Constant pressure molecular dynamics on a hypercylinder

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A Lagrangian formalism for variable-cell-shape molecular dynamics is derived from first principles. It is based on consideration of a crystal as arranged on the surface of hypercylinder in an extended coordinate frame. The artificial curvature along the additional degrees of freedom upsets the balance of forces acting on every atom in a periodically repeating cell. Since the distance between atoms is not the metric tensor the proposed method provides an essential simplification of the equations of motion compared to those of Parinello and Rahman approach. The Lagrangian of the system eliminates the cell orientation from the dynamics, thus avoiding symmetry-breaking effects and physically irrelevant cell rotation. The change from a fully flexible cell to an isotropically flexible cell is realized within the same computational framework. Simulations for the transformation of a model He lattice under isotropic applied pressure are used to illustrate the application of this method.

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INTRODUCTION

The success of numerous applications of the molecular dynamics (MD) method and especially of *ab initio* MD calculations is mainly due to a limited number of particles used. To reduce finite cell-size effects for an extended system, periodic boundary conditions are introduced. However, this suppresses fluctuations in the volume and shape of the MD cell which, in particular, are responsible for structural phase transitions. Necessary flexibility of the simulation cell under periodic boundary conditions can be provided by various special methods. The first allowing the change of the cell volume was introduced by Andersen [1]. The volume Ω of a cubic simulation cell was considered as a dynamical variable thus allowing for volume fluctuations driven by the dynamic imbalance between the imposed external pressure p and the actual instantaneous internal pressure σ as given by the virial theorem. Apart from this, the particle coordinates $\mathbf{r}_i$ were replaced by scaled coordinates $\mathbf{s}_i = \mathbf{r}_i / \Omega^{1/3}$. As a result the kinetic energy of the particles is measured in a frame that ''breathes'' with the cell. The fictitious ''mass'' associated with volume fluctuation does not have the dimension of mass.

The generalization of this idea was proposed by Parinello and Rahman [2] (PR) to allow for changes in both the volume and the shape of the cell. Three edge vectors of the MD cell are regarded as dynamical variables, and the coordinate and momentum of a particle are expressed in scaled forms. As a result, the Lagrangian has a time-dependent metric tensor. Many encouraging results have been obtained in MD simulations of structure phase transitions [2–4], in spite of the fact that Lagrangians of ''scaled'' models have not been obtained from first principles. The latter partly explains some shortcomings of the PR method pointed out by several authors: it does not reduce to the Andersen result as a special case, it is not invariant under modular transformation, the consistency between the condition of mechanical equilibrium and the virial theorem is only verified in the large N limit, and it has spurious cell rotation [5–8]. More complicated equations of motion have been proposed to avoid some of these problems [5,7–9].

A new approach for the variable-cell-shape MD method evaluated from the first principle was proposed recently in a short note [10]. It is based on consideration of the crystal as arranged on a surface of the hypercylinder in extended configuration space and the artificial curvature upsets the balance of forces acting on every atom in the periodically repeating cell, supplementary degrees of freedom enable the crystal to relax along the curvature directions until the minimum of free energy is reached.

The aim of this paper is to provide further development of this idea in terms of a general Lagrangian formalism. The paper is organized as follows. In Sec. II we illustrate the idea of solid state equilibrium in extended space with the example of a one-dimensional crystal, e.g., atomic chain. Simple generalization of the one-dimensional (1D) case to 3D in Sec. III make it possible to reproduce Andersen's results of isoshape MD [1]. Further evaluation of the general case of MD with variable cell shape in Sec. IV starts from the consideration of the 2D ideal crystal to clear up main peculiarities of 3D case. Section V contains results of simulation of a phase change in the high pressure helium lattice near 300 K. This model system has been studied in detail [11] by the PR method and then easier calculations are a convenient check for the given method.

I. ONE-DIMENSIONAL CHAIN

To illustrate the idea of introducing additional dimensions, consider a set of N classical particles of mass m and lattice period d constituting the ideal atomic chain with the coordinates $x_i^0 = i d_v$, $i = 1, \ldots N$ and cyclic boundary conditions. If the particles interact via a pairwise potential $\phi(r)$, each experiences equal but opposite forces $F_x = \Sigma_{j<i} f_{ij} = \Sigma_{j<i} \nabla_i \phi(x_i^0 - x_j^0) \neq 0$. These forces exactly compensate as a result of periodic boundary conditions. To reveal the stress, bend the atomic chain, thereby introducing an additional degree of freedom (see Fig. 1). Assuming the curvature radius R to be the same for all particles, their new positions

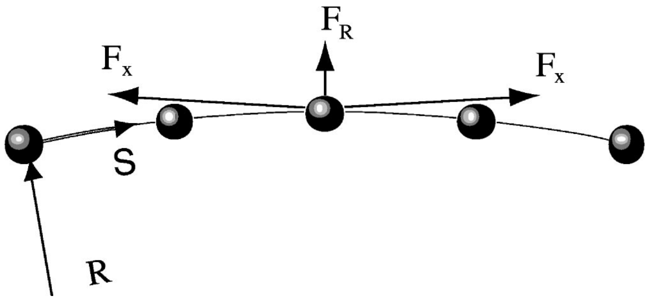

FIG. 1. Balance of forces on a curved linear chain of atoms with coordinates $[R,s_i]$. Preliminary compression due to a mismatch in the lattice constant $(F_x\neq 0)$ is revealed by the radial component of force F_R as a result of curvature.

