Elastic Constants of Hard-Sphere Crystals

In a recent letter,[1] Jarić and Mohanty reported the calculations of elastic constants, obtained with the density-functional theory. Their results suggest that a perfect icosahedral quasicrystal is unstable with respect to a small "martensitic" deformation. Jarić and Mohanty also observed that the same density-functional theory predicts that a hard-sphere (HS) solid close to its melting point should have a negative Poisson's ratio. This is a remarkable prediction. If a substance with a negative Poisson's ratio is elongated in one direction, it will also expand in the transverse directions. Such behavior is rarely observed in nature and is certainly unexpected for crystals of particles interacting via pairwise-additive central forces. It is important to know whether the predicted Poisson's ratio is due to the peculiar nature of the HS solid or to an artifact of the density-functional theory employed by Jarić and Mohanty.

We have computed the elastic constants of fcc crystals of HS's over a range of densities, including the melting density, from molecular-dynamics simulations of slightly distorted unit cells. The elastic constants were extracted from stress-strain relations,[2] with strain parameters varying between 0.0025 and 0.01. Nonlinear corrections to the relevant components of the stress tensor were found to be negligible in this regime. The results are shown in Table I.

The elastic constants have a free-volume–like density dependence $C \propto (\rho_0/\rho - 1)^{-2}$, possibly with small higher-order corrections. Poisson's ratio varies approximately linearly with density, from about 0.2 at close packing up to about 0.4 in the thermodynamically unstable state $\rho/\rho_0 = 0.7$. It is always positive. These results indicate that density-functional theory, which is known to yield quite accurate predictions of the melting transition in a system of HS's,[3] can lead to qualitatively incorrect elastic constants. Why this should be so is not clear. However, the fact that density-functional theory obtains the wrong sign for Poisson's ratio in the HS solid casts doubt on the theory's prediction of a "martensitic" instability in icosahedral quasicrystals.

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TABLE I. Isothermal elastic constants C_{11}, C_{12}, and C_{44} of an fcc crystal of HS's, as a function of reduced density ρ/ρ_0 (ρ_0 is the density of close-packed spheres). All simulations were for 108 HS's of diameter σ, except for the data at $\rho/\rho_0 = 0.8333$ which was obtained for 32 spheres. Poisson's ratio ν is calculated with the relation $\nu = (C_{12}+P)/(C_{11}+C_{12})$, where P is the pressure. The elastic constants quoted here are second derivatives of the Helmholtz free energy with respect to Lagrangean strain parameters, per unit volume (Ref. 2).

ρ/ρ_0	C_{11} (σ^3/k_BT)	C_{12} (σ^3/k_BT)	C_{44} (σ^3/k_BT)	ν	P (σ^3/k_BT)
0.7	46 ± 2	11.8 ± 3	33.5 ± 1	0.376	9.904 ± 0.007
0.736	68 ± 3	18.2 ± 2	46 ± 1	0.347	11.672 ± 0.006
0.8	133 ± 3	34.6 ± 2	94 ± 2	0.306	16.641 ± 0.02
0.8333	207 ± 8	56.8 ± 6	150 ± 2	0.294	20.79 ± 0.03
0.9	627 ± 12	149 ± 11	478 ± 10	0.241	37.69 ± 0.08