Stress relaxation in a perfect nanocrystal by coherent ejection of lattice layers

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We show that a small crystal trapped within a potential well and in contact with its own fluid, responds to large compressive stresses by a novel mechanism — the transfer of complete lattice layers across the solid-fluid interface. Further, when the solid is impacted by a momentum impulse set up in the fluid, a coherently ejected lattice layer carries away a definite quantity of energy and momentum, resulting in a sharp peak in the calculated phonon absorption spectrum. Apart from its relevance to studies of stability and failure of small sized solids, such coherent nanospallation may be used to make atomic wires or monolayer films.

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Solids subject to large uniaxial deformations, relieve stress either by the generation and mobility of dislocations and/or by the nucleation and growth of cracks. What is the nature of stress relaxation when conditions are arranged such that these conventional mechanisms are suppressed? Nano-indentation experiments show that if small system size prevents the generation of dislocations, solids respond to tensile forces by shedding atoms from the surface layer. In this Letter, we study equilibrium and dynamical aspects of this process in detail using Monte Carlo and molecular dynamics simulations for a model system, analyzing our results in the light of existing theory and simulation experiments show that if small system size prevents the generation of dislocations, solids respond to tensile forces by shedding atoms from the surface layer.

We create a dislocation-free nanosolid by trapping a collection of atoms in their crystalline state within a potential well of depth $-\mu$ over a finite region $S$ placed in contact with its fluid (Fig. 1). Trapping of atoms such as alkali metals and noble gases may be achieved by optical and magneto-optical techniques, using laser powers ranging from $1 - 10^2$ mW. On the other hand, colloidal solids may be manipulated using a number of optical techniques or surface templates.

To see that this trapped nanosolid is dislocation-free, we study the equilibrium behaviour of a model 2-dimensional (2d) nanosolid using a Monte Carlo simulation in the constant number ($N$), area ($A$) and temperature ($T$) ensemble with usual Metropolis moves using the Hamiltonian $H = \sum_{ij} V_{ij} + \sum_i \phi(r_i)$, where $V_{ij}$ is the 2-body potential and $\phi$ is the trap potential, here approximated as a rectangular potential well of depth $-\mu$ (Fig. 1). For numerical convenience we choose a system of hard disks (Fig. 1): our main results trivially extend to particles interacting with any form of repulsive potential, or even when the interactions are augmented by a short-range attraction, provided we choose $\mu$ deeper than the depth of the attractive potential. While all our simulations are carried out in 2d, our qualitative results should extend to three dimensions (we shall use the generic words ‘layer’ and ‘surface’ to describe the 1-dimensional line of atoms). The equilibrium density profile (Fig.1b) is obtained for different $\mu$ at fixed average density $\eta$.

The ‘phase diagram’, a plot of the density difference across the interface $\Delta \eta/\eta \equiv (\eta_s - \eta_l)/\eta$ versus $\mu$ (Fig. 2), shows a sharp jump at $\mu \approx 8$. This transition is associated with an entire close-packed layer entering $S$ thereby increasing the number of solid layers by one.
FIG. 1: (a) A 2d crystal of \( N_s \) atoms confined to a central region \( S \) of area \( A_s = L_x \times L_y \) by means of an optical trap with a potential \( \phi(r) = -\mu \) for \( r \in S \) which increases sharply to zero elsewhere over a width \( \delta \). The trapped solid of density \( \eta_s \) is in contact with its fluid of density \( \eta_f < \eta_s \), such that the average density in the entire simulation cell of \( N \) atoms occupying an area \( A = L_x \times L_y \) is \( \eta = \pi N/4A \). The atoms interact with a hard disk potential \[ V_{ij} = 0 \text{ for } |r_{ij}| > \sigma \text{ and } V_{ij} = \infty \text{ for } |r_{ij}| \leq \sigma, \] where \( \sigma \) is the hard disk diameter which sets the scale of length and \( r_{ij} = r_j - r_i \), the relative position vector of the particles. We have chosen \( \delta = \sigma/4 \). We set the energy scale by \( k_B T \). (b) Equilibrium behaviour for different \( \mu \) at fixed \( \eta = 0.699 \) (density at freezing \( \eta_f = 0.706 \)) obtained by Monte Carlo simulations in the constant NAT ensemble with periodic boundary conditions in both directions \( (N = 1200 \text{ particles occupy an area } A = 22.78 \times 59.18 \text{ with the solid occupying the central third of the cell of size } L_s = 19.73) \). The trap depth \( \mu = 6 \), supports an equilibrium solid of density \( \eta_s = 0.753 \) in contact with a fluid of density \( \eta_f = 0.672 \). The closest-packed lines of the solid in \( S \) are parallel to the solid - fluid interfaces which lie, at all times, along the lines where \( \phi(y) \rightarrow 0 \). The density profile \( \eta(y) \) coarse grained over strips of width \( \sigma \) (averages taken over \( 10^3 \) MC configurations each separated by \( 10^3 \) MCS), varies from \( \eta_f \) to \( \eta_s \) as we move into \( S \). The horizontal lines are predictions of a simple free-volume based theory (see Fig. 2) for \( \eta_s \) and \( \eta_f \). (c) Superposition of particle configurations from the MC run in (b) showing a solid like order (red : high \( \eta \)) gradually vanishing into the fluid (yellow : low \( \eta \)) across a well defined solid-fluid interface.

