

Fluctuations and thermodynamic response functions in a Lennard-Jones solid

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Thermodynamic response functions of a nearest-neighbor Lennard-Jones solid—heat capacity, thermal-expansion coefficient, compressibility, and elastic constants—are calculated directly from fluctuations using molecular-dynamics simulations. The algorithm used is the earlier Parrinello-Rahman molecular dynamics modified to take into account symmetry and rotation invariance of the system under investigation. The convergence is very fast and results are in good agreement with existing Monte Carlo and molecular-dynamics results.

Molecular-dynamics (MD) simulations have been used extensively in the past decade for investigating problems in statistical mechanics and thermodynamics,¹ particularly in the area of phase transitions, structures of defects, and transport properties. However, most molecular-dynamics simulations are performed in the microcanonical and canonical ensembles where the total energy or the temperature is held invariant, respectively, as is the total volume, or the shape, of the MD cell. Certain fluctuations of thermodynamic quantities from their equilibrium values in these molecular-dynamics methods are suppressed; since fluctuations and responses of a system depend on the ensemble that the molecular-dynamics trajectories generate,² most of the thermodynamic response functions, particularly those relevant to structural variations, are not available.

Recently proposed molecular-dynamics techniques attempt to remedy these difficulties. Andersen³ was the first to use volume as a dynamic variable to allow fluctuation of the MD cell. Using this technique, he was able to extend molecular dynamics from microcanonical and canonical ensembles to constant pressure and temperature (*NPT*) and constant pressure and constant enthalpy (*NPH*) ensembles. This idea of using macroscopic quantities as dynamic variables led Parrinello and Rahman⁴ (PR) to propose a new molecular-dynamics method that allows not only volume but also shape, or symmetry, variations of the MD cell. With Parrinello-Rahman molecular dynamics (PRMD), it is possible to study complicated problems like structural phase transitions and mechanical properties of materials where structural change is the primary concern. Most importantly, the response functions related to this change, such as elastic constants⁵ and the thermal-expansion coefficient, can be obtained.

Despite the promise of Parrinello-Rahman molecular dynamics, in practice it has been found to have several severe problems which make it difficult and unambiguous to interpret simulation results and, worst of all, lead to unphysical results. The primary problem is *symmetry variance*, or MD cell distortion, which happens when a stable or equilibrium structure is used in a simulation and occurs even at zero temperature when thermal fluctuations are completely absent. In these cases, the MD cell

distorts in a continuous manner and finally ends up in a structure of totally different symmetry. For example, fcc to bcc distortion has been observed and interpreted as a consequence of using pair potentials.⁴ This is disturbing when investigating structure changes induced by structural phase transitions or mechanical deformation, because one cannot tell whether or not the structure variations are artificial or arise from true physical causes. (For example, the Bain transformation in iron involves the tetragonal distortion of the fcc cell.) Additionally, it has been found that PRMD often leads to MD cell *rotation*, which has been observed in molecular systems⁶ as well as in simple Lennard-Jones solids (which will be described in detail below). Rotation of the MD cell indicates that the structure being simulated is not in mechanical equilibrium.⁷ The direct consequence of such rotation is that it is almost impossible to find an equilibrium reference state for the calculation of strains and elastic constants. Besides, rotated coordinates make it difficult to interpret simulation results. The last and most practical issue is the very *slow convergence* of PRMD in calculating thermodynamic quantities such as the thermodynamic response functions, which are directly related to fluctuations or to derivatives of structure variations. It has been reported⁸ that elastic constants of a simple Lennard-Jones (LJ) solid have been obtained, but with very slow convergence. However, those results have not been confirmed as yet.^{5,9} In contrast, the present authors found that it is impossible to calculate the elastic constants in nearest-neighbor LJ solids using PRMD, due to the above-mentioned distortions and rotations. Furthermore, there are no reports of heat capacity, thermal expansion, and compressibility calculated directly from fluctuations in Parrinello-Rahman MD simulations, even though extensive work has been done related to structural changes.

