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Elastic properties of a hard-sphere crystal

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Recent calculations for the elastic properties of the hard-sphere crystal gave quite peculiar results, including negative values for the Poisson's ratio. Here we claim that these results were due to the density-functional expansion used in these calculations. We report the elastic constants given in a different functional approach, which are in full disagreement with the previous calculations.

The density-functional formalism (DFF) has been applied during the last several years to the problem of crystallization.[1-12] The advantage of the DFF over other approaches rests on the fact that it provides a unified description of the fluid and the crystal, so that the thermodynamic potentials of both phases may be directly compared and the phase transition localized. The study of crystallization requires a very careful choice of the approximations used to evaluate the free-energy density functional, $F[\rho(\mathbf{r})]$. So far, two types of approximations have been successfully used in the description of crystalline solids within DFF. In both cases the ideal-gas contribution is exactly evaluated, while the rest,

$$\Delta F[\rho(\mathbf{r})] \equiv F[\rho(\mathbf{r})] - F_{\mathrm{id}}[\rho(\mathbf{r})] \ , \tag{1}$$

is approximated in different ways.

The first DFF theory of crystallization was developed by Ramakrishnan and Yussouff[1,2] (RY). It uses a functional Taylor expansion of $\Delta F[\rho(\mathbf{r})]$ around a uniform reference density, truncated at second order,

$$\Delta F[\rho(\mathbf{r})] \approx \Delta F[\rho_0] + \Delta\mu_0 \int d\mathbf{r}[\rho(\mathbf{r}) - \rho_0] - \frac{k_B T}{2} \int d\mathbf{r} \int d\mathbf{r}' c_0(|\mathbf{r}-\mathbf{r}'|)[\rho(\mathbf{r}) - \rho_0][\rho(\mathbf{r}') - \rho_0] \ , \tag{2}$$

where $\Delta\mu_0$ is the excess over ideal gas for the chemical potential and $c_0(|\mathbf{r}-\mathbf{r}'|)$ is the direct correlation function, both evaluated at the uniform reference system, so that they may be obtained from standard methods in the theory of liquids.[13]

Most of the correlation structure in a simple fluid may be described in terms of a reference hard-sphere (HS) system, so many efforts have been devoted to the study of HS crystallization. In particular, the RY approach has been used[4-8] with several criteria for the description of the density distribution in the solid and the choice of the uniform reference density ρ_0.

The second DFF approach to the problem of crystallization takes

$$\Delta F[\rho(\mathbf{r})] = \int d\mathbf{r}\, \rho(\mathbf{r}) \Delta\Psi(\bar{\rho}(\mathbf{r})) \ , \tag{3}$$

where $\Delta\Psi(\rho)$ is the excess over the ideal gas for the free energy per particle in a homogeneous fluid of density ρ. The "averaged density" $\bar{\rho}(\mathbf{r})$ is defined as

$$\bar{\rho}(\mathbf{r}) \equiv \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|, \bar{\rho}(\mathbf{r})) \ , \tag{4}$$

with a normalized weight function $w(r,\rho)$ which is fixed to reproduce the linear response function, or the direct correlation function of the bulk fluid. This kind of density-functional model was first introduced in the study of electronic systems,[14] with the name of averaged-density approximation (ADA) and later reinvented for classical fluids.[9,15] Several versions of the ADA have been applied to the problem of the crystallization of hard spheres, and the more developed versions[10-12] show substantial agreement with the results of computer simulations.

Having achieved a good description of the hard-sphere solid from these density-functional models, a step forward was given by Jones[16] and Jaric and Mohanty[17] with the evaluation of the elastic constants of the HS crystal, in both cases with the RY approach described above. The DFF clearly constitutes a good approach to the evaluation of the elastic constants, as they are defined in terms of the second derivatives of the free energy with respect to the crystal lattice. For the fcc lattice of the hard-sphere solid there are only three independent elastic constants (in the usual notation of cubic crystals):

$$C_{11} \equiv (1/V)\partial^2 F/\partial A_{11}\partial A_{11} \ , \tag{5}$$

$$C_{12} \equiv (1/V)(\partial^2 F/\partial A_{11}\partial A_{22} - \partial F/\partial A_{11}) \ , \tag{6}$$

$$C_{44} \equiv (1/V)\partial^2 F/\partial A_{12}\partial A_{12} \ , \tag{7}$$

where V is the volume of the unstrained crystal, and A_{ij} are the elements of the strain tensor. The derivatives with respect to A_{ij} in (5)–(7) are evaluated at the unstrained crystal, $A_{ij} = \delta_{ij}$, and they have to include the full relaxation of the particle distribution in the unit cell. This is usually done by parametrizing the particle density in terms of a set of free parameters $\{\lambda_p\}$ ($p = 1$ to n), so that for any value of the strain tensor, F is given by the minimum of the resulting parametrized free energy with respect to all these parameters. The second derivatives of F, including the relaxation of the parameters $\{\lambda_p\}$, may be written[16] as

