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Rapid Equilibration by algorithmic quenching the ringing mode in molecular dynamics

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ABSTRACT

Long wavelength acoustic phonons are normally weakly coupled to other vibrational modes in a crystalline system. This is particularly problematic in molecular dynamics calculations where vibrations at the system-size scale are typically excited at initiation. The equilibration time for these vibrations depends on the strength of coupling to other modes, so is typically very long. A very simple deterministic method is presented which removes this problem. Examples of equilibration in lithium and a martensitic phase transition in sodium are used to demonstrate the method.

INTRODUCTION

Molecular dynamics is a very powerful method for simulating the behaviour of a many-atom system. It is particularly useful and flexible when used for studying phase transitions, since it makes no assumption about the preferred crystal structure. However if the system is not initiated in an equilibrium structure, it may take some time to equilibrate. There is no good theory that enables one to say how long the equilibration will take.

Indeed, within statistical mechanics, it is difficult to define what a non-equilibrium state even means. Provided the molecular dynamics is based on some underlying Lagrangian, any simulation will be initiated in a valid microstate of the appropriate ensemble. The reason why this microstate is "non-equilibrium" lies outside the realm of statistical mechanics.

Probably the only sensible way to address this is via the equipartition theorem, which holds that each degree of freedom has, on average, an equal amount of energy. One might then argue that if a single degree of freedom in a microstate has a *macroscopic* amount of energy - i.e. a finite fraction of the total energy - then the microstate is atypical and "non-equilibrium". One can think here of non-equilibrium situations in the Cartesian coordinate system \mathbf{r}_i , e.g. a radiation damage simulation where the primary knock-on atom has keV of energy, or of non-equilibrium in the normal modes \mathbf{u}_i , a simulation in which one phonon mode is massively excited.

Unfortunately, even this definition fails in general because of the nonunique definition of degrees of freedom. One can always recast the degrees of freedom in any linear combination - including a linear combination \mathbf{q}_i , chosen such that all the kinetic energy is in one degree of freedom \mathbf{q}_i . It is likely that such a perverse choice would have entangled degrees of freedom very far from the normal modes, which describe a typical near-harmonic crystal system. As such, the energy in \mathbf{q}_i , would disperse quickly into the other \mathbf{q}_j modes.

In this paper, we adopt the following definition of a "non-equilibrium microstate": *a microstate in which one degree of freedom has a macroscopic energy, and retains that macroscopic energy for many iterations of the system dynamics.*

In this definition, the degree of freedom with macroscopic energy can be regarded as a thermodynamic variable. Since we are interested in constant pressure molecular dynamics, the specific degree of freedom considered here will be the size of the MD supercell.

THEORY

The most common method for implementing constant pressure molecular dynamics is the Parrinello Rahman barostat [1].

The Parrinello-Rahman method (PR) can be used in molecular dynamics to describe the NPE or NPT ensemble when applied with a thermostat such as Nose [2]. PR has a number of well-known anomalies [3-5], including lack of rotational invariance and missing cross terms in the derivatives, however in the current work we consider the original method, which is widely used in molecular dynamics packages. In this, nine fictitious degrees of freedom are introduced corresponding to the components of the vectors defining the supercell **a**, **b**, **c**. Each degree of freedom then has its own equation of motion, derived from the Lagrangian

$$L = \frac{1}{2} \sum_i m_i \dot{\mathbf{x}}_i' h' h \dot{\mathbf{x}}_i - U_{coh} - P(\Omega - \Omega_0) + \frac{1}{2} W \text{Tr} \dot{h}' \dot{h} - \frac{1}{2} \text{Tr} [h_0^{-1} (\mathbf{S} - P) h_0' \Omega_0 h' h]$$

in which **x** are the fractional coordinates within the supercell and the 3x3 "boxmatrix" $h=[\mathbf{a},\mathbf{b},\mathbf{c}]$ define the simulation volume. The scalar W is the equivalent of a mass associated with the box degrees of freedom. P is the external hydrostatic pressure, \mathbf{S} is the external stress (assumed hydrostatic in the original work). A constant term $\Omega \text{Tr}(\mathbf{S}-P)$ is ignored.

The atomic positions \mathbf{r}_j are written as a product of fractional coordinates

$$\mathbf{r}_j = h \mathbf{x}_i$$

from which a strain matrix with respect to a reference structure h_0 is defined by

$$\epsilon = \frac{1}{2} (h_0'^{-1} h' h h_0^{-1} - 1)$$

where prime denotes the transpose.

