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Geometry explains the large difference in the elastic properties of fcc and hcp crystals of hard spheres

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As is well known, hard-sphere crystals of the fcc and hcp type differ very little in their thermodynamic properties. Nonetheless, recent computer simulations by Pronk and Frenkel indicate that the elastic response to mechanical deformation of these two types of crystal are quite different [S. Pronk and D. Frenkel, Phys. Rev. Lett. **90**, 255501 (2003)]. By invoking a geometrical argument put forward by Martin some time ago [R. M. Martin, Phys. Rev. B **6**, 4546 (1972)], we suggest that this is largely due to the different symmetries of the fcc and hcp crystal structures. Indeed, we find that elastic constants of the fcc hard-sphere crystal can be mapped onto the equivalent ones of the hcp crystal to very high accuracy, as a comparison with the computer simulation data of Pronk and Frenkel shows. The same procedure applied to density functional theoretical predictions for the elastic properties of the fcc hard-sphere crystal also produces remarkably accurate predictions for those of the hcp hard-sphere crystal.

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In a recent publication [1], Pronk and Frenkel report on a computer simulation study of the elastic properties of fcc and hcp crystals of hard spheres. They find the various elastic constants to differ by up to 20%, despite that the thermodynamic properties of both types of hard-sphere crystal are barely distinguishable. Indeed, the free energies, pressures and compressibilities of the two crystal types deviate from each other by less than 0.1% for conditions not too far removed from the melting point [1]. In this work, we point out that the difference in the elasticity of fcc and hcp hard-sphere crystals is less surprising than claimed by Pronk and Frenkel, and that it can be explained by the geometry of the packing of the particles within each lattice type.

The relation between the elastic moduli of hcp and fcc crystals have been studied theoretically and experimentally by a number of authors [2–6]. Of particular interest is the work of Martin [4], who derived an approximate transformation of the elastic moduli of the fcc crystal to those of the hcp lattice, making use of the fact that both lattice types can be constructed from tetrahedral units. The tetrahedral blocks in the fcc lattice are equally oriented, while the hcp lattice can be built up from two tetrahedra oriented differently from each other and from the fcc tetrahedron. The transformation of any tensor in the fcc system of coordinates, defined as usual along the cubic axes, to either of the two representations of this tensor in the trigonal geometry of the hcp crystal can be made by two simple rotations $R^{(1)}$ and $R^{(2)}$, where

$$R^{(1)} = \begin{pmatrix} \sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} \\ -\sqrt{\frac{1}{6}} & \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{6}} \\ -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \end{pmatrix}, \quad (1)$$

$$R^{(2)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} R^{(1)}.$$

This suggests that the transformation of the elastic moduli tensor, C^{FCC} , from the fcc geometry to that of the trigonal geometry of the hcp lattice, \bar{C}^{HCP} , could simply be the average (or superposition) of the two trigonal tensors [6],

$$\bar{C}_{ijkl}^{HCP} = \frac{1}{2} (R_{ir}^{(1)} R_{js}^{(1)} R_{kt}^{(1)} R_{lu}^{(1)} C_{rstu}^{FCC} + R_{ir}^{(2)} R_{js}^{(2)} R_{kt}^{(2)} R_{lu}^{(2)} C_{rstu}^{FCC}), \quad (2)$$

where the subscripts have their usual meaning. It so happens, however, that the two unequal tetrahedra of the hcp lattice are not independent, but attached to each other. Hence, the elastic response of the hcp lattice to an external strain should be the *combined* response of both tetrahedra, not just a simple average, implying that Eq. (2) requires a correction for the internal strain that the connectedness of and interaction between the tetrahedra produces. We refer to Ref. [4] for further details.