$$(\partial^2 F/\partial A_{ij}\partial A_{kl})_{\mathrm{rel}} = \partial^2 F/\partial A_{ij}\partial A_{kl} - \sum_{p,q} (\partial^2 F/\partial A_{ij}\partial\lambda_p) E_{pq}^{-1} (\partial^2 F/\partial A_{kl}\partial\lambda_q) \ , \tag{8}$$

where the second derivatives in the right-hand side (rhs) of this equation are taken independently with respect to the strain tensor and the free parameters. The subscript "rel" denotes a relaxed derivative, and E_{pq}^{-1} is the pq element of the matrix inverse of

$$E_{pq} = \partial^2 F/\partial\lambda_p\partial\lambda_q \ . \tag{9}$$

All the derivatives in (8) and (9) should be evaluated at the equilibrium unstrained crystal.

The outcome of the DFF calculations of the elastic constants of the hard-sphere solid was very surprising. Both calculations gave negative values for the C_{12} constant, which is reflected in very low values of the bulk modulus and negative Poisson's ratio. The question arises whether these unusual results are a defect of the theoretical model or respond to a real feature of the hard-sphere system, which may be associated to the strong discontinuity in the interatomic potential. Some speculations were also done on the possible relation of the peculiar elastic properties and crystal instabilities which may lead to quasicrystalline structures.[17]

In order to explore this problem we have performed the calculation of the elastic constants of the hard-sphere solid using the ADA instead of the density-expansion approach. We use a Gaussian parametrization for the density distribution, which in a deformed state with strain tensor A is taken as

$$\rho(\mathbf{r}) = [\det(\alpha)/\pi^3]^{1/2} \times \sum_{\mathbf{R}} \exp[-(r_i - A_{ik}R_k)\alpha_{ij}(r_j - A_{jl}R_l)] \ , \tag{10}$$

where $\mathbf{R} = (R_1, R_2, R_3)$ runs over the vectors of the original undeformed fcc lattice, α_{ij} are the elements of a symmetric matrix which are used as free parameters and sum over repeated indices is assumed. This particle density is normalized to have one particle per unit cell.

For the unstrained crystal $A_{ij} = \delta_{ij}$, and by symmetry the matrix parameter α has to reduce to $\alpha_{ij} = \alpha_0\delta_{ij}$ with a single Gaussian decay constant, α_0, to be used as parameter. Then (9) reduces to the form

$$\rho(\mathbf{r}) = (\alpha/\pi)^{3/2} \sum_{\mathbf{R}} \exp[-\alpha_0(\mathbf{r} - \mathbf{R})^2] \ , \tag{11}$$

which was used in the evaluation of the liquid-crystal coexistence in previous ADA calculations.[9,10] Here we use the prescription for the weight function given in Refs. 10 and 18. The parameters of the liquid-solid transition are given in Table I, in units of the hard-sphere diameter σ.

By symmetry, the diagonal elements of the strain tensor are only coupled [through the cross derivatives in (8)] to the diagonal elements of α, so that the evaluation of the elastic constants C_{11} and C_{12} (5) and (6) only requires three free parameters to represent the diagonal terms α_{ii}, $i = 1,2,3$. The elastic coefficient C_{44} measures the response of the system to shear stress, say in the $x = y$ direction, and the particle distribution will tend to deform itself in the same direction when this stress is applied, giving nonzero off-diagonal elements of α. Hence, our results for C_{44} may only be considered as an upper bound, within the Gaussian parametrization (10), as pointed out by Jones.[16] Anyway, the elastic constant C_{44} seems not to be associated to the peculiar behavior observed in the RY calculations.

The derivatives of F with respect to A_{ij} and α_{kl} were evaluated directly from Eqs. (3) and (4) for the free-energy functional. We have checked several sum rules, which relate the derivatives with respect to A_{ii} and α_{jj} of the general expression for the free energy of the strained crystal, and the derivatives with respect to the density and the scalar Gaussian decay parameter α_0 in the relaxed crystal. Namely,

$$\begin{aligned} &4\rho\partial F/\partial\rho + 3\rho^2\partial^2 F/\partial\rho^2 = \partial^2 F/\partial A_{11}^2 + 2\partial^2 F/\partial A_{11}\partial A_{22} \ , \\ &\partial^2 F/\partial\alpha_0\partial\rho = -(1/\rho)(\partial^2 F/\partial A_{11}\partial\alpha_{11} + 2\partial^2 F/\partial A_{11}\partial\alpha_{22}) \ , \\ &\partial^2 F/\partial\alpha_0^2 = 3\partial^2 F/\partial\alpha_{11}^2 + 6\partial^2 F/\partial\alpha_{11}\partial\alpha_{22} \ . \end{aligned} \tag{12}$$

The results for the elastic constants, the bulk modulus,

$$B = (C_{11} + 2C_{12})/3 \ , \tag{13}$$

and Poisson's ratio,

$$\nu = C_{12}/(C_{11} + C_{12}) \ , \tag{14}$$

are given in Table II, for several values of the solid density. The liquid and the solid coexist at the first density, while the solid is more stable at the rest of the densities. As can be seen from the table, C_{12} is always positive and the value of Poisson's ratio is very close to the experimental results for fcc crystals.[19] The bulk modulus also gives sensible results, comparable to the dense fluid. All these results are to be contrasted with the previous DFF calcu-

TABLE I. Coexistence data for liquid-solid transition in units of the hard-sphere diameter ($\sigma = 1$). The results given in Ref. 10 have been numerically improved in the present work.