The boxmatrix introduces nine additional degrees of freedom, three stretches, three shears and three rotations. Equations of motion for these degrees of freedom come from the stresses on the

supercell and an equivalent kinetic energy term from their time derivatives and the fictitious mass.

The scalar W is the equivalent of a mass associated with the box degrees of freedom. It determines how rapidly the box changes shape in response to stress and can be related loosely to elastic constants. Typically it takes a value of similar order of magnitude to the sum of the atomic masses. From all this analysis, the equation of motion for the boxmatrix degrees of freedom is

$$W\ddot{h} = (\pi - P)\sigma - h[h_0^{-1}(\mathbf{S} - P)h'_0\Omega_0]$$

where π is the internal stress tensor from the kinetic energy and virial and σ is defined by:

$$\sigma = \{b \times c, c \times a, a \times c\}.$$

The practical difficulty with this, and other barostats, is that the box degrees of freedom are typically coupled only weakly to the atomic degrees of freedom. Thus if equipartition of energy between box and atoms is not established at the start of the simulation, then equilibration times become very long. This is particularly annoying because one is not generally interested in the box degrees of freedom. They are simply used to enable the cell to adjust its shape, to ensure that the simulation is properly hydrostatic, or to facilitate phase transitions. It is easy to start the box degrees of freedom with an equipartitioned kinetic energy, however the potential energy stored in the strain field is *macroscopic*, and not generally known – and sometimes this is what one is trying to find. Furthermore, the Parrinello-Rahman method was designed to facilitate phase transitions, but when a phase transition occurs in an MD simulation it is associated with a macroscopic release of strain energy - all of which goes initially into the boxmatrix degrees of freedom.

The excess energy in the box degrees of freedom manifests itself in nearly harmonic oscillations of the entire system: these are long wavelength phonons. Because they correspond to the acoustic degrees of freedom, they are referred to as ringing modes. The important insight here is that NPT simulations are out of equilibrium in this well-defined way.

Now that the problem is well defined, we can seek a bespoke solution to stop the ringing mode. Critical damping would be ideal, but that would require a priori knowledge of the ringing frequencies in order to determine the damping coefficient. An alternative is to use an algorithmic rather than Lagrangian formulation. We are trying to remove both potential and kinetic energy from one mode. Removing kinetic energy is easy, one simply sets \dot{h} to zero. However, if this is done on each step, the cell shape cannot change, which defeats the purpose of the PR method. The most efficient strategy is to remove the kinetic energy at the point where the potential energy is minimised. This can be done for each component of h independently with a single IF statement:

$$\text{IF } (\dot{h}_{ij} \cdot \ddot{h}_{ij} < 0) \text{ THEN } \dot{h}_{ij} = 0$$

In most practical cases, this is extremely effective, however there are two problems. Applying the algorithm to a single off-diagonal component is equivalent to applying a torque to the system, which is undesirable. This traces back to the fact that Parrinello-Rahman introduces

nine fictitious variables, but three of these are rotations that should not affect the energy. In most practical MD codes, net rotation of the cell can occur due to rounding errors in the stress tensor, and are eliminated automatically. An alternative is to transform \mathbf{h} and its derivatives into volume expansion, five shears and three rotations, apply the algorithm only to the first six.

A second problem is that the algorithmic removal of energy does not correspond to any Hamiltonian, and therefore does not obey time-reversibility and conservation of the Hamiltonian energy. The resolution to this depends on what the simulation is meant to be doing. Energy conservation can be restored by rescaling the velocities of all the individual atoms in the system, so as to compensate for the lost energy. This is effectively introducing a strong, fictitious, anisotropic coupling between box and atom degrees of freedom to resolve the weak-coupling problem. An alternative is to observe that the ringing mode comes from assuming that the acoustic mode is localized in a region the size of the supercell, as a consequence of the periodic boundary condition approximation. If one relaxes the approximation and assumes that sound wave can travel away from the explicitly modelled region, then the loss of energy from the boxmatrix modes makes perfect physical sense.

The algorithmic quench was implemented in NPTp ensemble calculations in the open source molecular dynamics code MOLDY [6].

To demonstrate its efficacy two examples are considered. In both cases we use a many-body empirical potential [7], first in simple equilibration of a large system of 16000 lithium atoms, and second for a small system of 2000 sodium atoms undergoing a martensitic phase transition.