In practice, constant energy and shape (*EhN*) or constant temperature and constant shape (*ThN*) ensemble PRMD⁵ are used to calculate C_p or C_v , respectively, as well as adiabatic or isothermal elastic constants, while constant (*NPT*) or (*NPH*) ensemble PRMD are used to obtain equilibrium structures.¹⁰ Since the volume and shape of a MD cell in constant (*EhN*) and (*ThN*) ensem-

ble MD are fixed, distortions and rotations of the MD cell are no longer a concern. The calculation of elastic constants and heat capacities using these fixed-volume (or shape) PRMD has been found to converge very quickly.⁵ However, it is inconvenient and time consuming to switch between different ensemble molecular dynamics in order to obtain the desired structures, fluctuations, and response functions. Especially, when the evolution of fluctuations and responses is needed for cases like phase transitions and structural variations, such shuffling among two or three different ensemble MD becomes quite a burden. Furthermore, since most experiments are performed under constant temperature and pressure, it is desirable for one to use constant (*NPT*) PRMD in which volume is allowed to fluctuate, to compare the results with experimental ones under the same conditions.

In this paper we present our simulation results for the calculation of thermodynamic response functions directly from the fluctuations of the energy, volume, and shape of a MD cell. We are primarily interested in the heat capacity, compressibility, thermal-expansion coefficient, and elastic constants. The molecular-dynamics algorithm is a version of the Parrinello-Rahman type with a modified kinetic-energy term associated with the phenomenological dynamic variable of shape, or symmetry. Our results are in good agreement with those from existing Monte Carlo simulations^{11,12} and those from constant shape, or symmetry, molecular-dynamics simulations.⁵ All of these results have been obtained with fast convergence of only about 10^5 MD time steps.

In Parrinello-Rahman molecular dynamics the shape (or symmetry) of the simulation MD cell is used as a phenomenological dynamic variable. The cell is a parallelepiped with its edges represented by the three vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} . The positions and velocities of particles in the MD cell are scaled by a matrix h , that is, $\mathbf{r}_i = h\mathbf{s}_i$ and $\dot{\mathbf{r}}_i = h\dot{\mathbf{s}}_i$, where $h = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$. The Lagrangian proposed by Parrinello and Rahman includes phenomenological kinetic- and potential-energy terms

$$L = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{s}}_i^t G \dot{\mathbf{s}}_i - \sum_{i=1}^N \sum_{j>i} \phi(r_{ij}) + \frac{W}{2} \text{Tr}(\dot{h}^t \dot{h}) - P_{\text{ext}} \Omega, \quad (1)$$

where $G = h^t h$ is the metric tensor (h^t is the transpose of h), $\Omega = \det|\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|$ is the volume of the MD cell, and P_{ext} is the externally applied pressure. W is the fictitious mass associated with the phenomenological dynamic variable h . A pairwise interaction $\phi(r_{ij})$ is assumed. The equations of motion for the time evolution of the $3N$ particles and h matrix take the form

$$m_i \ddot{\mathbf{s}}_i = - \sum_{j \neq i} \chi_{ij} \mathbf{s}_{ij} - m_i G^{-1} \dot{G} \dot{\mathbf{s}}_i, \quad (2)$$

$$W \ddot{h} = [\sigma - P_{\text{ext}} I] A, \quad (3)$$

where $A = \partial \Omega / \partial h = \Omega h^{-t}$ is the area tensor (h^{-t} is the transverse transpose of h). σ is the microscopic stress tensor, which is defined as

$$\sigma = \Omega^{-1} \left[\sum_i \frac{\mathbf{p}_i \mathbf{p}_i}{m_i} - \sum_{i>j} \chi_{ij} \mathbf{r}_{ij} \mathbf{r}_{ij} \right], \quad (4)$$

with linear momentum $\mathbf{p}_i = m_i h \dot{\mathbf{s}}_i$ and $\chi_{ij} = r_{ij}^{-1} [\partial \phi(r_{ij}) / \partial r_{ij}]$. In PRMD the strain tensor is defined as¹³

$$\epsilon = \frac{1}{2} h_0^{-t} [G - I] h_0^{-1}, \quad (5)$$

where $h_0 \equiv \langle h \rangle$ is the equilibrium MD cell used as the reference for strain calculation and $\langle \rangle$ stands for time average.