The resulting solid is a triangular lattice with a small rectangular distortion \( \epsilon_d(\eta_s, L_s) \). The qualitative features of this phase diagram may be obtained by a simple thermodynamic theory (Fig. 2) with harmonic distortions of the solid, ignoring contributions from spatial variations of the density. We find that the jump in the fractional density difference is sensitive to \( L_s \) and vanishes for large \( L_s \) or \( \delta \), the sharpness of the trap.

Adiabatically cycling the trap depth \( \mu \) across the jump obtains a sharp rectangular hysteresis loop: this indicates that ‘surface’ steps (dislocation pairs) nucleated in the course of adding (or subtracting) a solid layer, have a vanishingly short lifetime. Consistent with this we find that the jump in \( \Delta \eta(\mu)/\eta \) vanishes when the system is minimised at each \( \mu \) with a constraint that the solid contains a single dislocation pair. Interestingly, a dislocation pair forced initially into the bulk, rises to the solid-fluid interface due to a gain in strain energy \[ \epsilon_d \], where they form surface indentations flanked by kink-antikink pairs. The confining potential, which prefers a flat interface, may remove these indentations either by bending lattice layers or annealing the kink-antikink pair incorporating particles from the adjacent fluid. The second process always costs less energy and happens

FIG. 2: Plot of the equilibrium fractional density change \( \Delta \eta/\eta \) as a function of \( \mu \) (points (MC data), thick solid line (approximate theory)), showing discontinuous jump at \( \mu \approx 8 \). The MC data are obtained by averaging over \( 10^3 \) configurations each separated by \( 10^3 \) MCS, while the system is equilibrated for \( > 10^5 \) MCS starting from a uniform fluid with density \( \eta = 0.699 \). The approximate theory is based on the assumption that a change in \( \mu \) produces a uniform geometric strain \( \epsilon_d \) from a reference triangular lattice with the same number of atomic layers. The geometric strain \( \epsilon_d \) is an oscillatory function\[ \[ \epsilon_d \] of \( L_s \), with an amplitude which decays as \( 1/L_s \). The Helmhotz free energy of the harmonic solid is then given by \( f_s = f_s + 1/2 \Delta \kappa \varepsilon_d^2 \), where \( \Delta \kappa \) and \( \Delta \kappa \) are the free energy and Young’s modulus respectively, of an undistorted triangular lattice which may be obtained from simple free-volume theory\[ \[ \epsilon_d \] \]. Minimising the total free energy density of the fluid + solid regions, \[ f = x[f_s(\eta_s, L_s) - 4\eta_s\mu/\pi] + (1 - x)f_l(\eta_f) \] with the constraint \( \eta = x\eta_s + (1 - x)\eta_f \), where \( x \) is the area fraction occupied by \( S \) and \( f_l(\eta_f) \) is the free energy of the hard disk fluid\[ \[ \epsilon_d \] \] produces the jump in \( \Delta \eta(\mu)/\eta \). Inset (top) shows a cycle-averaged hysteresis loop as \( \mu \) is cycled at the rate of \( 0.2 \) per \( 10^3 \) MCS. (bottom) A plot of the tensile stress \( \gamma_d \) against strain \( \epsilon_d \). The arrows show the behaviour of these quantities as \( \mu \) is increased from the points marked A – D. The corresponding points in the \( \Delta \eta/\eta \) vs. \( \mu \) plot is also marked for comparison. The state of stress in the solid jumps discontinuously from tensile to compressive from B to C due to an increase in the number of solid layers by one accomplished by incorporating particles from the fluid. This transition is reversible and the system relaxes from a state of compression to tension by ejecting this layer as \( \mu \) is decreased.
quickly. The question is how quickly?