Three quantities are monitored to detect three distinct forms of equilibration:

- 1/ Equilibration with respect to external work, the system volume,
- 2/ Equilibration with respect to the First Law, energy.
- 3/ Equilibration with respect to the Second Law, entropy.

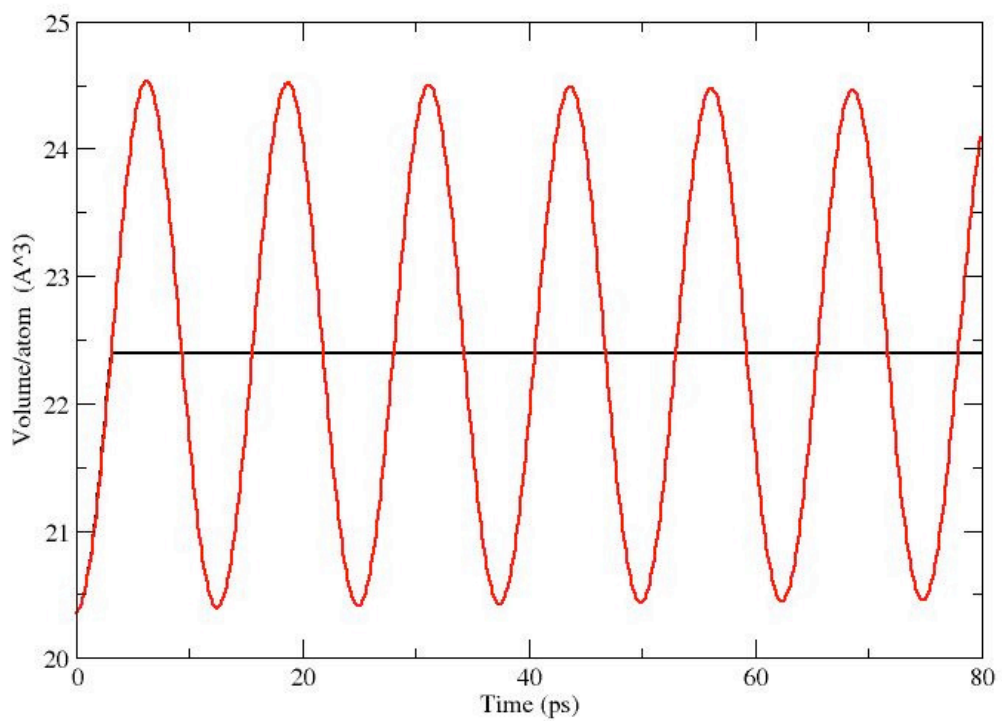
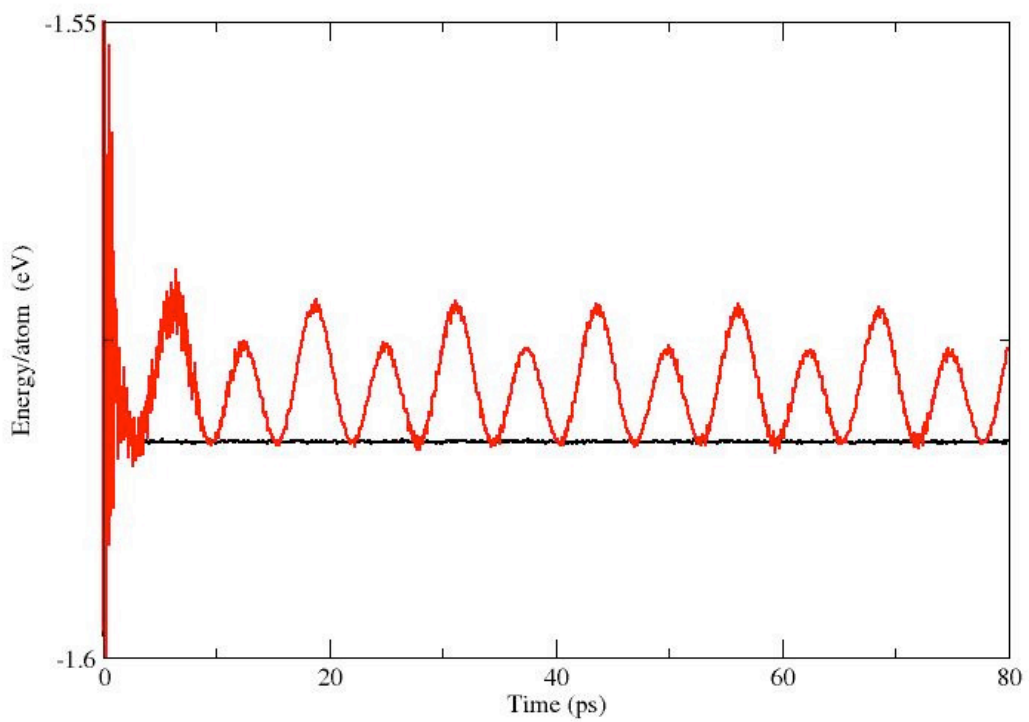
The first two are the standard measures of equilibration, but thermodynamic equilibrium is defined by point at which the system no longer generates entropy. The entropy is calculated by integrating the Central equation of thermodynamics:

