"Martensitic" Instability of an Icosahedral Quasicrystal

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A density-functional theory is developed to calculate the elastic moduli of crystals and quasicrystals. It is found that the nonaffine character of deformations below the unit-cell scale causes the Poisson ratio of a hard-sphere solid to be negative. An elastic instability is found for the icosahedral quasicrystals which lowers their symmetry to D_3 or D_5. The distortions of the diffraction pattern are in qualitative agreement with experiments.

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During the last several years there has been a renewed interest in theories of solid-liquid transition. The appeal of the density-functional theory put forward by Ramakrishnan and Yussouff[1] is in its simplicity, accuracy, and the fact that it contains no adjustable parameters. The accuracy is controlled by the truncation of an expansion around a reference uniform state. The only assumption enters through a description of this state. This theory is quite successful in predicting solidification parameters for hard-sphere (HS)[2] and Lennard-Jones (LJ)[3] fluids. Such theory was also used to study submonolayer phases of rare gases on graphite,[4] the glass transition,[5] and most recently the stability of icosahedral quasicrystals.[6] Several authors have proposed that a similar approach can be used for "first-principles" calculations of such quantities as defect energy,[7] liquid-solid interface,[8] elastic moduli,[9] etc.

In this Letter we develop a density-functional theory for calculating the elastic moduli of crystals and quasicrystals. A novelty of our calculation is that we allow for the relaxation of the strained crystal density. Although our main interest is in quasicrystals, we first consider the elastic moduli of HS, LJ, and (hypothetical) cobalt fcc crystals.[10] We then focus our attention on the elastic moduli of a hypothetical cobalt icosahedral quasicrystal.[11]

In the case of the HS system we used the Percus-Yevick liquid structure factor at the freezing point. For the LJ calculation we make use of the supercooled-liquid structure factor determined by computer simulations near the glass transition.[12] For the Co calculation we used the experimentally determined amorphous cobalt structure factor[13] which we assume to be similar to the structure factor of supercooled-liquid Co near its estimated glass point. Because of the lack of relevant experimental and theoretical results, we cannot make an independent check of calculated crystal moduli. However, the results which are available at different points in the phase diagrams indicate that our moduli are of the correct order of magnitude. We have also found that the density relaxation is crucial for HS, important for LJ, but negligible for Co. An interesting result of our investigation is the discovery that a HS crystal has negative Poisson ratio at the melting point. The Poisson ratio is driven negative by the density relaxation of purely geometric (entropic) origin.

Recently, several authors analyzed the role of "phasons"[14] in elastic and hydrodynamic properties of icosahedral quasicrystals.[15] A goal of this Letter is to complement their analysis by calculation of the elastic moduli. Our starting point is the density-functional determination of icosahedral quasicrystalline structures,[6] with the exception that instead of the *linear* extrapolation, we used a *flat* extrapolation of the "liquid" Co structure factor to a value consistent with the compressibility of Co. Note that single-component HS or LJ liquids do not seem to lead to a (meta)stable icosahedral phase. By extending our calculations for crystals, we evaluated the elastic modulus tensor for icosahedral Co.[11] This tensor has the usual "phonon" components of an isotropic solid and the new "phason" components associated with the relative displacement of the incommensurate density waves. While the phonon part of the tensor is positive, we found that the full tensor has one negative eigenvalue revealing an elastic instability and a spontaneous deformation of the icosahedral quasicrystal. If this deformation is small, it will be generated by a phonon-phason eigenstrain associated with the negative eigenvalue. The most likely (minimal) reduction of the icosahedral symmetry due to such spontaneous strain would be to D_5 or D_3 symmetry.[16] Diffraction patterns of such distorted quasicrystals are shown in Fig. 1. The main feature seen is the staggering of the spots which would otherwise lie on a line. This is in qualitative agreement with some recent experiments.[17]

The above results raise questions as to whether the icosahedral quasicrystals are elastically stable and whether the observed shifts might not reflect this instability rather than inhomogeneities caused by the growth direction.[17] The fact that the growth axis coincides with the threefold axis seems to suggest that the reduced symmetry is (crystallographic) D_3. On the other hand, D_5 symmetry is suggested by the fact that the more stable decagonal phase is often observed accompanying the

