Response to “Comment on ‘New phase for one-component hard spheres’” [J. Chem. Phys. 120, 11686 (2004)]

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The comment raises some technical issues regarding our recent work and it provides an alternative interpretation of our simulation results. The critique is not supported by any new simulation data.

It is argued that the new phase could be an artifact caused by such factors as the choice of canonical (N-V-T) ensemble instead of an isobaric-isothermal (N-P-T) ensemble, cell shape and number of particles used in the simulation. These are generic issues that are common to many molecular simulation studies. It is reasonable to infer from past simulation experience that these issues will have a quantitative effect on our results, e.g., the numerical values of the compressibility factors may change. However, in the absence of any new simulation data, it is impossible to conclude that such considerations would change the nature of the phenomena observed. The same phenomena were observed irrespective of the number of particles but the influence of the shape of the simulation cell was not investigated. As noted in our work, deviations from the traditional hard-sphere phase diagram have also been observed in molecular dynamics studies with the N-P-T ensemble. In view of this, it appears unlikely that the results are simply an artifact of the N-V-T ensemble.

Blaak et al. explain the new phenomenon in terms of “microscopic coexistence between liquid and solid, or the presence of crystalline grain boundaries.” This alternative interpretation is understandable in view of the highly ordered nature of the new phase and the apparent zigzag pattern in the configurational snapshot. However, our investigations did not find any evidence for two-phase coexistence. The new phase is remarkably homogeneous and stable as evident from our analysis of the self-intermediate scattering function. The new phase is certainly unlike any conventional crystalline phase with the hard spheres exhibiting a considerable degree of mobility. Blaak et al. make an interesting suggestion to further test the stability of the new phase. To facilitate investigations by other workers, we have made the configuration files for the snapshots freely available via the internet.

In the addendum, Blaak et al. have used our data to analyze the structural properties of the new phase and they provide snapshots at different orientations. Their analysis of our data indicates that the new phase is highly ordered and that it is different from the conventional metastable phase. These findings are consistent with the structural analysis that we reported originally. Indeed, the relative differences in the structure (W₆ term) that they obtained for the solid, metastable, and new phases are similar to trends that we reported for the distributions of the number of connections per particle in a system of 32 000 hard spheres.

It is suggested that compressing the system has resulted in a stress which has induced an artificial ordering of the hard spheres stabilized by the periodic boundary conditions. Although this suggestion appears plausible, it is not supported by the simulation data. In Fig. 1, we illustrate different three-dimensional perspectives for a postequilibration configuration of the new phase. The central simulation box is surrounded by its six adjacent periodic images. If the new phase were a stress-induced artifact of the periodic boundary conditions, we would expect to see discontinuities at the boundaries of the simulation box. That is, the configuration observed in the central simulation box would not align correctly with its periodic images. It is apparent from Fig. 1, that there are no such discontinuities between the central simulation box and its periodic images. There is no obvious indication of stress in the system.

As discussed in the original work, the case for a new phase is supported by considerations other than simply differences in the compressibility factor and radial distribution functions compared to that expected for conventional solid and isotropic liquid phases. Analysis of the connections per particle for a thermally equilibrated system clearly indicates that the phase does not have a conventional crystalline structure. The structure factors obtained for the new phase are also significantly different to that expected from either an isotropic phase or a nearly crystalline state. The same distinction between phases is also apparent from values of the translational order parameter, which are also time independent. The stability of the new phase has been checked by determining the self-intermediate scattering function. Irrespective of the packing fraction the function goes to zero, which indicates that a stable equilibrium has been reached. Both Monte Carlo and molecular dynamics simulations show that the properties of the new phase are independent of the duration of the postequilibration period.

In conclusion, the available simulation data, obtained via both Monte Carlo simulation and molecular dynamics...
support the existence of a new phase for hard spheres. Although it is not possible to totally exclude an alternative interpretation of the results, the phenomenon itself is unlikely to be simply an artifact of the simulation procedure. To facilitate further investigation of this interesting new phase, we have made the relevant configuration files freely available via the internet.3

![FIG. 1. Different three-dimensional perspectives of a postequilibrium configuration of the new phase. The central simulation box is surrounded by its six adjacent periodic images.](image)

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3The configuration files are available by following the “Software & Data” link found at http://www.it.swin.edu.au/centres/cms/