Comment on "New phase for one-component hard spheres" [J. Chem. Phys. 120, 11686 (2004)]

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In a recent paper, Wu and Sadus[1] claim the existence of a new third thermodynamic stable phase for a hard sphere system based on computer simulations. The phase is obtained via a slow compression of near-freezing configurations, and is found at volume fractions between $\eta = 0.508$ and $\eta = 0.686$.

The claim that this phase is neither liquid nor solid, is based on the observation that the compressibility factor is found to lie between that of the liquid and solid. In addition, structural properties such as the radial distribution function and other order parameters do not coincide with that of either of the two phases.

Although it is not impossible that unexpected behavior is found in a system that has been studied in great detail and thought to be fully understood, the claim that this traditional system, that of one-component hard spheres, shows a third, and so far unknown, stable phase, on the basis of the evidence shown, is at least premature. Without other indications, a much more likely explanation would be that the observed phase is a microscopic coexistence between liquid and solid, or the presence of crystalline grain boundaries.

One major concern is that the simulations are performed in the canonical ensemble, rather than in the isobaric ensemble. This allows for the possibility of microphase separation, and complicates the structural analysis enormously. Hence, before measuring any quantity, one should ensure that one only consider a single phase, and not possibly a partly liquid and partly solid phase, or two or more crystal regions with different orientations.

Moreover, it appears that the simulations of Ref. 1 have been performed in a cubic simulation box. For reasons of symmetry this is allowed for the liquid phase. The presence of a solid phase, however, will break the isotropic symmetry. If the crystal orientation of the solid does not match that of the simulation box, e.g., when the crystal is rotated, a cubic simulation box will lead to the presence of stress in the system and an anisotropic pressure tensor. Unfortunately, this has not been checked.

The radial distribution function that is found to be in between that for the liquid and solid, i.e., what one would obtain if one has a coexistent liquid and solid phase in a single simulation box, and for small number of particles (500) the presence of different crystallites and grain boundaries will also destroy the pure crystal radial distribution function. The snapshot that is shown of the phase, is difficult to judge, because it is a partial projection of several configurations. The order that appears to be present, however, points to some kind of order that is not aligned with the simulation box, e.g., a rotated crystal, and the zig-zag pattern could be a sign of grain boundaries.

Another issue is the history dependent behavior pointed out by the authors. The "phase" described as phenomenon III is observed by a sufficiently slow compression of near freezing configurations of the liquid branch by Monte Carlo or by molecular dynamics simulations. That a sufficiently slow compression rate has to be used would be consistent with homogeneous nucleation of the ordinary face-centred-cubic(fcc) crystal phase, leading as explained above to a "badly crystallized" sample. However, configurations obtained by relaxing a perfectly aligned fcc crystal by molecular dynamics, do not on compression convert in the "new phase."

An interesting possibility to test the stability of the "new phase," is to prepare a constant stress system that consist of 50% of this phase in contact with 50% of a perfect fcc crystal. If thermodynamically stable, one should be able to find a pressure at which it grows at the expense of the fcc crystal.

In conclusion, the claim of the authors that they have observed a new thermodynamic phase in one-component hard spheres is not supported by the data presented. The deviations from the traditional phase diagram can be explained by the usage of the *NVT* ensemble, which enables the system to phase separate in a liquid-solid system and/or the formation of several crystallites with different orientations and the presence of grain boundaries.

In response to our proceding comment, the authors have made available three configurations[2] corresponding to the three "different" phases they observe in a 500 particle system. The analysis of these three configurations, confirms our point of view that no new phase is observed.

For the configurations published in Ref. 2, we show a histogram of the bond-orientational order parameters per particle in Fig. 1, where we used particles within a distance of
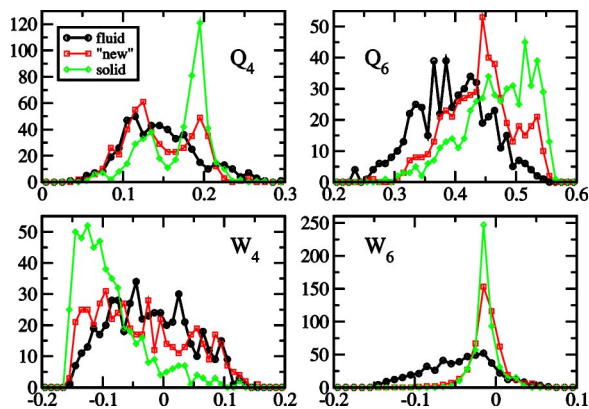
FIG. 1. Histogram of the four main bond-orientational order parameters per particle for the three different phases.

FIG. 2. The configuration corresponding to the "new phase," from left to right, top view, titled by 15°, and tilted by 40°.

1.4σ. The Q_4, Q_6, and W_4 order parameters for the "new phase" do indeed show a behavior deviating from the metastable liquid and the solid. The W_6 order parameter, however, which is much less sensitive to distortions, is almost identical to that of the fcc solid phase.

To understand the nature of the "new phase" we need to characterize its structure. In Fig. 2 we show the configuration of this phase provided[2] as seen from three different angles. The top view does not reveal anything but a slight zig-zag pattern mentioned by the authors. In the two, with different angles, tilted configurations, however, one can easily identify the layered structure. A top view from these layers reveals the hexagonal structure expected from a fcc crystal, although the layers in the second tilt have more defects. Furthermore
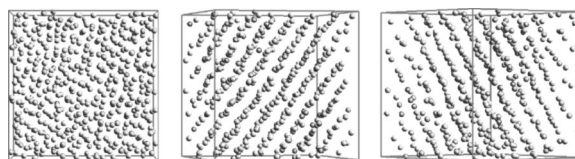
the layers are correlated in a random hcp like stacking.

The fact that not a perfect fcc or hcp crystal is found, is explained by the tilted snapshots as well, as they reveal that in both cases one actually is looking at single hexagonal layer. These layers are artificially stabilized by periodic boundary conditions. The incommensurate nature of these tilted layers in a cubic simulation box leads to a necessary deformation of the perfect, thermodynamical stable crystal phase, and explains the deviations of structural quantities as the bond-order parameters and radial distribution function from that of the stable solid. It also results in an anisotropic pressure tensor and stress being buildup in the system on compression, which explains the deviations for the compressibility with respect to the solid found by the authors.

In summary, although based on the analysis of a single configuration, the new phase is a by periodic boundaries stabilized, artificial phase. It is, therefore, not a "new phase" as claimed by the authors.

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[1] G.-W. Wu and R. J. Sadus, J. Chem. Phys. **120**, 11686 (2004).
[2] The configuration files are available by following the Software & Data link found at http://www.it.swin.edu.au/centres/cms/