The resulting strain-corrected expression for the elastic moduli tensor of the hcp lattice, C^{HCP} , reads [4]

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$$C_{ijkl}^{HCP} = \bar{C}_{ijkl}^{HCP} - \Delta_{ijrs} (\bar{C}_{rstu}^{HCP})^{-1} \Delta_{tukl}, \quad (3)$$

where \bar{C}_{ijkl}^{HCP} is given by Eq. (2) and Δ is a correction tensor identical to it except that the difference is taken instead of the sum. There are six independent elastic moduli in the trigonal representation. The relations between the elastic moduli of the fcc lattice and the ones in the trigonal representation are expressed in the following formulas (using the standard Voigt notation):

$$\begin{aligned} \bar{C}_{11} &= (C_{11}^{FCC} + C_{12}^{FCC} + 2C_{44}^{FCC})/2, \\ \bar{C}_{12} &= (C_{11}^{FCC} + 5C_{12}^{FCC} - 2C_{44}^{FCC})/6, \\ \bar{C}_{13} &= (C_{11}^{FCC} + 2C_{12}^{FCC} - 2C_{44}^{FCC})/3, \\ \bar{C}_{14} &= (C_{11}^{FCC} - C_{12}^{FCC} - 2C_{44}^{FCC})/3\sqrt{2}, \\ \bar{C}_{33} &= (C_{11}^{FCC} + 2C_{12}^{FCC} + 4C_{44}^{FCC})/3, \\ \bar{C}_{44} &= (C_{11}^{FCC} - C_{12}^{FCC} + C_{44}^{FCC})/3. \end{aligned} \quad (4)$$

The elastic moduli of the hcp lattice can then be calculated from the following relations:

$$\begin{aligned} C_{11}^{HCP} &= \bar{C}_{11} - \bar{C}_{14}^2/\bar{C}_{44}, \\ C_{12}^{HCP} &= \bar{C}_{12} + \bar{C}_{14}^2/\bar{C}_{44}, \\ C_{13}^{HCP} &= \bar{C}_{13}, \\ C_{14}^{HCP} &\equiv 0, \\ C_{33}^{HCP} &= \bar{C}_{33}, \\ C_{44}^{HCP} &= \bar{C}_{44} + \bar{C}_{14}^2 \left[\frac{1}{2}(\bar{C}_{11} - \bar{C}_{12}) \right]. \end{aligned} \quad (5)$$

The mapping of C^{FCC} onto C^{HCP} implicit in Eqs. (4) and (5) agrees well with experimental data on ZnS, a compound that can crystallize both in an fcc and in an hcp lattice [4]. In fact, the mapping works very well for fcc and hcp crystals of hard spheres too, as we demonstrate next.

In Fig. 1, we have plotted the relative difference between the various moduli of the fcc and hcp crystals of hard spheres, $\delta_{ij} \equiv |C_{ij}^{FCC} - C_{ij}^{HCP}|/C_{ij}^{FCC}$, as a function of the dimensionless crystal density $\rho_S \sigma^3$ with σ the diameter of the spheres, using the computer simulation data of Pronk and Frenkel (obtained from Table I of Ref. [1]) and the prediction of Martin, given by Eqs. (1)–(5) [4]. The deviation between the two is within the numerical error of the computer simulations (not shown for clarity) [1]. Hence, we can conclude that the approximate theory outlined above, and which is based entirely on a geometric argument, explains the difference between the elastic moduli of fcc and hcp crystals. In other words, geometry plausibly explains the found differences in elastic behavior of fcc and hcp crystals of hard

