PHYSICAL REVIEW A VOLUME 38, NUMBER 8 OCTOBER 15, 1988

Elastic constants of the hard-sphere solid from density-functional theory

Hong Xu and Marc Baus
Faculté des Sciences, Code Postal 231, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium

(Received 2 May 1988)

The isothermal elastic constants of the perfect fcc hard-sphere crystal are computed from our approximate density-functional theory and found to be in qualitative agreement with the computer-simulation results over the full density region ranging from marginal stability of the solid up to the close-packing density.

Recently, several authors[1–7] have considered the problem of the first principles determination of the elastic constants of the hard-sphere fcc crystal from either density-functional theory[1–5] or from computer simulations.[6,7] The resulting situation has raised some doubts[3,5,7] and it is hoped that the present report may clarify the situation. Most of the problems originate from the conflicting results which have been obtained from two different versions of the density-functional theory,[3–5] whereas the two independent sets of simulation results,[6,7] although not identical, are mutually consistent and require no further comments on our part. The results of Jarić and Mohanty[3] and Jones[4] are qualitatively incorrect since they predict a negative elastic constant (C_{12}) not seen in the simulations.[6,7] To understand the origin of this discrepancy it is necessary to recall here that the theory used by these authors[3,4] is based on a second-order expansion of the free energy in the relative density change between the solid and the liquid. As we have shown elsewhere,[8,9] this approximation predicts only a metastable *perfect* crystal which can be further stabilized within this second-order theory only by considering a very *imperfect* crystal with an unphysically large concentration of about 10% vacancies. It is thus not surprising that such a loose solid should also exhibit an unusual elastic behavior. Contrary to a recent claim[5] it seems fair to us to conclude from this that the unexpected elastic properties found within this theory are artefacts of the underlying approximation scheme and not of the density-functional theory *per se.* To show this more explicitly we have computed the elastic constants of the perfect fcc hard-sphere crystal within our own version[8–10] of the density-functional theory.[11] The basic thermodynamic potential used to determine the isothermal elastic properties is the Helmholtz free energy, F, of a system of N particles enclosed in a volume V at temperature T and of local number density $\rho(\mathbf{r})$ such that $\int_V d\mathbf{r}\,\rho(\mathbf{r})=N$, which we briefly denote $F[\rho]$. Elasticity is concerned then with the behavior of $F[\rho]$ with respect to a small deformation of the system away from its equilibrium state (see Jones[4] for a more detailed account). Such a deformation can be produced by a small *uniform* strain induced by the linear point transformation, $r_i(\epsilon)=r_i+\epsilon u_{ij}r_j$ for any point $\mathbf{r}=[r_i]$ of the undeformed system (here i and j are running over the Cartesian coordinates, with a summation over repeated indices, while ϵ is a smallness parameter). Several sets of elastic constants can be defined according to whether one considers the elastic response to the "small-strain tensor," $\epsilon_{ij}=(\epsilon/2)(u_{ij}+u_{ji})$, which governs the change in the position of the points, or with respect to the "finite-strain tensor," $\eta_{ij}=(\epsilon/2)(u_{ij}+u_{ji}+\epsilon u_{ki}u_{kj})$, which governs the change in the distances between the points. Unfortunately, these different definitions have been denoted invariably C_{ijkl} in the recent literature.[1–7] When the undeformed system ($\epsilon=0$) is in an equilibrium state, the linear term of the expansion with respect to the strain of the free energy of the deformed state, say, $F[\rho_\epsilon]$, around the free energy of the equilibrium state, $F[\rho_{\epsilon=0}]$, has to be balanced[4] by the equilibrium stresses of the undeformed state, T_{ij}, which for the present system correspond to an isotropic pressure p, $T_{ij}=-p\delta_{ij}$. Hence with either strain tensor one has

$$T_{ij}=\frac{1}{V}\frac{\partial F[\rho_\epsilon]}{\partial \epsilon_{ij}}\bigg|_{\epsilon=0}=\frac{1}{V}\frac{\partial F[\rho_\epsilon]}{\partial \eta_{ij}}\bigg|_{\epsilon=0}, \tag{1}$$

where V is the undeformed volume. The elastic response of the system is defined then by the second-order term of this expansion. Using the small-strain tensor ϵ_{ij} one obtains the elastic constants used in Ref. 1–3, which in order to avoid confusion, we will denote here A_{ijkl}:

$$A_{ijkl}=\frac{1}{V}\frac{\partial^2 F[\rho_\epsilon]}{\partial \epsilon_{ij}\partial \epsilon_{kl}}\bigg|_{\epsilon=0}, \tag{2}$$

whereas the elastic constants, say, B_{ijkl}, used in Ref. 6 and 7,

$$B_{ijkl}=\frac{1}{V}\frac{\partial^2 F[\rho_\epsilon]}{\partial \eta_{ij}\partial \eta_{kl}}\bigg|_{\epsilon=0}, \tag{3}$$

