# High-pressure mechanical instability in close-packed Hooke's-law crystals[a)]

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Lattice dynamics and molecular dynamics are used to study close-packed crystals with pairwise-additive Hooke's-law interparticle potentials. Lattice dynamics describes a mechanical soft-mode instability at high pressure. In two dimensions molecular dynamics reveals that a thermodynamic transition, from the triangular close-packed lattice to the square lattice, occurs before the soft-mode instability density is reached. Similar phenomena occur in the three-dimensional close-packed lattices.

When a solid is subjected to large stresses, such as those associated with shock waves, plastic and viscous flows can occur, in addition to elastic deformation. In exploratory computer-simulation studies of inelastic behavior in solids, the piecewise-linear-force model[1–3] has some advantages over more realistic force laws. In particular, there is a close correspondence between the microscopic Hamiltonian and the macroscopic strain-energy function.[2] As a preliminary to future molecular dynamics simulations of shock-induced plastic flow, the properties of the two-dimensional close-packed triangular lattice are examined here. The work reveals an interesting high-pressure "soft-mode"[4] instability.

Our model is a periodic two-dimensional triangular lattice with an $L\times L$ atom parallelogram unit cell. The interatomic potential is of the form

$$\phi(r)=\begin{cases}(1/2)\kappa(r-d_0)^2-\kappa w^2, & r< d_0+w,\\ -(1/2)\kappa(r-d_0-2w)^2, & d_0+w< r< d_0+2w,\\ 0, & d_0+2w< r\,.\end{cases} \quad (1)$$

The force derived from this potential is continuous. For all values of $r$ less than $d_0+w$ (where the "width" $w$ is typically $0.15d_0$), this potential is equivalent to a purely harmonic Hooke's-law interaction. The nearest-neighbor lattice dynamics for this model is worked out in the Appendix as a function of the reduced density $\rho=V_0/V$, where the (two-dimensional) stress-free "volume" is $(3/4)^{1/2}Nd_0^2$. This $V_0$ is exactly the volume occupied by $N$ hard disks of diameter $d_0$ in a close-packed triangular lattice. For a potential width $w=0.15d_0$, second-neighbor interactions would need to be included for densities greater than 1.78. If we exclude such higher-neighbor interactions, then the $2(N-1)=2(L^2-1)$ vibrational normal-mode frequencies have the form

$$(m/\kappa)\omega^2=(2-\rho^{1/2})T_{ij}\pm\rho^{1/2}U_{ij},\quad i=1,2,\ldots L,\quad j=1,2,\ldots L, \quad (2)$$

where $T_{ij}$ and $U_{ij}$ are density-independent functions of $i$ and $j$, given in the Appendix, and where the case $i=j=L$, corresponding to center-of-mass translation, is excluded. The + and − signs in Eq. (2) correspond, in certain symmetry directions, to longitudinal and transverse modes.

The longitudinal and transverse sound speeds can be obtained from a long-wave expansion of Eq. (2):

$$(m/\kappa d_0^2)c^2=(3/8\rho)[4-\rho^{1/2}(2\mp 1)]. \quad (3)$$

The transverse sound speed [plus sign in Eq. (3)] is zero at a density of 16/9, indicating a shear instability at that density. A detailed numerical study of the dispersion relation (2) shows that this is, in fact, the lowest compressive instability density. The "soft" modes that result are centered on the three symmetry lines in the Brillouin zone which correspond to correlated shear motion of close-packed rows of atoms.[5] A comparison of the dispersion relations at the stress-free density ($\rho=1$) and at a density ($\rho=1.75$) very close to the instability density is shown in Fig. 1. The low-frequency soft shear modes show up as deep valleys parallel to and centered on the symmetry lines.

Similar shearing modes cause instabilities, corresponding to shearing parallel to close-packed planes in the three dimensional close-packed lattices, where the instability density is $1.2^3=1.728$. The single-particle Einstein model predicts only a higher-density lattice instability: at $\rho=4$ (rather than 1.778) in a two-dimensional triangular lattice and at 3.375 (rather than 1.728) in the three-dimensional face-centered-cubic lattice.

