# 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[1] and/or by the nucleation and growth of cracks[1, 2]. What is the nature of stress relaxation when conditions are arranged such that these conventional mechanisms are suppressed? Nano-indentation experiments[3] show that if small system size prevents the generation of dislocations[4], 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[5] for a model system, analyzing our results in the light of existing theory[4, 6, 7]. Briefly, we discover that a small solid, constrained to remain defect free by being, at all times, in contact with its own liquid (a situation easily realised using optical traps[8]), responds to stress by exchanging surface atomic layers with the adjacent liquid. Impacting the solid with a momentum pulse[9] of sufficient strength dislodges an entire crystalline layer coherently, which travels into the liquid as a distinct though short-lived entity, with a lifetime determined by the fluid viscosity[7]. A curious feature of this process is that weaker pulses *do not* dislodge partial layers, leading to a novel resonance phenomenon distinguished by a pronounced peak in sound absorption[7]. We believe that our work may be useful for undertanding the failure behaviour and sound and heat[10] absorption properties of nanostructures[11, 12]. Since coherent scattering of momentum pulses occur over a narrow window of incident energies, this phenomenon may also be used as a detector/analyzer for weak acoustic shocks. Free standing, cleaved single atomic layers[13] have recently been shown to posses interesting mechanical and electrical properties. Coherent spallation[9] of nanocrystals, as discussed here, may be a practical way to produce such atomic layers or for making nanowires or nanosurface coatings[14] in the future.

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 $\mathcal{S}$ 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 [8], using laser powers ranging from $1 - 10^2$ mW. On the other hand, colloidal solids[15] may be manipulated using a number of optical techniques[16, 17] or surface templates[18].

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[4, 5] using the Hamiltonian $\mathcal{H} = \sum_{ij} V_{ij} + \sum_i \phi(\mathbf{r}_i)$, 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[20] for different $\mu$ at fixed average density $\eta$.

The 'phase diagram', a plot of the density difference across the interface $\Delta\eta/\eta \equiv (\eta_s - \eta_\ell)/\eta$ versus $\mu$ (Fig. 2), shows a sharp jump at $\mu \approx 8$. This transition is associated with an entire close-packed layer entering $\mathcal{S}$ thereby increasing the number of solid layers by one.

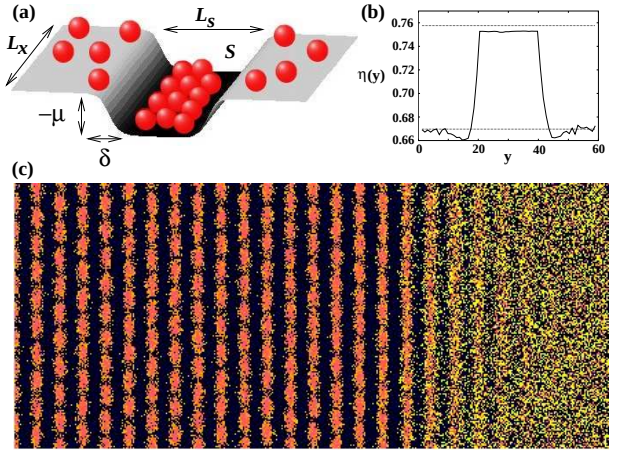


FIG. 1: (a) A 2d crystal of $N_s$ atoms confined to a central region $\mathcal{S}$ of area $A_s = L_x \times L_s$ by means of an optical trap with a potential $\phi(\mathbf{r}) = -\mu$ for $\mathbf{r} \in \mathcal{S}$ which increases sharply to zero elsewhere over a width $\delta$. The trapped solid of density $\eta_s$ is in contact with its fluid of density $\eta_l < \eta_s$, 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[4, 19, 21] $V_{ij} = 0$ for $|\mathbf{r}_{ij}| > \sigma$ and $V_{ij} = \infty$ for $|\mathbf{r}_{ij}| \leq \sigma$, where $\sigma$ is the hard disk diameter which sets the scale of length and $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ the relative position vector of the particles. We have chosen $\delta = \sigma/4$. We set the energy scale by $k_BT$. (b) Equilibrium behaviour for different $\mu$ at fixed $\eta = .699$ (density at freezing $\eta_f = .706$[19]) obtained by Monte Carlo simulations in the constant NAT ensemble with periodic boundary conditions in both directions ($N = 1200$ particles occupy an area $A = 22.78 \times 59.18$ 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 $\eta_s = .753$ in contact with a fluid of density $\eta_\ell = .672$. The closest-packed lines of the solid in $\mathcal{S}$ are parallel to the solid -fluid interfaces which lie, at all times, along the lines where $\phi(y) \to 0$. 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 $\eta_\ell$ to $\eta_s$ as we move into $\mathcal{S}$. The horizontal lines are predictions of a simple free-volume based theory (see Fig. 2) for $\eta_s$ and $\eta_\ell$. (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.