The equation of motion for \mathbf{s}_i in constant (*NPT*) ensemble PRMD takes the form

$$m_i \ddot{\mathbf{s}}_i = f^{-2} \left[- \sum_{j \neq i} \chi_{ij} \mathbf{s}_{ij} - m_i (f^2 G^{-1} \dot{G} + 2f \dot{f}) \dot{\mathbf{s}}_i \right]. \quad (6)$$

The Nosé scaling method¹⁴ is used to fix the temperature, and f is the Nosé scaling variable. The equation of motion for h remains the same as in (3).

Using the equations of motion (3) and (6), we simulated a nearest-neighbor Lennard-Jones solid. We used 500 atoms arranged in a cubic cell with the fcc structure. Temperature and pressure are set equal to 0.3 and 0.0 (in reduced LJ units), respectively. The fifth-order Gear's predictor-corrector algorithm is used to solve the equations of motion. The length of time step in our MD runs is 0.005 (in reduced LJ units). It is found that the cubic MD cell rotates continuously, accompanied by a tetragonal distortion. For a typical run, at 500 MD steps the MD cell $h = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ looks like

$$\begin{bmatrix} 1.56 & -7.27 & -2.46 \\ 5.32 & 2.93 & -5.04 \\ 5.55 & -0.89 & 5.73 \end{bmatrix},$$

with $|\mathbf{a}| = 7.84$, $|\mathbf{b}| = 7.89$, and $|\mathbf{c}| = 8.02$, and the angles between each of the vectors are $\theta_{ab} = 90.64$, $\theta_{bc} = 91.80$, and $\theta_{ac} = 88.95$. With such rotation and distortion it is virtually impossible to find an equilibrium reference h_0 to calculate strain and elastic constants.

Since the PR molecular dynamics used above is not derived from first principles, in order to modify PRMD one must first check the invariance or conservation of dynamic and structural variables. First, the kinetic-energy term associated with the h matrix is not invariant with the choice of the h matrix, or MD cell (which has been observed also by other researchers; Nosé and Klein,⁶ Cleveland,¹⁵ and Wentzcovitch¹⁶). However, in a system with translational symmetry two different choices of h are related by a transformation matrix B such that $h_2 = h_1 B$ and $\dot{h}_2 = \dot{h}_1 B$. Any dynamic or structural variable in such a system must be invariant with respect to the transformation. A simple choice of a new kinetic-energy term

$$K_h = \frac{W}{2} \text{Tr}(\dot{h} Q \dot{h}^t), \quad (7)$$

where Q is chosen to be any linear function of $h^{-1} h^{-t}$, would eliminate the dependence of K_h on the choice of MD cell. Such a choice of Q makes the transformation of K_h with respect to different choices of MD cell invariant,

that is,

$$K_{h_2} = \frac{W}{2} \text{Tr}(\dot{h}_2 Q_2 \dot{h}_2^t) = \frac{W}{2} \text{Tr}(\dot{h}_1 Q_1 \dot{h}_1^t) = K_{h_1},$$

where $Q_1 = h_1^{-1} h_1^{-t}$ and $Q_2 = h_2^{-1} h_2^{-t}$. After replacing K_h , the new Lagrangian leads to a new equation of motion for the h matrix,

$$W\dot{h} = \Omega^{-1}[\sigma - P_{\text{ext}}I]h - W\Omega^{-2}[-2\Omega\dot{\Omega}h + \text{Tr}(\dot{h}Q\dot{h}^t)h + \dot{h}Q\dot{G} - \Omega A\dot{h}^t h]. \quad (8)$$

The equation of motion for variable s_i remains the same as in Eq. (2).

In addition, the total angular momentum in PRMD is not formally conserved. In an equilibrium system the conservation of total angular momentum keeps the shear stress tensor symmetric, and thus the strain tensor symmetric, leaving the system unrotated.⁷ Unlike most constant-volume MD, the Parrinello-Rahman MD has an orientational degree of freedom for the MD cell (the h matrix has nine components, six of which specify shape and volume and the additional three of which describe orientation). Because of this, nonconserved total angular momentum can lead to net rotations at the end of a simulation, as we in fact observed. (Although the use of periodic boundary conditions also leads to total angular-momentum nonconservation, weighting over a long time might be expected to average out such an effect.) Using the modified equations of motion (8) and (6) we observed that the MD cell distortion and rotation are kept within the scale of normal fluctuations during simulations, and,

at the end, the distortion and rotation completely disappear from time averaging.