$$S = \int \frac{dU}{T} + \int \frac{PdV}{T}$$

where the integral is converted to a time integral using the chain rule:

$$dU = \frac{dU}{dt} dt; \quad dV = \frac{dV}{dt} dt$$

with the changes in U,V calculated numerically over a 0.1ps window.



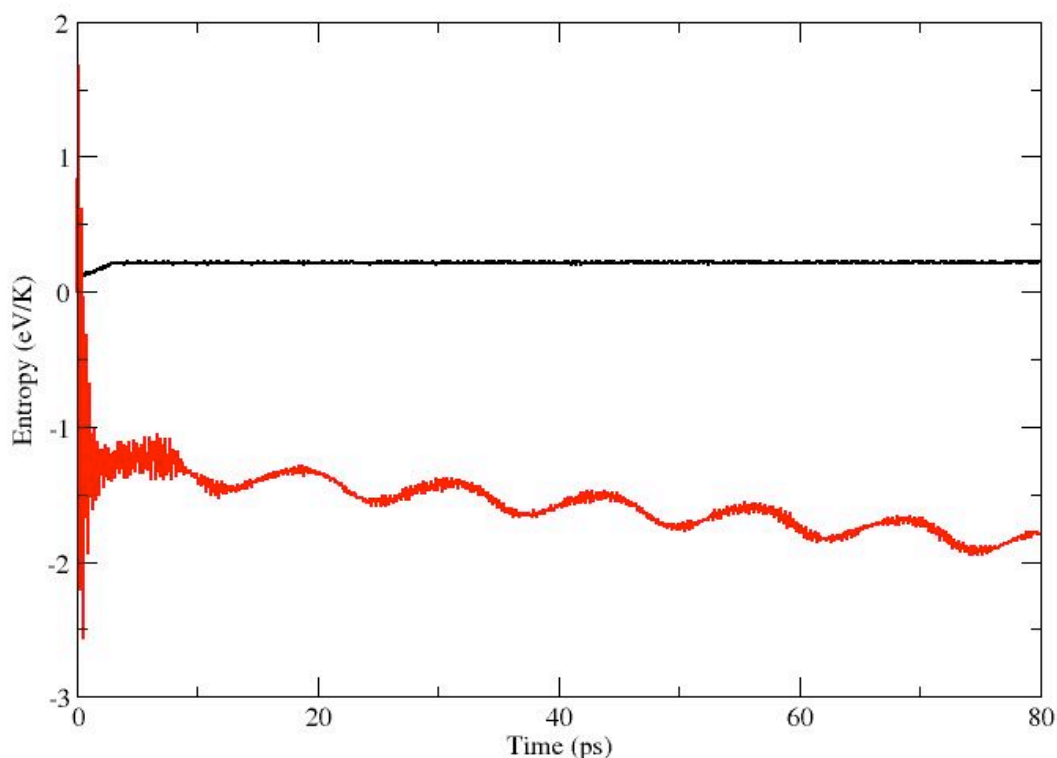


Figure 1 Volume, energy and entropy changes with time, the red (grey), strongly oscillating curves use are the standard Parrinello Rahman method, black curves add algorithmic quench

NPE Crystal Equilibration

We consider first the case of equilibration of lithium [7] with a Finnis-Sinclair style potential [8] at 280K, where the bcc structure is expected to be stable. The structure is set up with atoms on the perfect lattice structure, with the lattice parameter determined from static relaxation.