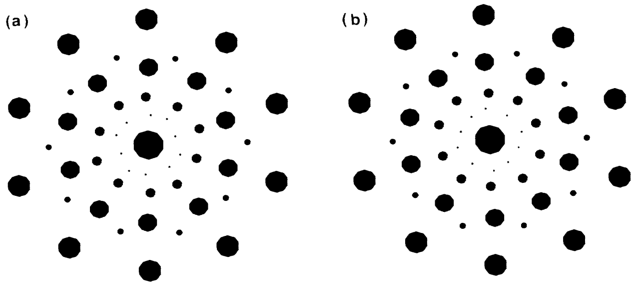

FIG. 1. Diffraction patterns perpendicular to a pseudo fivefold symmetry axis for (a) D_3 and (b) D_5 strains. The strain magnitude is 0.03 and the thickness of the reciprocal-space slice is 0.03 of the fundamental wave vector. Areas of the spots are proportional to their intensities. Only the spots with indices 0 or ±1 are shown. In order to see the staggering, the figure should be viewed at a glancing angle.

iscosahedral phase.[18] It is intriguing to note that Landau theory with an appropriate order parameter and with commensurate lock-in terms can predict a change of symmetry not only to D_5 but also to D_{10}.[19]

The isothermal elastic modulus tensor C of a solid is defined by expansion of the elastic free energy E_{el} to second order in the strain tensor ε,

$$E_{\text{el}}=H_\varepsilon-H+p(V_\varepsilon-V)=\tfrac{1}{2}\varepsilon^T{:}C{:}\varepsilon+\cdots, \tag{1}$$

where H is the Helmholtz potential of the solid, V its volume, and p its equilibrium pressure. Subscript ε indicates corresponding quantities for the strained solid. The infinitesimal strain ε is assumed to be defined on the surface of the solid so that a point at x is moved to $x_\varepsilon=(1+\varepsilon)\cdot x$ and the volume V is changed to $V_\varepsilon=V/\|1+\varepsilon\|$. The number N_S of particles in the solid and the temperature T are kept constant.

The potentials H and H_ε as well as the solid densities $n(x)$ and $n_\varepsilon(x)$ are evaluated within a density-functional approach.[1] In this approach one calculates the grand canonical potential G (which is Legendre transform of H) as the minimum of a variational potential W whose "energy" contribution is expanded around that of a reference liquid:

$$\begin{aligned}(p_L-p_S)V&=G(\mu_S,V,T)-G(\mu_L,V,T)\\&=\min_{n(x)}\Delta W\end{aligned} \tag{2}$$

and

$$\Delta W=-N_S(\mu_S-\mu_L)-(N_S-N_L)+\int_V n(x)\ln\frac{n(x)}{n_L}-\frac{1}{2}\int_V\int_V[n(x)-n_L]C_L(|x-y|)[n(y)-n_L]+\cdots, \tag{3}$$

where all energies are in units of k_BT, μ denotes chemical potential, the direct pair correlation function of the liquid is C_L, and subscripts S and L denote the solid and the liquid, respectively.

It has been observed in the past that for simple solids a remarkably simple and accurate theory of freezing is obtained by expansion of the solid density into Gaussians centered at the sites of a Bravais lattice. With this *Ansatz* the density $n(x)\equiv n(x;n_S,a,\alpha)$ depends on the average solid density n_S, the 3×3 matrix of lattice constants a, and the symmetric 3×3 Gaussian-width matrix α. Consequently, the functional ΔW becomes a *function* of these parameters and the minimization is greatly simplified.

In order to determine the free energy of a strained crystal, one must first determine its equilibrium density $n_\varepsilon(x)$. If the crystal is viewed as a uniform continuum, then $n_\varepsilon(x)$ would be simply given by $n[(1+\varepsilon)^{-1}\cdot x]/\|1+\varepsilon\|=n((1+\varepsilon)^{-1}\cdot x;n_S,a,\alpha)/\|1+\varepsilon\|$. However, this formula does not generally hold below the unit cell scale. Consequently,

$$n_\varepsilon(x)=n((1+\varepsilon)^{-1}\cdot x;n_S,a_\varepsilon,\alpha_\varepsilon)/\|1+\varepsilon\|, \tag{4}$$

where $a_\varepsilon\equiv a+\Delta a$ and $\alpha_\varepsilon\equiv\alpha+\Delta\alpha$ are to be determined by minimizing ΔW_ε given by Eq. (3) with $n(x)$ replaced by $n_\varepsilon(x)$, V by V_ε, and μ_S by $\mu_{S\varepsilon}$. The chemical potential $\mu_{S\varepsilon}$ of the strained solid is fixed by the condition that the parameter n_S should indeed minimize ΔW_ε. Therefore, the equilibrium strained density is characterized by the average $n_S/\|1+\varepsilon\|$, the lattice constants $(1+\varepsilon)\cdot a_\varepsilon$, and the Gaussian width $(1+\varepsilon)\cdot\alpha_\varepsilon\cdot(1+\varepsilon)$.