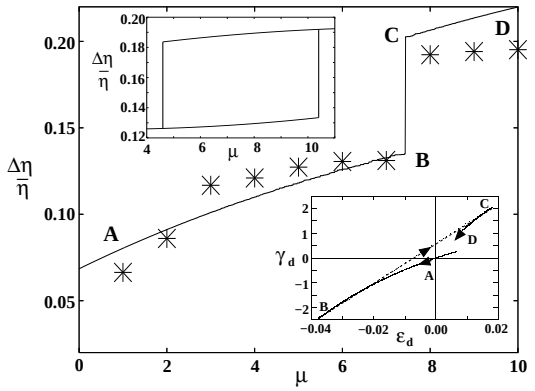


FIG. 2: Plot of the equilibrium fractional density change $\Delta\eta/\eta$ as a function of $\mu$ (points (MC data), thick solid line (approximate theory)), showing discontinuous jump at $\mu \approx 8$. The MC data are obtained by averaging over $10^3$ configurations each separated by $10^3$ MCS, while the system is equilibrated for $> 10^7$ MCS starting from a uniform fluid with density $\eta = .699$. The approximate theory is based on the assumption that a change in $\mu$ produces a *uniform* geometric strain $\varepsilon_d$ from a reference triangular lattice with the same number of atomic layers. The geometric strain $\varepsilon_d$ is an oscillatory function[4] of $L_s$, with an amplitude which decays as $1/L_s$. The Helmholtz free energy of the harmonic solid is then given by $f_s = f_\Delta + \frac{1}{2}K_\Delta\varepsilon_d^2$, where $f_\Delta$ and $K_\Delta$ are the free energy and Young's modulus respectively, of an undistorted triangular lattice which may be obtained from simple free-volume theory[4, 22]. Minimising the total free energy density of the fluid + solid regions, $f = x\,[f_s(\eta_s, L_s) - 4\eta_s\mu/\pi] + (1-x)f_l(\eta_\ell)$ with the constraint $\eta = x\eta_s + (1-x)\eta_\ell$, where $x$ is the area fraction occupied by $\mathcal{S}$ and $f_l(\eta_\ell)$ is the free energy of the hard disk fluid[23] produces the jump in $\Delta\eta(\mu)/\eta$. Inset (top) shows a cycle-averaged hysteresis loop as $\mu$ is cycled at the rate of .2 per $10^6$ MCS. (bottom) A plot of the tensile stress $\gamma_d$ against strain $\varepsilon_d$. 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 → 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.

The resulting solid is a triangular lattice with a small rectangular distortion $\varepsilon_d(\eta_s, L_s)$ [4]. 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[6], 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

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[5], with the unit of time given by $\tau = \sqrt{m\sigma^2/k_BT}$, where $m(=1)$ is the mass of the hard disks[24]. Using values of $m$ and $\sigma$ typical for atomic systems like Ar or Rb, $\tau \approx$ 1ps. 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 $\Delta F L_s l$, going from a 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 $l \geq l^* \sim 1/L_s$. For small $L_s$, 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[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[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 ($v_y(t=0) = V_0$) over a thin region in $y$ spanning the length $L_x$ of the cell, which results in a weak acoustic shock[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[7, 10]. For large enough pulse strengths $V_0$, 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$^2$[9] usually available only during impulsive loading conditions; the ejected layer is a "chunk" of the surface. This difference comes about