If anharmonic forces are included, as, for example, in the long-range part of a piecewise-linear-force model (1), then a phase transition to another lattice structure occurs, rather than the one-phase catastrophic instability. A static-lattice calculation of energies for the piecewise-linear-force model with $w=0.15d_0$ indicates a first-order triangular-to-square lattice transition at a pressure of $0.21\kappa$, with coexisting densities of 1.25

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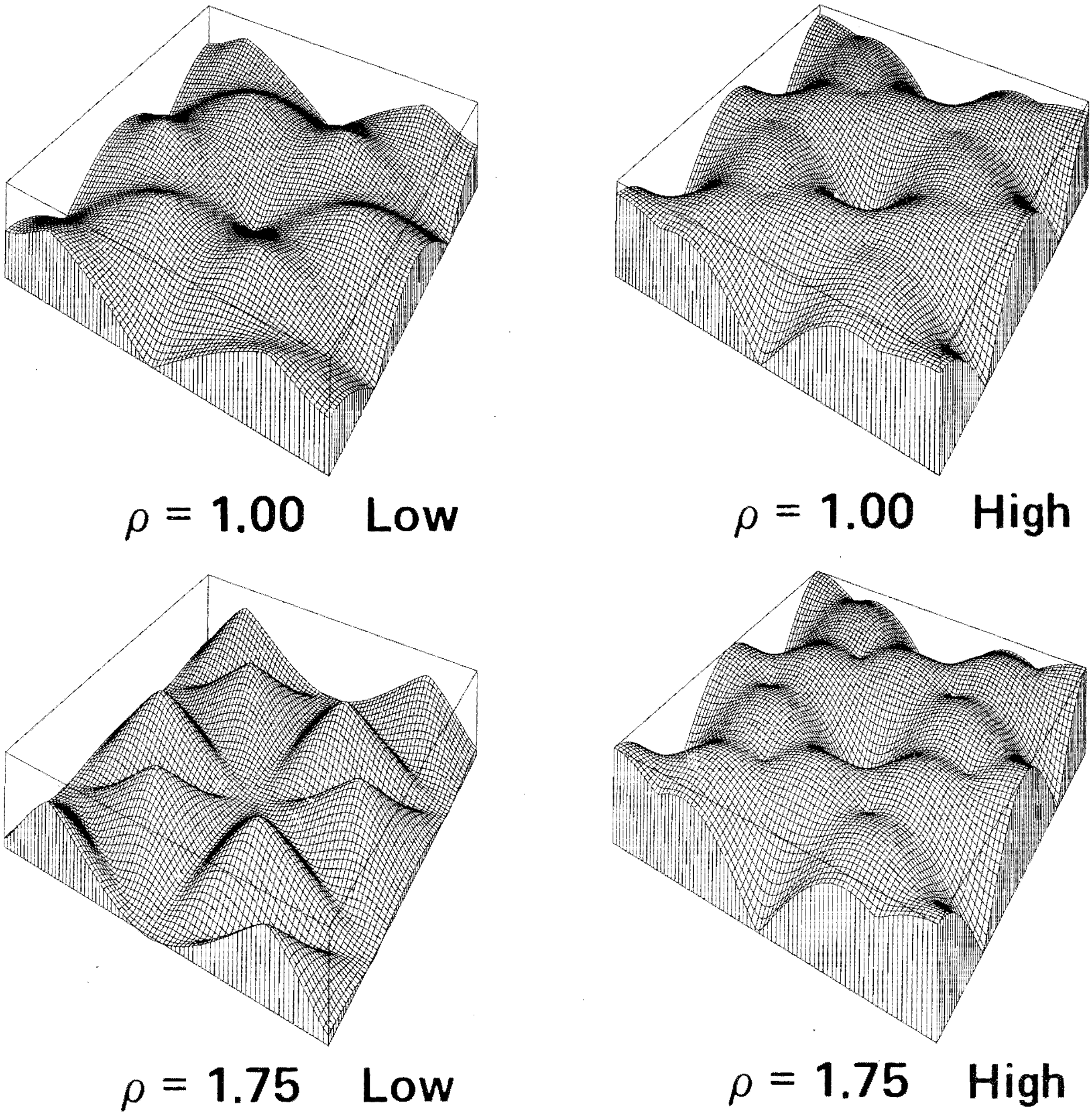