We are mostly interested in the fluctuations and the related thermodynamic response functions which have not been obtained previously from PRMD. To obtain such quantities we used the fluctuation formulas directly.¹⁷ In our case, response functions are related to the fluctuations in the (NPT) ensemble by

$$\langle (\delta H)^2 \rangle = k_B T^2 C_P, \quad (9)$$

$$\langle (\delta \Omega)^2 \rangle = \Omega k_B T \kappa_T, \quad (10)$$

$$\langle (\delta \Omega \delta H) \rangle = \Omega k_B T^2 \alpha_P, \quad (11)$$

$$\langle (\delta \epsilon_{ij} \delta \epsilon_{kl}) \rangle = \frac{k_B T}{\Omega} C_{ijkl}^{-1}, \quad (12)$$

where Ω is the equilibrium volume and T is the preassigned temperature. H is the total enthalpy giving by $H = E + P_{\text{ext}}\Omega$, where E is the total energy. C_P , κ_T , α_P , and C_{ijkl} are the isobaric heat capacity, volume isothermal compressibility, thermal-expansion coefficient, and isothermal elastic constants, respectively. The time average of fluctuations is given by $\langle \delta A \delta B \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle$, where A and B are functions of the dynamic variables. The elastic constants are inversely related to the strain fluctuations.¹³

We used the modified equations of motion (8) and (6) in simulations of the nearest-neighbor LJ solid under the same conditions stated earlier. The mass associated with h is chosen as 0.042 for the runs. During the simulation the averaged MD cell remains cubic and no net rotation

TABLE I. Thermodynamic response functions of a nearest-neighbor Lennard-Jones solid from modified Parrinello-Rahman (NPT) molecular dynamics. σ and ϵ are the Lennard-Jones potential parameters, N is the total number of atoms, and k_B is the Boltzmann's constant. $\tau=0.005$ is the time step used in the simulation. MD runs is the number of time steps used for obtaining averages.

MD runs (τ)	$R_{NN}(\sigma)$	$C_P(Nk_B)$	$\alpha_P(k_B/\epsilon)$	$\kappa_T(\sigma^3/\epsilon)$
5 000	1.149 33	3.401	0.0783	0.028 53
10 000	1.149 01	3.560	0.2377	0.034 57
15 000	1.148 99	3.168	0.1669	0.035 74
20 000	1.148 95	3.253	0.1669	0.036 13
25 000	1.148 93	3.242	0.1796	0.034 00
30 000	1.148 94	3.327	0.1796	0.034 77
35 000	1.148 97	3.423	0.1897	0.034 77
40 000	1.148 97	3.592	0.2251	0.036 71
45 000	1.148 94	3.518	0.2378	0.035 94
50 000	1.148 93	3.359	0.2378	0.034 39
55 000	1.148 93	3.317	0.2251	0.034 19
60 000	1.148 76	3.338	0.2125	0.034 58
65 000	1.148 92	3.401	0.2403	0.035 94
70 000	1.148 90	3.380	0.2454	0.035 36
75 000	1.148 90	3.571	0.2479	0.039 05
210 000	1.148 90	3.401	0.2454	0.037 50
Monte Carlo ^a	1.148 39	3.53	0.2765	0.0362 ^c
MD data ^b	1.148 66	3.49		0.0355 ^c

^aReferences 11 and 12.

^bReference 18.

^cObtained from the bulk modulus using $\kappa_T = 1/B_T$. In Ref. 18 the bulk modulus is obtained through relation $B_T = \frac{1}{3}(C_{11} + 2C_{12})$.

TABLE II. Isothermal elastic constants in units $Nk_B T/\Omega$ from modified Parrinello-Rahman (*NPT*) molecular dynamics. The data shown here are taken after 30 000 time steps, since before that they have large fluctuations.