To study the lifetime of the kink-antikink pairs (surface step), we resort to a molecular dynamics (MD) simulation using a velocity Verlet algorithm\textsuperscript{[2]} with the unit of time given by \( \tau = \sqrt{m\sigma^2/k_BT} \), where \( m (= 1) \) is the mass of the hard disks\textsuperscript{[24]}. Using values of \( m \) and \( \sigma \) typical for atomic systems like Ar or Rb, \( \tau \approx 1 \)ps. Starting with an equilibrium configuration at \( \mu = 9.6 \) (and \( k_BT = 1 \)) corresponding to a 22-layer solid, we create a unit surface step of length \( l \) by removing a few interfacial atoms and ‘quench’ across the transition to \( \mu = 4.8 \), where the 21-layer solid is stable. A free energy audit involving a bulk free energy gain \( \Delta F_L l \), going from 22 to 21 layered solid (Fig. 2), and an elastic energy cost \( \propto \log(l) \) for creating the step, reveals that a surface step is stable only if \( l \geq l^* \sim 1/L_x \).

For small \( L_x \), the critical size \( l^* \) may therefore exceed \( L_x \), the total length of the interface. Indeed, we observe all steps, save a complete removed layer, get annealed by particles from the adjacent fluid over a time scale of order \( \tau \). The solid therefore relieves stress only by the loss or gain of an entire lattice layer, since all other avenues of stress relief entail higher energy costs.

This mechanism of stress relaxation via the transfer of an entire layer of atoms may be exploited for a variety of practical applications, provided we can eject this layer of atoms deep into the adjoining fluid and enhance its lifetime. Highly stressed monoatomic layers tend to disintegrate or curl up\textsuperscript{[13]} as they separate off from the parent crystal. It may be possible to bypass this eventuality, if the time scale of separation is made much smaller than the lifetime of the layer. Can acoustic spallation\textsuperscript{[9]} be used to cleave atomic layers from a metastable, stressed nanocrystal? Imagine, therefore, sending in a sharp laser (or ultrasonic) pulse, producing a momentum impulse \( (v_\nu(t = 0) = V_\nu) \) over a thin region in \( y \) spanning the length \( L_y \) of the cell, which results in a weak acoustic shock\textsuperscript{[9]} (corresponding to a laser power \( \approx 10^2 \) mW and a pulse duration 1ps for a typical atomic system).

The initial momentum pulse travels through the solid and emerges at the far end (Fig. 3 (a)-(c)) as a broadened Gaussian whose width, \( \Delta \), is a measure of absorption of the acoustic energy of the pulse due to combined dissipation in the liquid, the solid and at the interfaces\textsuperscript{[2, 10]}. For large enough pulse strengths \( V_\nu \), this is accompanied by a coherent ejection of the (single) outer layer of atoms into the fluid; such coherent nanospallation involves surface stresses of the order \( k_BT/\sigma^2 \approx 10^{-5} \) N/cm\(^2\) (Fig. 3(d)). In contrast, spallation in bulk solids like steel needs acoustic pressures in excess of \( 10^5 \) N/cm\(^2\)\textsuperscript{[4]} usually available only during impulsive loading conditions; the ejected layer is a “chunk” of the surface. This difference comes about because unlike a bulk system, a strained nanocrystal on the verge of a transition from a metastable \( n + 1 \) to a \( n \) layered state readily absorbs kinetic energy from the pulse. The fact that surface indentations are unstable (see Fig. 4(a)) unless of a size comparable to the length of the crystal, \( L_x \), ensures that a full atomic layer is evicted almost always, leading to coherent absorption of the pulse energy. The coherence of this absorption mechanism is markedly evident in a plot of \( \Delta^2 \) against \( V_\nu \) which shows a sharp peak (Fig. 4 (b)). Among the two systems studied by us, \textit{viz.}, a metastable \( (\mu = 4.8) \) and a stable \( (\mu = 9.6) \) 22 layered solid, the former shows
The spallated solid layer emerges from the solid surface into the fluid, and travels a distance close to the mean free path; whereupon it disintegrates due to viscous dissipation (Fig. 3 (d)). The lifetime of the layer is around 2-3 time units (τ) which translates to a few ps for typical atomic systems. The lifetime increases with decreasing viscosity of the surrounding fluid. Using the Enskog approximation [23] to the hard disk viscosity, we estimate that by lowering the fluid density one may increase the lifetime by almost three times. The lifetime enhancement is even greater if the fluid in contact is a low density gas (when the interparticle potential has an attractive part [26]).

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