FIG. 1. (a) Low-frequency modes at the stress-free density. Frequency is plotted as a function of $k$. The region of $k$ space shown has an area equivalent to four Brillouin zones. (b) High-frequency modes at the stress-free density. (c) Low-frequency modes at $\rho = 1.75$. Note the deep valleys in $k$ space corresponding to the soft-mode instability analyzed in the text. (d) High-frequency modes at $\rho = 1.75$.

and 1.53. The square lattice, which is always unstable with just nearest-neighbor forces, is stabilized by second-neighbor interactions.

Consider, for example, a density of 1.50. The nearest-neighbor spacing is then $0.81650d_0$ in the triangular lattice and $0.75984d_0$ in the square lattice. With $w = 0.15d_0$ the second neighbors (at $1.41421d_0$ in the triangular case and $1.07457d_0$ in the square case) lie within the range of the potential $1.3d_0$ only in the square-lattice case. The energy per particle is $-0.0170\kappa d_0^2$ in the triangular case and $-0.0268\kappa d_0^2$ in the square case. Except at zero temperature, dynamical simulations must be used to establish stability.

We performed a series of simulations using molecular dynamics to solve the equations of motion for systems interacting with the potential (1). Molecular dynamics simulations at finite temperatures indicate that the triangular lattice is stable up to densities of about 1.2, and that the square lattice is stable at densities greater than 1.6. The melting temperatures of both lattices are of order $0.01\kappa d_0^2/k$, in agreement with previous estimates.[3]

The Helmholtz free energy of the triangular quasiharmonic lattice is, in the thermodynamic limit,

$$A/NkT = (\kappa d_0^2/kT)[1.5(\rho^{-1/2} - 1)^2 - 3(w/d_0)^2]$$

$$+2\ln(h\nu_E/kT) - \Delta S/Nk\ . \tag{4}$$

The first term is the static lattice contribution; the second is the uncorrelated single-particle (Einstein) contribution to the free energy; and the last term gives the collective normal-mode correction to the Einstein free energy. The Einstein frequency is

$$\omega_E/(2\pi) \equiv \nu_E = [3(\kappa/m)(2-\rho^{1/2})]^{1/2}/(2\pi)\ , \tag{5}$$

and $\Delta S/Nk$ is computed by averaging, over all nonvanishing normal-mode frequencies, the high (+) and low (−) frequency contributions to the vibrational entropy:

$$\Delta S/Nk = \langle \ln(\nu_E^2/\nu^+\nu^-)\rangle\ . \tag{6}$$

The sum over frequencies has been worked out analytically at $\rho=1$ by Huckaby,[6] with the result $\Delta S/Nk = 0.273$. At the instability density we find $\Delta S/Nk = (1/2)\ln 12 = 1.242$.

To analyze the mechanical soft-mode instability we consider the transverse modes that lie close to the symmetry line $k_1=k_2$ (see the Appendix). We choose $\theta_i = \theta+\delta\theta$, $\theta_j=\theta-\delta\theta$, and $\delta\rho=\frac{16}{9}-\rho$. We find that in the thermodynamic limit the minimum frequency varies as $(\delta\rho)^{1/2}$. The variation of frequencies near the minimum is parabolic in $\delta\theta$, with an effective width also proportional to $(\delta\rho)^{1/2}$:

$$(m/\kappa)(\omega^-)^2$$
$$=(1-\cos\theta)(2\delta\theta^2+(9/8)\delta\rho)+\text{higher-order terms.} \tag{7}$$

The contribution of each mode to the pressure is proportional to the "mode gamma" $\gamma=\partial\ln\omega/\partial\ln\rho$. For small $\rho$, the Brillouin-zone average can be calculated by integrating over $\theta_i$ and $\theta_j$ with the result

$$\langle\gamma\rangle = \langle(-2\delta\theta^2-(9/8)\delta\rho)^{-1}\rangle = -2\delta\rho^{-1/2}\ , \tag{8}$$

where the average includes all modes in the low-frequency $\omega^-$ branch.