result from an expansion with respect to the finite-strain tensor η_{ij}. Finally, a third definition, used in Ref. 4 and 5, results from an expansion of the stress tensor of the deformed system, say, $T_{ij}(\epsilon)$:

$$C_{ijkl}=\frac{\partial T_{ij}(\epsilon)}{\partial \epsilon_{kl}}\bigg|_{\epsilon=0}=\frac{\partial T_{ij}(\epsilon)}{\partial \eta_{kl}}\bigg|_{\epsilon=0} \tag{4}$$

which amounts to formulating a generalized Hooke's law. These different definitions are not equivalent and lead, for the cubic crystals under consideration, to the relations

$$\begin{aligned} C_{11}&=B_{11}-p=A_{11}\ ,\\ C_{12}&=B_{12}+p=A_{12}+p\ ,\\ C_{44}&=B_{44}-p=A_{44}\ , \end{aligned} \tag{5}$$

where we have used the Voigt notation $A_{\alpha\beta}\equiv A_{(ij)(kl)}$, etc., with $\alpha=1=(x,x)$, $\alpha=2=(y,y)$, $\alpha=3=(z,z)$, $\alpha=4=(x,y)$, etc. As seen from (5) it is only when the equilibrium system is taken at zero pressure, which is impossible for the hard-sphere crystal, that the three sets of elastic constants [Eqs. (2)–(4)] coincide. Henceforth, we consider C_{ijkl} of (4) as our basic set and determine them by using for $F[\rho_\epsilon]$, the approximate free-energy density functional proposed elsewhere[8–10] but evaluated now for the deformed system of local density $\rho_\epsilon(\mathbf{r})$, which we parametrize by Gaussians centered around the deformed lattice sites $R_i(\epsilon)=R_i+\epsilon u_{ij}R_j$:

$$\rho_\epsilon(\mathbf{r})=\left[\frac{\det\alpha(\epsilon)}{\pi^3}\right]^{1/2}\times\sum_{\mathbf{R}}\exp\{-[r_i-R_i(\epsilon)]\alpha_{ij}(\epsilon)[r_j-R_j(\epsilon)]\} \tag{6}$$

and with a modified (or relaxed) inverse width matrix $\alpha_{ij}(\epsilon)$.

In order to keep the algebra reasonably simple further approximations are required with the purpose of limiting the number of additional degrees of freedom describing the deformed system. For simplicity we have left the structural scaling condition (which fixes the effective liquid[8–10] used to describe the direct correlations of the solid) unchanged and focused our attention on $\alpha_{ij}(\epsilon)$ for which we took the simple form $\alpha_{ij}(\epsilon)=(\alpha_0+\epsilon\alpha_1)\delta_{ij}+\epsilon\alpha'_{ij}$, with α'_{ij} proportional to u_{ij}, $\alpha'_{ij}=\alpha' u_{ij}$. Here α_0 is the isotropic width parameter of the equilibrium crystal ($\epsilon=0$) determined previously[8–10] and α_1 describes its relaxation in the deformed state whereas α' takes into account the possible strain-induced anisotropy of the width matrix. The two new variational parameters α_1 and α' are then determined perturbatively[4] by minimizing the second-order-in-ϵ expansion of $F[\rho_\epsilon]$ for a given ϵ value. We found that the results do depend here much more sensitively on the number of variational parameters than was the case[10] for the undeformed state ($\epsilon=0$). For instance, with only one additional variational parameter ($\alpha'=0$), very large overestimates of the elastic constants were found. With the two variational parameters used here the improvement is already considerable but it is our impression that in order to reach convergence within the Gaussian approximation (6) a larger parameter space may be required. The origin of this difficulty is easily understood in terms of the increased anisotropy of the deformed crystal.

To proceed, the three elastic constants C_{11}, C_{12}, and C_{44} can now be determined stepwise[6] by computing the quantity

$$e=\frac{1}{V}\frac{\partial^2 F[\rho_\epsilon]}{\partial^2\epsilon}\bigg|_{\epsilon=0}$$

for three independent deformations u_{ij}. First, we consider an isotropic compression, $u_{ij}=\delta_{ij}$, for which $e_1=3(C_{11}+2C_{12}-2p)$, where e_1 is the corresponding value of e and p the pressure of the equilibrium solid.