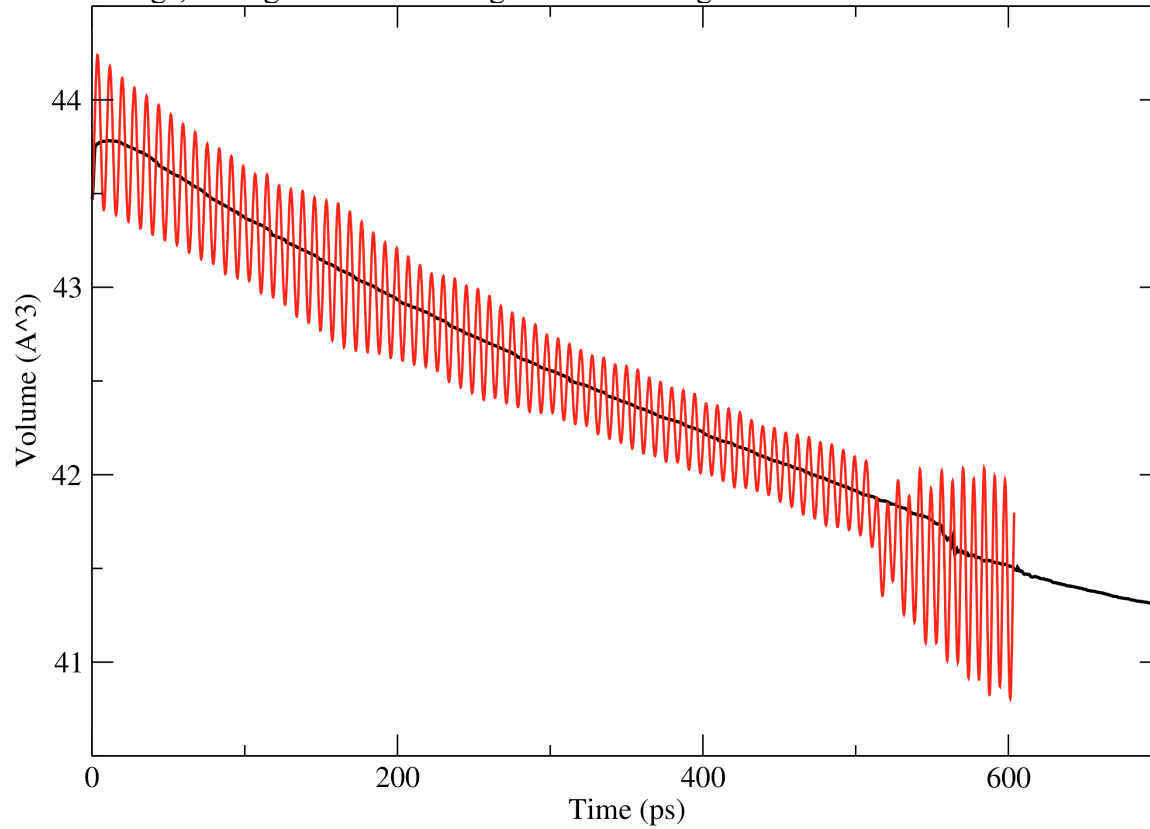
Temperature is initialized at 280K by setting initial particle velocities, and maintained through use of a Nose thermostat.

Due to neglect of thermal expansion, the initial volume is too small. This triggers the ringing, and Figure 1(a) shows that without quenching there is almost no sign of attenuation of the ringing mode. By contrast, the algorithmic quench kills the ringing within 5ps at the equilibrium value, and subsequent oscillations are too small to discern.

The energy of the non-fictitious modes fluctuates at double the frequency of the volume, and the alternating peak heights in the unquenched case shows that the effect of ringing on the other modes is intrinsically anharmonic, despite which the removal of energy from the mode is very slow. Again, the algorithmic quench stabilizes the energy in the system from its first application. Although the quench continues to remove energy from the fictitious modes of the system, such

that the Hamiltonian energy reduces, the effect on the atomic modes is negligible and cannot even be discerned in the figure.

The entropy of the quenched system increases in the equilibration period and is then stable. In the unquenched case, the system entropy increases in expansion phases, and reduces in contraction. The overall downward slope indicates that the ringing is creating entropy in the surroundings, and again there is no sign of this abating.