The average indicated in Eq. (8) is to be carried out in the Brillouin zone described by the oblique coordinates $\theta_1$ and $\theta_2$. Sixfold rotational symmetry within the zone allows us to use the region within which $\theta_1$ varies from 0 to $\pi$ and $\theta_2$ is restricted to a narrow strip near $\theta_1$. The integral of gamma over this region must then be divided by one sixth the zone area, namely, $\pi^2/3^{1/2}$, to obtain $\langle\gamma\rangle$. Because the integrand depends only on $\delta\theta$, not $\theta_1$ and $\theta_2$ separately, the $\theta_1$ integration can be performed to give a multiplicative factor of $\pi$. The remaining integral $-(3/2\pi)\int d\delta\theta/[\delta\theta^2+(9\delta\rho/16)]$ reproduces the result just given in Eq. (8).

At intermediate densities we calculated the frequency sums numerically, using crystals of up to 160 000 atoms, in order to estimate the large-$N$ limit. The data for $\Delta S/Nk$ can be fitted within 0.001 by the function

$$\Delta S/Nk = (1/2)\ln(12)\exp[-\delta\rho^{1/2}(1.811-0.16\delta\rho^2)]\ . \tag{9}$$

The contribution to the compressibility factor $PV/NkT$ from all the soft shear modes, calculated in Eq. (8), agrees with a numerical calculation (giving 2.00 as the coefficient of $-\delta\rho^{-1/2}$) of the pressure from lattice dynamics at densities near the instability density. In the three-dimensional case an average of the form (8) would lead to a logarithmic singularity in the pressure.

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## APPENDIX: LATTICE DYNAMICS FOR THE TRIANGULAR HOOKE'S-LAW CRYSTAL

Using an oblique coordinate system (see Ref. 2 for details) to index the particles, the linear restoring force on the central (00) atom, in terms of the Cartesian displacements from the lattice sites, is

$$\begin{aligned}F_x = -\kappa[&2x_{00}-x_{01}-x_{0-1}+(1-\Gamma^2\rho^{1/2})\\ &\times(4x_{00}-x_{10}-x_{-10}-x_{1-1}-x_{-11})\\ &+(\Gamma/2)\rho^{1/2}(-y_{10}-y_{-10}+y_{1-1}+y_{-11})]\ ,\\ F_y=-\kappa[&(1-\rho^{1/2})(2y_{00}-y_{01}-y_{0-1})\\ &+(1-\tfrac{1}{4}\rho^{1/2})(4y_{00}-y_{10}-y_{-10}-y_{1-1}-y_{-11})\\ &+(\Gamma/2)\rho^{1/2}(-x_{10}-x_{-10}+x_{1-1}+x_{-11})]\ ,\end{aligned} \tag{A1}$$

where $\Gamma$ is $(3/4)^{1/2}$. By using Dean's method for diagonalizing the dynamical matrix,[7] the eigenfrequencies of the lattice are found to be given by Eq. (2) of the text, with

$$T_{ij}=3-\cos\theta_i-\cos(\theta_i-\theta_j)-\cos\theta_j\ ,$$
$$U_{ij}=[\cos^2\theta_i+\cos^2(\theta_i-\theta_j)+\cos^2\theta_j-\cos\theta_i\cos\theta_j$$
$$-(\cos\theta_i+\cos\theta_j)\cos(\theta_i-\theta_j)]^{1/2}\ ,$$

with

$$\theta_i=k_1\Gamma d=2\pi i/L\ ,\quad \theta_j=k_2\Gamma d=2\pi j/L\ . \tag{A2}$$

The expression for the frequencies reduces to Dean's result in the stress-free case $\rho=1$.

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