Liquid density at coexistence	0.9412
Solid density at coexistence	1.0563
Gaussian decay parameter for solid	161.65

TABLE II. Elastic constants of the hard-sphere solid in units of $\sigma = k_B T = 1$.

ρ	α_0	C_{11}	C_{12}	C_{44}	B	ν
1.0563	161.65	71.1	34.4	61.5	46.6	0.33
1.0663	175.25	76.9	36.7	66.3	50.1	0.32
1.0763	207.28	89.8	41.5	77.7	57.6	0.32

lations in the RY approach. We have been informed of a very recent computer simulation[20] to evaluate the same elastic constants which is in sharp disagreement with the earlier DFF attempts.

Thus it seems clear now that the truncated density expansion used in the RY approach to crystallization may give a good description of the unstrained solid but fails dramatically in the evaluation of the elastic constants. We may think of two explanations for this effect. The derivatives of the free energy with respect to the strain tensor elements may be regarded as the changes of F associated to a particular change in the density distribution, so that they are the projection of the second functional derivative of $F[\rho(\mathbf{r})]$ on the derivatives of $\rho(\mathbf{r})$ with respect to the strain tensor

$$\partial^2 F/\partial A_{ij}\partial A_{kl} = \int d\mathbf{r} \int d\mathbf{r}' [\delta^2 F/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')] \times [d\rho(\mathbf{r})/dA_{ij}][d\rho(\mathbf{r}')/dA_{kl}] \ , \tag{15}$$

where the derivatives have to be evaluate at the unstrained solid, and include the full relaxation of the free parameters.

The second functional derivative of $F[\rho]$ may be written[21] as

$$(1/k_B T)[\delta^2 F/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')] = \delta(\mathbf{r}-\mathbf{r}')/\rho(\mathbf{r}) - c(\mathbf{r},\mathbf{r}') \ , \tag{16}$$

where $c(\mathbf{r},\mathbf{r}')$ is the direct correlation function of the crystal, which is in general a function of $\mathbf{r}$ and $\mathbf{r}'$ independently. However, in the RY approach, $F[\rho]$ is expanded from the reference uniform system, up to second order, so that it is equivalent to approximate $c(\mathbf{r},\mathbf{r}')$ by the reference-fluid direct correlation function, $c_0(|\mathbf{r}-\mathbf{r}'|)$, which is isotropic. Therefore, letting aside the ideal-gas contribution, which gives the purely local first term in the rhs of (16), the RY approach uses a fully isotropic and homogeneous response function for the crystal. It is not too surprising then that the elastic coefficient C_{12}, which measures the anisotropy of the crystal response function, may not be well reproduced, and unphysical estimates may be obtained. This problem could be corrected, at least partially, if the functional expansion in (1) is extended up to third order.[4] This would already give some anisotropic dependence to $c(\mathbf{r},\mathbf{r}')$ evaluated at the crystal. The main problem for this extension of the theory is the lack of information for the three-particle correlations in bulk fluids.[22]

The second problem which may present the calculation in the RY approach is the lack of full thermodynamic consistence in the evaluation of the strained crystal free energy. The reference density ρ_0 at which $F[\rho]$ is expanded in (1) is fixed for the equilibrium, unstrained solid, but it will depend on its density. In fact, the criterion to fix the reference density is one of the crucial points in that approach to crystallization. In the evaluation of the elastic constants, the reference system is considered fixed, but as the sum rule (12) expresses, a suitable combination of variations with respect to the diagonal terms of the strain tensor should be equivalent to changes with respect to the density in the fully relaxed crystal. It is clear that in the RY approach this is not obtained, because ρ_0 is considered as fixed when evaluating the derivatives with respect to the strain tensor, while it has to be allowed to change in the evaluation of the unstrained crystal free energy as a function of the solid density. The failure in reproducing the sum rule (12) is therefore a serious thermodynamic inconsistency of this approach.

To summarize, the peculiar values of the elastic constants obtained for the HS crystal seem to be a result of the pathological behavior of the density expansion used in their evaluation. The alternative method which has been used in the study of the hard-sphere crystallization (ADA) seems, however, to be able to correctly reproduce the elastic properties of the system. This is probably because the latter approach has full thermodynamic consistency, reflected in the sum rules (12), and at the same time reproduces the anisotropy of the crystal response function.

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