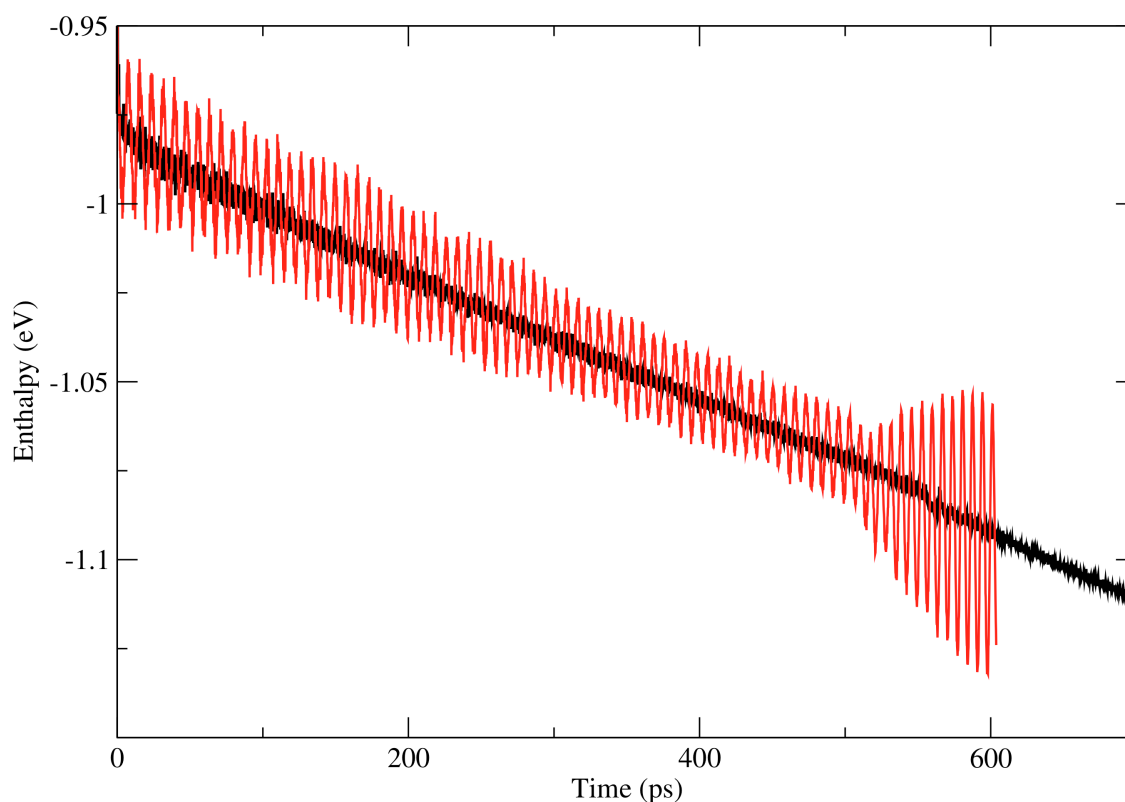


Figure 2 Volume and enthalpy changes with time, in a simulation cooling sodium from bcc to fcc simulations start at 500K and cool at 1.5ps/K, so that the transition after 500ps occurs at about 150K. Curves with high frequency oscillation are the standard Parrinello Rahman method, black curves the same simulation adding algorithmic quench

Martensitic transition

In the second case, we consider the phase transition on cooling in sodium [7]. The system is initiated in the ground state fcc structure at 10K. It is then heated by incrementing the thermostat target temperature at the rate of 1.5ps/K. The potential describes two transformations, fcc-bcc and melting. At this heating rate, typical of MD simulation, the figure shows that with standard NPT ensemble the ringing mode is barely suppressed and, moreover, at the phase transition it is enhanced. With the algorithmic quench, equilibration is reached quickly.

One expects some hysteresis in a martensitic transition [9], and it is notable here that the ringing simulation transforms first, at a lower temperature. The ringing presumably helps to overcome the kinetic barrier to transformation.

DISCUSSION

The "ringing" mode is the slowest-equilibrating mode in NPE molecular dynamics calculations. It is a dirty secret of molecular dynamics, seldom shown in published work, sometimes not even calculated and even present as pressure oscillations in NVT simulations. The ringing mode is excited whenever the initial configuration is not at equilibrium, and again at any stage in the simulation where a phase transformation occurs. In practical applications, it is therefore

unavoidable. Using a simple algorithm to remove energy from the mode, we show that equilibration can be achieved many orders of magnitude faster than with standard Parrinello Rahman Lagrangian. Although the algorithm does not correspond to a Lagrangian, and lacks strict time-reversibility, we show that the equilibrated systems have the same energy and volume properties as the Parrinello-Rahman simulations do on average.

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