MD Runs (τ)	$\frac{1}{3}(C_{11} + C_{22} + C_{33})$	$\frac{1}{3}(C_{12} + C_{13} + C_{23})$	$\frac{1}{3}(C_{44} + C_{55} + C_{66})$
30 000	177.92	68.43	103.28
35 000	160.15	72.73	100.67
40 000	152.99	68.30	98.25
45 000	158.42	71.32	87.72
50 000	165.59	73.07	88.26
55 000	167.84	71.86	85.86
60 000	166.11	70.34	86.42
65 000	160.73	67.41	89.21
70 000	162.52	67.79	92.01
75 000	158.04	60.14	91.43
80 000	160.31	63.74	89.90
85 000	162.22	65.78	87.71
210 000	158.16 \pm 5.82	69.12 \pm 5.53	84.30 \pm 5.83
Monte Carlo ^a	157.1 \pm 1.0	69.3 \pm 0.9	82.2 \pm 0.2
MD data ^b	164.6 \pm 5.9	76.2 \pm 5.4	82.0 \pm 1.7

^aReference 11.

^bReference 18.

is observed at the end. In Table I we show the equilibrium nearest-neighbor distance R_{NN} , heat capacity C_P , thermal-expansion coefficient α_P , and compressibility κ_T . These results are compared with those from Monte Carlo calculations.^{11,12} One can see that the convergence of the quantities is very fast, especially for the nearest-neighbor distance R_{NN} which converges after 10^4 time steps. After about 10^4 time steps C_P , α_P , and κ_T approach their stable values, and in less than 10^5 time steps all of the elastic constants reach equilibrium values. In Table II we give the isothermal elastic constants C_{11} , C_{12} , and C_{44} , which are actually obtained by averaging over three equivalent independent elastic constants, respectively. After 30 000 time steps the typical deviations from their averaged values are within 1.0%, 15.0%, and 20.0%, respectively. However, with increasing run time (up to 10^5 time steps) we are able to reduce the deviations to about 5.0%, while the averaged values are not changed greatly (in Table II the average elastic constants from a run of 2.1×10^5 time steps are listed for illustration). Same calculation has been performed also on the system with temperature at 0.5 (reduced LJ units) and results are listed in

Table III. Similar isothermal elastic constants calculated with fixed shape and volume from constant (*ThN*) molecular dynamics¹⁸ are presented for comparison. Both results agree well with Monte Carlo results.

To summarize, we have shown that the earlier Parrinello-Rahman molecular dynamics using MD cell shape or symmetry as a phenomenological dynamic variable has been hindered in its application by lack of preservation of symmetry (or MD cell distortion from the equilibrium state), MD cell rotation, and by the slow convergence or nonconvergence of fluctuations and response functions. This is observed to be related to the dependence of K_h on the choice of MD cell and to nonconservation of the total angular momentum. A modified PRMD has been obtained by replacing the MD cell kinetic energy K_h by $K_h = W/2 \text{Tr}(\dot{h}Q\dot{h}^{-1})$ from the original PR Lagrangian. Using this modified Parrinello-Rahman molecular dynamics we have calculated the response functions directly from fluctuations. The convergence is quite satisfactory, and the results are in good agreement with existing Monte Carlo and other molecular-dynamics results. This gives us more confidence to use this

TABLE III. Thermodynamic response functions of a nearest-neighbor Lennard-Jones solid from modified Parrinello-Rahman (*NPT*) molecular dynamics. Temperature is fixed at 0.5.

MD runs (τ)	$R_{NN}(\sigma)$	$C_P(Nk_B)$	$\alpha_P(k_B/\epsilon)$	$\kappa_T(\sigma^3/\epsilon)$
45 000	1.178 12	4.303	0.4266	0.007 07
Monte Carlo ^a	1.174 54	4.28	0.4348	0.010 668
MD runs (τ)	$\frac{1}{3}(C_{11} + C_{22} + C_{33})$	$\frac{1}{3}(C_{12} + C_{13} + C_{23})$	$\frac{1}{3}(C_{44} + C_{55} + C_{66})$	
45 000	57.34 \pm 5.17	21.02 \pm 1.91	30.39 \pm 2.72	
Monte Carlo ^b	61.7 \pm 0.7	22.8 \pm 0.8	33.8 \pm 0.2	

^aReferences 11 and 12.

^bReference 11.

molecular-dynamics method to study complicated thermodynamic and statistical-mechanical systems in the future.

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