A nonzero Δa corresponds to a change in the number of defects as the solid is strained. Because of long characteristic times for diffusion of vacancies and interstitials it is probably a good approximation to assume that in a realistic experiment this number is constant. We shall therefore take $a_\varepsilon=a$.[20] On the other hand, a nonzero $\Delta\alpha$ roughly corresponds to a change in the mean square displacements of the atoms. As we already mentioned this can be an important effect which has been previously neglected.

It is generally not a simple task to minimize ΔW_ε with respect to six components of α_ε. However, since to lowest order $\Delta\alpha\propto\varepsilon$ and the elastic energy is $O(\varepsilon^2)$, the elastic modulus C can be determined from an expansion of ΔW_ε to order $\Delta\alpha^2$. Therefore, Eq. (1) is replaced by

$$E_{\text{el}}=\min_{\Delta\alpha}(\tfrac{1}{2}\varepsilon{:}C_0{:}\varepsilon+\Delta\alpha{:}C_1{:}\varepsilon+\tfrac{1}{2}\Delta\alpha{:}C_2{:}\Delta\alpha), \tag{5}$$

where the fourth-rank tensors C_0, C_1, and C_2 can be directly evaluated by expansion of ΔW_ε. Explicit expressions for these tensors in terms of reciprocal-lattice sums involve first and second derivatives of the liquid structure factor and will be given elsewhere.[10] A minimization of Eq. (5) trivially leads to the elastic modulus $C=C_0-C_1^T{:}C_2^{-1}{:}C_1$. The second term in C reflects the nonaffine density deformation at the length scale of the unit cell.

We base our calculation of quasicrystal elastic modulus on a recent density-functional calculation of quasicrystal density.[6] The density of an incommensurate crystal can always be represented as a cut through a higher-dimensional periodic crystal. The physical and experimentally relevant icosahedral quasicrystal density $n^{\parallel}(x^{\parallel})$ can be viewed as a particular three-dimensional cut through a six-dimensional simple-cubic crystal density $n(x^{\parallel},x^{\perp})$. That is, $n^{\parallel}(x^{\parallel})=n(x^{\parallel},x^{\perp}=0)$, where the superscripts $\parallel$ and $\perp$ denote the three-dimensional physical subspace and its three-dimensional orthogonal complement, respectively. It can be also shown that minimization of Eq. (2) with respect to $n^{\parallel}(x^{\parallel})$ is *formally* equivalent to minimization of a six-dimensional ΔW with respect to $n(x^{\parallel},x^{\perp})$. The hypothetical six-dimensional and the physical liquid structure factors are related via $C_L(Q^{\parallel},Q^{\perp})\equiv C_L^{\parallel}(Q^{\parallel})$.

The quasicrystal minimization of ΔW was performed with use of the Gaussian expansion of the density in six dimensions and $C_L^{\parallel}$ was taken to be the structure factor of amorphous Co.[6] It was found that the quasicrystal is more stable than the reference liquid. The diffraction pattern determined from the calculated quasicrystal density was in good qualitative agreement with experiments on real alloys.

From the explicit form of ΔW in six dimensions it can be easily verified that it is invariant under displacements $x\rightarrow x+u$. The $u^{\parallel}$ compoennt of u is the usual physical displacement whereas the component $u^{\perp}$ corresponds to relative displacement of the density waves. *Small* constant $u^{\parallel}$ and $u^{\perp}$ label independent degenerate densities. The long-wavelength limit of corresponding excitations can be considered by allowing uniform $x^{\parallel}$ dependence in u: $u^{\parallel}=\varepsilon^{\parallel,\parallel}\cdot x^{\parallel}$ and $u^{\perp}=\varepsilon^{\perp,\parallel}\cdot x^{\parallel}$. Therefore, the calculation as outlined for elasticity in three dimensions can be applied to six dimensions. One must keep in mind that the only nonzero blocks of ε are the physical strain $\varepsilon^{\parallel,\parallel}$ and the new strain $\varepsilon^{\perp,\parallel}$.