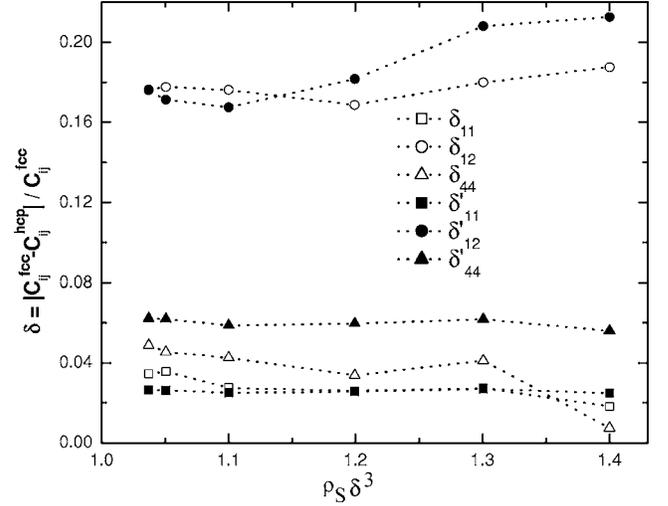


FIG. 1. Relative difference $\delta_{ij} \equiv |C_{ij}^{FCC} - C_{ij}^{HCP}|/C_{ij}^{FCC}$ between the various elastic moduli of hcp and fcc crystals of hard spheres as a function of the dimensionless density, $\rho_S \sigma^3$, where σ denotes the hard-sphere diameter. Shown are the results of the computer simulations of Pronk and Frenkel for the two crystal types [1], indicated by the open symbols (δ_{ij}), and those obtained by applying the relations Eqs. (1)–(5) to the simulation results for the fcc crystal, indicated by the closed symbols (δ'_{ij}).

spheres. This makes these differences not as surprising as previously claimed [1].

In order to further verify Eqs. (1)–(5), we calculate the elastic moduli of the hcp hard-sphere crystal using results for the elastic moduli of fcc crystals of hard spheres obtained from density functional theory (DFT) [7]. We use the predictions of the modified weighted-density approximation DFT, MWDA DFT, because they are known to agree very well with the results of computer simulations [7]. Classical DFT has its roots in the quantum mechanical theory and makes use of the fact that the Helmholtz free energy F is a unique functional of the density distribution $\rho(\mathbf{r})$ for all positions \mathbf{r} in the system. This functional $F[\rho]$ can be represented as a sum of an ideal functional $F_{id}[\rho]$ for noninteracting particles and an excess-free energy $F_{ex}[\rho]$, which arises due to the inter-particle interactions, so $F[\rho] = F_{id}[\rho] + F_{ex}[\rho]$. The equilibrium single-particle density can be calculated by the minimization of $F[\rho]$. The expression for the ideal part of the free energy $F_{id}[\rho]$ is known exactly,

$$F_{id}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) [\ln \rho(\mathbf{r}) - 1], \quad (6)$$

while the excess free energy is not and requires (often ad hoc) approximations. The MWDA DFT uses the following expression for it

$$\frac{1}{\rho_S V} F_{ex}[\rho] = f_{ex}^L[\bar{\rho}], \quad (7)$$

where $f_{ex}^L[\bar{\rho}(\mathbf{r})]$ is the excess free energy per particle of a uniform liquid, V is the volume of the system, ρ_S is the