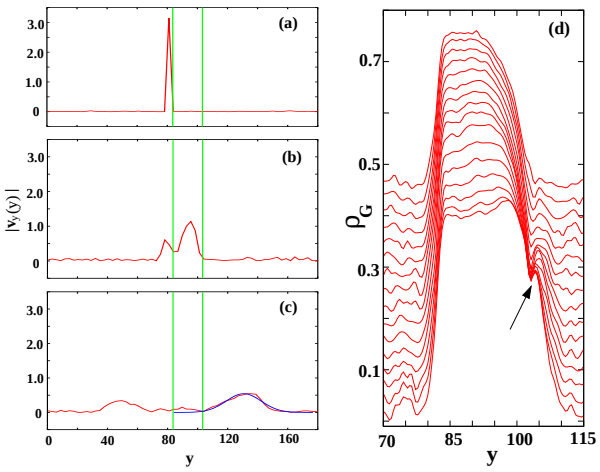


FIG. 3: (a)-(c) Plot of the absolute value of the momentum $|v_y(y)|$ for molecular dynamics times $t = .0007$ (a), .2828 (b) and 2.8284 (c). The green lines show the position of the solid - fluid interfaces. The parameters $L_s = 19.73$, $\eta_s = .789$ and $\mu = 4.8$. The fit to a Gaussian (blue line) is also shown in (c). The initial momentum pulse with strength $V_0 = 6.$ is given within a narrow strip of size $\sim \sigma$, just to the left of the solid region and the Gaussian fitted (and the width $\Delta^2$ extracted) when the maximum of the pulse reaches a fixed distance of 44.1 from the source. A reflected pulse can also be seen. To reduce interference from the reflected pulse through periodic boundary conditions, we increase the fluid regions on either side, so that for the MD calculations we have a cell of size $22.78 \times 186.98$ comprising 3600 particles. (d) A plot of the time development of the Fourier component of the local density correlation $\rho_{\mathbf{G}}(y,t)$ obtained by averaging, at each time slice $t$, the sum $\sum_{j=1,N} \exp(-i\,\mathbf{G}\cdot(\mathbf{r_j} - \mathbf{r_i}))$ over all particle positions $\mathbf{r_i}$ within a strip of width $\sim \sigma$ centered about $y$ and spanning the system in $x$. The wavenumber $\mathbf{G} = (2\pi/d)\hat{\mathbf{n}}$ where $d = .92$ is the distance between crystal lines in the direction $\hat{\mathbf{n}}$ normal to the fluid-solid interface. The solid (central region with $\rho_{\mathbf{G}}(y,t) \neq 0$) ejects a layer (shown by an arrow) which subsequently dissolves in the fluid. The curves from bottom to top correspond to time slices at intervals of $\Delta t = .07$ starting from $t = 1.06$ (bottom). We have shifted each curve upward by $.03t/\Delta t$ for clarity. Curves such as in (a)-(d) are obtained by averaging over $100-300$ separate runs using different realizations of the initial momentum distribution.

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 $V_0$ which shows a sharp peak (Fig. 4 (b) ). Among the two systems studied by us, *viz.*, a metastable ($\mu = 4.8$) and a stable ($\mu = 9.6$) 22 layered solid, the former shows

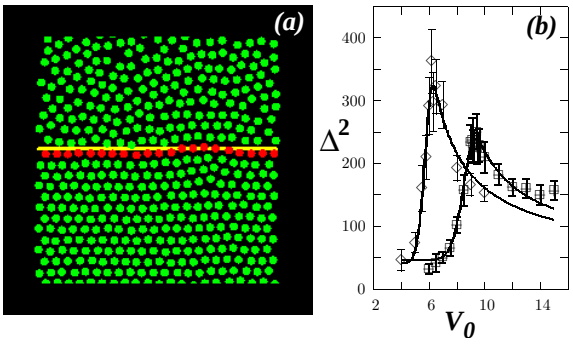


FIG. 4: (a)(color on-line) Configuration snapshot from a portion of our MD cell showing hard disk atoms (green circles) at the solid (bottom)- liquid interface (yellow line) as a weak momentum pulse ($V_0 = 2.$) emerges into the liquid. The pulse initially ejects a few atoms of the interfacial crystalline layer (red circles) of a metastable 22 layered solid at $\mu = 4.8$. The resulting large non- uniform elastic strain evidenced by the bending of lattice layers, however, causes these atoms to be subsequently pulled back into the solid. Only a stronger pulse capable of ejecting a complete lattice layer succeeds in reducing the number of solid layers by one leading to overall lower elastic energy. (b) Plot of the squared width $\Delta^2$ of the momentum pulse after it emerges from the solid as a function of $V_0$ for $\mu = 4.8\,(\diamond)$ and $9.6\,(\square)$. The solid line is a guide to the eye. The absorption of momentum is largest when the available kinetic energy of the pulse exactly matches the potential energy required to eject a layer. The peak in $\Delta^2(V_0)$ so produced is more prominent for the metastable 22 layered solid $\mu = 4.8$ than for the stable ($\mu = 9.6$) system showing a more coherent momentum transfer in the former case.

a sharper resonance. The eviction of the atomic layer is therefore assisted by the strain induced interlayer transition and metastability of the 22 layered solid discussed above. Spallation is also facillitated if the atomic interactions are anisotropic so that attraction within layers is stronger than between layers (eg. graphite and layered oxides[13]), for our model, purely repulsive, hard disk solid, an effective, intralayer attractive potential of mean force is induced by the external potential[4].

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 ($\tau$) which translates to a few ps for typical atomic systems. The lifetime increases with decreasing viscosity of the surrounding fluid. Using the Enskog approximation[25] 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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