The strain ε has fifteen independent components and the "elastic" modulus tensor C can be considered as a 15×15 matrix. For icosahedral quasicrystals C has only five independent components. The usual elastic energy $\frac{1}{2}\varepsilon^{\parallel,\parallel}\cdot C^{\parallel,\parallel;\parallel,\parallel}\cdot\varepsilon^{\parallel,\parallel}$ is isotropic because of high icosahedral symmetry. Consequently, the block $C^{\parallel,\parallel;\parallel,\parallel}$, which is the usual elastic modulus tensor, has only two independent components. The block $C^{\perp,\parallel;\perp,\parallel}$ has also only two independent components, but their tensorial structure is more complicated. Finally, the block $C^{\perp,\parallel;\parallel,\parallel}$ has only a single component and its tensorial structure is also nontrivial.[11] By contraction of appropriate components of C with the physical wave vector $q^{\parallel}$ one can obtain the phonon and phason energies.[15] All our conclusions about the number of independent components and their explicit tensorial structure agree with Ref. 15.

The tensor C can be diagonalized by the observation that the fifteen-dimensional representation of Y spanned by ε decomposes into irreducible components according to $\mathbf{15}=\mathbf{5}\oplus\mathbf{5}\oplus\mathbf{4}\oplus\mathbf{1}$. We find that the corresponding four eigenvalues are (in arbitrary units) -1724.6, 3163.1, 456.2, and 3078.9. Hence, the five-dimensional subspace associated with the first eigenvalue is unstable indicating that a "strained icosahedral" rather than icosahedral density minimizes ΔW.

The new stable structure could be determined by minimizing (3) with the use of a more general six-dimensional Bravais lattice. However, this is a very tedious and complicated process which can be avoided when the equilibrium distortion of the hypercubic lattice is small. In this case the "spontaneous" strain can be assumed to lie in the five-dimensional eigenspace of the negative eigenvalue and the associated Landau-Ginzburg free energy that should be minimized is given by

$$F(\psi)=-1724.6\,|\psi|^2+O(\psi^3)+O(\psi^4)+\cdots, \qquad (6)$$

where ψ denotes the five-dimensional eigenstrain. The tensorial structure of the Y-invariant cubic and quartic terms can be determined with use of group theory while the actual coefficients can be evaluated by expanding ΔW. The most likely symmetries of the spontaneous strain can be determined by group theory[21]: These are the maximal isotropy subgroups of the five-dimensional irreducible representation of Y. In this way we obtain D_3 and D_5.[16]

It turns out that the symmetries D_3 and D_5 completely fix the strain ψ except for its magnitude. Therefore, we can calculate corresponding strained densities and their diffraction patterns shown in Fig. 1. It can be seen that the shift of a diffraction spot at $Q^{\parallel}$ has the usual contribution $-(1+\psi^{\parallel,\parallel})^{-1}\cdot Q^{\parallel}$ and a "staggering" contribution $-(1+\psi^{\parallel,\parallel})^{-1}\cdot(\psi^{\perp,\parallel})^{T}\cdot Q^{\perp}$ which is proportional to $Q^{\perp}$.

To summarize, we have formulated a density-functional theory of elasticity. The principal results we have obtained are (1) the negative Poisson ratio for HS solid, and (2) a martensitic instability of icosahedral Co. The first result calls for an independent verification, e.g., by Monte Carlo simulations. In order to check the accuracy of our approach it will be also necessary to extend our calculation for the LJ solid to the entire liquid-solid transition line. Further work is necessary to explore potentially important contributions from the three-point correlations neglected in the lowest-order expansion in Eq. (3). The second result raises the question as to whether the icosahedral quasicrystalline structure is generally intrinsically unstable with respect to some other structure, or whether it only might become destabilized at a sufficiently low temperature where a martensitic transition would occur.[22] The present calculation cannot tell whether the lowering of the symmetry would also involve a loss of quasiperiodicity. This emphasizes the urgency of extending the calculations based on more realistic structure factors of two-species supercooled liquids. If the described martensitic distortion indeed occurs in known quasicrystals, then their diffraction patterns *must* show the staggering. Therefore, a careful experimental determination of the temperature dependence of the staggered shifts which could discriminate quenched strains is also desirable. Such experiments would also reveal whether the low-symmetry structure is incommensurate by observation of whether the relative distortions change continuously with temperature.

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