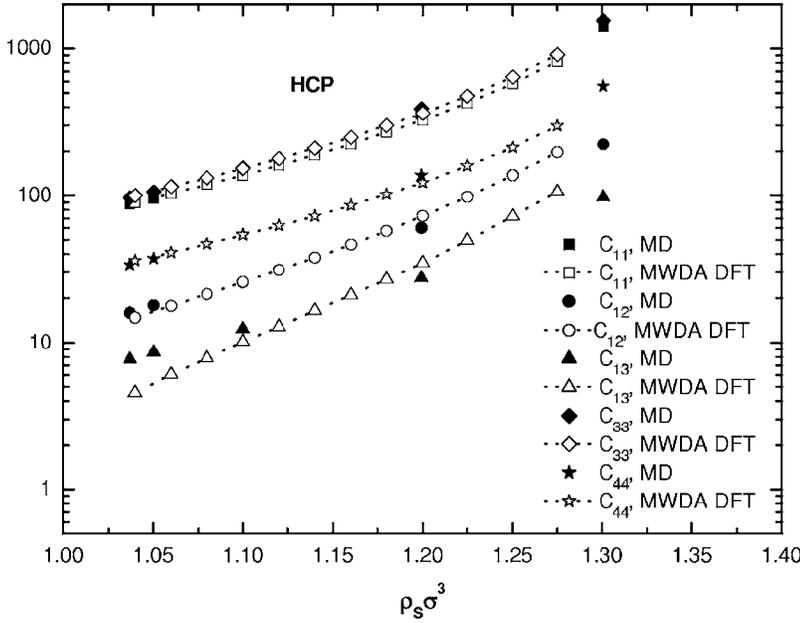


FIG. 2. Elastic moduli C_{ij} in units of $k_B T / \sigma^3$ [7], as a function of the dimensionless crystal density, $\rho_s \sigma^3$. Here, σ represents the particle radius and $k_B T$ the thermal energy. Represented by the open symbols are the results of the mapping of the fcc moduli calculated by means of the MWDA DFT onto the hcp moduli, using the relations Eqs. (1)–(5). Indicated by the closed symbols are the results of the MD computer simulations of Pronk and Frenkel [1].

density of the solid phase, and $\tilde{\rho}$ is the so-called uniform weighted solid density, defined as

$$\tilde{\rho} = \frac{\int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \tilde{w}(\mathbf{r} - \mathbf{r}', \tilde{\rho})}{\int d\mathbf{r}'' \rho(\mathbf{r}'')} \quad (8)$$

The equation for the weighting function $\tilde{w}(\mathbf{r} - \mathbf{r}', \tilde{\rho})$ adopts in Fourier space the form

$$-k_B T \hat{C}_L^{(2)}(q, \rho_L) = 2 \frac{\partial f_{ex}^L(\rho_L)}{\partial \rho_L} \hat{w}(q, \rho_L) + \rho_L \frac{\partial^2 f_{ex}^L(\rho_L)}{\partial^2 \rho_L} \delta_{q,0}, \quad (9)$$

with ρ_L the density of the fluid phase, q the momentum transfer, $\hat{C}_L^{(2)}(q, \rho_L)$ the Fourier transform of the direct correlation function of the particles in the fluid phase, and \hat{w} the Fourier transform of the weighting function.

The weighting function should satisfy the condition that the direct correlation function of the uniform liquid \hat{C}_L is equal to the direct correlation function of the solid if the liquid and solid densities are the same, $\rho(\mathbf{r}) = \rho_L$, i.e., the solid is treated as an inhomogeneous liquid. As usual, we presume the density distribution $\rho(\mathbf{r})$ to be Gaussian and centered around the lattice points. The direct correlation function of the fluid phase can be obtained by solving the Ornstein-Zernike equation for classical fluids invoking, e.g., the Percus-Yevick closure. Finally, the excess free energy per particle f_{ex}^L is calculated from the Carnahan-Starling equation of state. The results of the MWDA for the freezing of the

hard-sphere system show very good agreement with computer simulations [7].

The elastic moduli tensor obtainable from DFT and Hooke's law reads

$$C_{ijkl} = \left. \frac{1}{V} \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right|_{\eta=0}, \quad (10)$$

where η_{ij} denotes the elements of the strain tensor. For cubic symmetry the desired expressions for the elastic moduli are quite straightforward, e.g., see Ref. [7]. The predictions of the MWDA DFT for the elastic moduli of the fcc crystal show the best agreement with simulations in comparison to other DFTs [7] and seem therefore to be the most suitable for our purpose. The results of the mapping of the fcc moduli, calculated by means of the MWDA DFT, onto the hcp moduli are presented in Fig. 2, again as a function of the dimensionless density of the spheres. The agreement with the results of the computer simulations of Pronk and Frenkel [1] is quite good for all moduli except C_{13} , for which it is not as impressive but still satisfactory.

In conclusion, we believe to have demonstrated that the difference in elasticity between the fcc and hcp crystals of hard spheres is largely caused by the geometrical differences of these two types of crystal lattice. Even when the thermodynamic properties of fcc and hcp crystals are indeed similar to the point of being virtually indistinguishable, there is in fact no reason for their elastic properties to be similar too. The reason is that similarities in the free energy landscape at long wavelengths do not preclude differences at short wavelengths. Indeed, short wavelength distortions contribute much more significantly to the elastic constants than to the free energy itself [8].

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