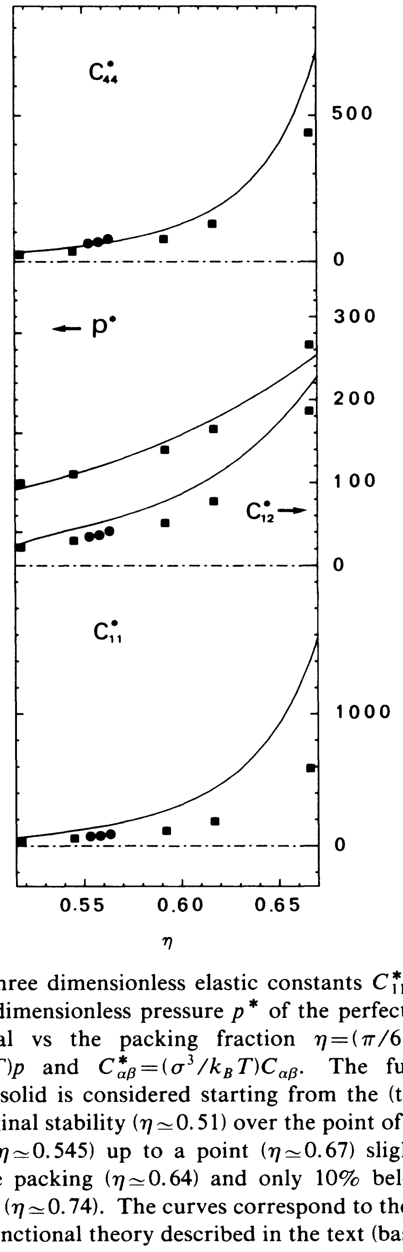

FIG. 1. Three dimensionless elastic constants C^*_{11}, C^*_{12}, and C^*_{44} and the dimensionless pressure p^* of the perfect fcc hard-sphere crystal vs the packing fraction $\eta=(\pi/6)\sigma^3\rho$ with $p^*=(\sigma^3/k_BT)p$ and $C^*_{\alpha\beta}=(\sigma^3/k_BT)C_{\alpha\beta}$. The full density range of the solid is considered starting from the (theoretical) point of marginal stability ($\eta\simeq0.51$) over the point of two-phase coexistence ($\eta\simeq0.545$) up to a point ($\eta\simeq0.67$) slightly above random close packing ($\eta\simeq0.64$) and only 10% below crystal close packing ($\eta\simeq0.74$). The curves correspond to the results of the density-functional theory described in the text (based on two variational parameters and the Percus-Yevick approximation). On this scale the single Monte Carlo point of Runge and Chester (Ref. 6) at $\eta\simeq0.545$ cannot be distinguished from the molecular-dynamics data (■) of Frenkel and Ladd (Ref. 7) which cover a much larger density range. The results (●) of Velasco and Tarazona (Ref. 5) are based on the Carnahan-Starling equation of state and use three variational parameters. The results of Jones (Ref. 4) are not shown here because they correspond to an imperfect crystal.

Next we perform a uniaxial stretch for which u_{ij} reduces to $u_{xx}=1$ and zero otherwise, leading to $e_2=C_{11}$. Finally, we consider a shear deformation with $u_{xy}=u_{yx}=1$ and u_{ij} zero otherwise, leading to $e_3=2(2C_{44}+p)$. From the knowledge of e_1, e_2, e_3, and p (computed previously 8–10) we determine C_{11}, C_{12}, and C_{44}. The results are shown in Fig. 1 where it is seen that (1) no unphysical values, such as those reported in Refs. 3 and 4, are found within the present density-functional theory, (2) the qualitative trends of the simulation results[7] are correctly reproduced over the *full* range of stability of the solid (previous investigations[3-6] have considered only a narrow density range around two-phase coexistence), (3) the quantitative overestimations are similar to those found elsewhere[8-10] and partly inherent to the underlying Percus-Yevick approximation used here up to the close-packing density. Notice also that at marginal stability of the solid the (theoretical) elastic constants appear to drop to zero discontinuously.

Finally, it should also be observed that the computation of the isothermal elastic constants is similar to the computation of the isothermal compressibility, a problem which is already notoriously difficult in the liquid phase even for present-day liquid-state theory. It may thus be somewhat vain, at present, to try to perform more sophisticated density-functional calculations in order to improve the quantitative agreement with the simulations, unless very accurate equations of state for the *metastable* liquid become available.

One of us (M.B.) acknowledges financial support from Fonds National Belge de la Recherche Scientifique and the Association Euratom-Etat Belge.

---

[1] T. V. Ramakrishnan, Pramana **22**, 365 (1984).

[2] M. D. Lipkin, S. A. Rice, and U. Mohanty, J. Chem. Phys. **82**, 472 (1985).

[3] M. Jarić and U. Mohanty, Phys. Rev. Lett. **58**, 230 (1987); **59**, 1170 (1987).

[4] G. L. Jones, Mol. Phys. **61**, 455 (1987).

[5] E. Velasco and P. Tarazona, Phys. Rev. A **36**, 979 (1987).

[6] K. J. Runge and G. V. Chester, Phys. Rev. A **36**, 4852 (1987).

[7] D. Frenkel and A. J. C. Ladd, Phys. Rev. Lett. **59**, 1169 (1987).

[8] M. Baus and J. L Colot, Mol. Phys. **55**, 653 (1985) (see Fig. 5).

[9] M. Baus, J. Stat. Phys. **48**, 1129 (1987).

[10] J. L. Colot and M. Baus, Mol. Phys. **56**, 807 (1985); J. L. Colot, M. Baus, and H. Xu, *ibid.* **57**, 809 (1986).

[11] For an alternative appraoch see, e.g., A. D. J. Haymet, Ann. Rev. Phys. Chem. **38**, 89 (1987).