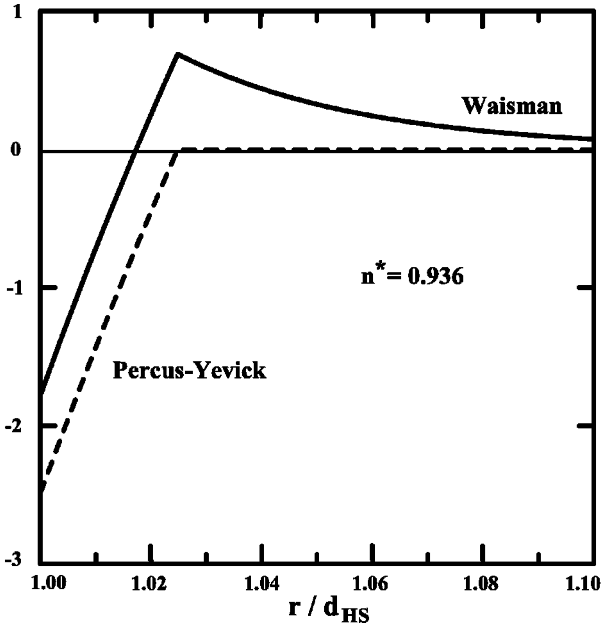

FIG. 1. The direct correlation function for hard spheres $\overline{C}(r)$ is plotted as a function of scaled distance, r/d_{HS} for a density $n^* = 0.936$. The function $\overline{C}(r)$ is the volume average of $c(r)$; the volume used is δ^3 where $\delta = 0.04 d_{HS}$. The solid line represents the Waisman parametrization [9], while the dashed line is the analytic Percus-Yevick solution [8].

That this reasoning is logically faulty can be seen as follows. First, the sensitivity of the thermodynamic quantities to the coarseness of the grid exists in both the *r*-space and *k*-space methods, a point on which both groups apparently agree. Second, the behavior of such quantities calculated with fine grids, and the existence (or not) of false secondary minima, is a separate issue. In fact, as noted above, the continuum (thermodynamic) limit is the only one of physical interest.

Now, consider calculations using coarse meshes that are typical of those used by DV. As we have shown [3], the grand potential difference has significant variation of its minima as the mesh coarsens. In their comment [6], DV agree that there is a quantitative change, with the location of the minimum in the grand-potential difference shifting from $L \sim 1.51 d_{HS}$ to $1.55 d_{HS}$. In addition, the values of the grand-potential difference do not lie on a smooth curve when viewed as a function of ''lattice constant'' of the inhomogeneous density, see Fig. 1 of their comment [6]. In that plot, the scatter in the *r*-space-generated values are a result of the interplay of the coarse mesh with the spatial variation of $c(r)$ when evaluating the second term in Eq. (1). Clearly, the smoothing method for calculating $c(r)$ employed by DV [Eq. (3) of their comment [6]] is insufficient to eliminate the above-mentioned scatter, which affects all thermodynamic quantities including the pressure. We believe that both the groups are in agreement on these points. In addition, any free-energy landscape will be affected by such discontinuities in thermodynamic functions.

We, now address what happens when refining the grid to achieve the continuum limit. Ostensibly both groups were using the PY approximation to $c(r)$, which is identically zero for values of r beyond the hard-sphere diameter. DV trace the existence of our false minima to the k-space effective $c(r)$ being slightly positive outside hard-sphere diameter (a Gibb's overshoot). However, more accurate representations of $c(r)$ are also positive in this region. In paricular, we plot in the accompanying figure the direct correlation in the Percus-Yevick [8] approximation along with the better parametrization by Waisman [9]. To approximate the ''smearing'' in DV's r-space method, we averaged $c(r)$ over a volume equal to that of one of their smaller elements. The comparison of this plot with that of DV in their Comment [6] shows that fortuitously the Gibbs overshoot gives a shift of almost identically the same form and magnitude as if one had used a better approximation to $c(r)$. Thus, more accurate DFT calculations would necessarily produce similar numerically induced false minima. Indeed, as DV show in Fig. 1 of their comment [6], an r-space solution using such a $c(r)$ (with nonzero positive weight beyond the hard-sphere diameter) does yield the grid-sensitive false minimum that we described using a k-space method [3]. Such a false minimum must be considered as an artifact of the use of a mesh and not due to the k-space method in and of itself. Hence, one must employ a finely spaced mesh (in either r or k space) to obtain accurate thermodynamic functions, which was the main message of our original work [3].

As DV stated in their comment [6] for the r-space method, quantitative differences arise from coarsening the mesh, which is similar to what we had previously shown (see Fig. 1 of Ref. [3]) for k-space results. They still need to substantiate why they ''believe'' that their coarse-mesh solutions are qualitatively correct, and are not dramatically affected by mesh coarseness. In their comment, they could have addressed this issue by plotting the grand-potential (and pressure) difference for several mesh spacings and including the resultant mesh-dependent scatter, since in their comment they describe such results for a range of granularities. However, they chose not to do so.

To summarize, using either r-space or k-space based methods, the dependencies on the granularity of the mesh must be understood and eliminated to obtain the correct thermodynamics, as we did so in our paper for a k-space method [3]. Numerically induced false minima will occur when using more realistic forms of $c(r)$ in both, r-space and k-space methods, as seen in calculations done by both groups [3,6]. And, finally, one should be careful in extrapolating results obtained from such calculations to the thermodynamic limit, a point in agreement with the sentiments in the last paragraph of Dagupta and Valls' 1999 article [7].

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