$[R\sin(s_i/R),R\cos(s_i/R)]$ in Cartesian coordinates can be written as $[R,s_i]$ in the curvilinear coordinate frame of circular arc s and radius R. Now the radial component of the overall force appears as a result of the curvature (see Fig. 1),

$$F_R=\frac{1}{R}\sum_{i\neq j} f_{ij}s_{ij}, \tag{1}$$

where $s_{ij}=s_i-s_j$, $|s_{ij}/R|\ll 1$. This force acts to make every atom move along the radius of curvature, decreasing the stress and transferring a part of elastic energy of the chain stored by the initial compression (or extension) to radial kinetic energy. As a result the chain period will oscillate near the equilibrium value determined by vanishing stress $\langle F_R\rangle =0$.

The Lagrangian for the curved atomic chain with the thermal vibration of atoms taken into account can be written as

$$L=\frac{m}{2}\sum_{i=1}^{N}(\dot R^2+v_i^2)-\sum_{i>j}^{N}\phi(|s_{ij}|), \tag{2}$$

$$v_i=\dot s_i-s_i\frac{\dot R}{R}.$$

The equations of motion are found from the Lagrangian Eq. (2):

$$\dot s_i=v_i+s_i\frac{\dot R}{R},$$

$$\dot v_i=-\frac{1}{m}\sum_j \nabla_i\phi(s_{ij})-v_i\frac{\dot R}{R}, \tag{3}$$

$$Nm\ddot R=\frac{\sigma}{R},$$

$$\sigma=m\sum_{i=1}^{N} v_i^2-\sum_{i>j}\nabla_i\phi(s_{ij})s_{ij}.$$

These equations describe the thermal motion of every atom along the circle as well as their collective motion along the circle radius R. The right-hand part of the equation for $\ddot R$ in Eq. (3) is the radial component of the resulting force caused by internal stress of the chain.

The solution of these equations of motion conserves the total energy of the system associated with the Lagrangian Eq. (2),

$$H=\frac{m}{2}\sum_{i=1}^{N}(\dot R^2+v_i^2)+\sum_{i>j}^{N}\phi(|s_{ij}|). \tag{4}$$

Fictitious dynamics of a linear chain can be obtained now by substitution $s_i\rightarrow x_i$ in Eqs. (2) and (3). It should be noted, that the initial transition from a straight to a curved atomic row defined by the Lagrangian of Eq. (2) results in a change of the potential energy caused by the replacement of rectilinear distances x_{ij} by segments s_{ij}. In principle, if the radius of curvature R is large enough the error involved in bringing in the interaction $\sim\phi'(x_{ij})(x_{ij}/R)^2$ is negligible. Nevertheless, the inverse conversion from a curved atomic row to a fictitious 1D one compensates this inaccuracy, so that Eq. (3) is not formally constrained to large radius.

Now introduce an external tension force f acting on atoms of the chain. The cell containing N atoms being under the cyclic boundary conditions $x_{N+1}^0=x_1^0+Nd$ is seen within the angle $\theta_N=Nd/R$. This angle remains constant while the radius and the row period change: $\dot d=d\dot R/R$. Hence, the equations of motion for the atoms with external force f are obtained from Eq. (3) by replacing σ by $\sigma+fd$, and the modified equations of motion conserve the energy

$$H=\frac{m}{2}\sum_{i=1}^{N}(\dot R^2+v_i^2)+\sum_{i>j}^{N}\phi(|x_{ij}|)+f\theta_N R, \tag{5}$$

$$v_i=\dot x_i-x_i\frac{\dot R}{R}.$$

The last term in Eq. (5), being equal to fNd, is written in the form displaying the direct dependence on R.

The average of the system over time, H being conserved, corresponds to the equilibrium state where the strain vanishes: $\langle\ddot R\rangle=\langle\sigma\rangle/N+f\langle d\rangle=0$. The radius oscillates near the equilibrium value with the frequency ω_R that depends on initial values of curvature radius R_0 and period d_0. According to Eq. (3) these values determine the angle $\theta_0=d_0/R_0$ (constant during the evolution for $v_i=0$). The expansion of the radial force in Eq. (3) over small deviation of R from the equilibrium value gives $\omega_R\sim\omega_0 d_0/R_0$, where $\omega_0=[\phi''(\langle d\rangle)/m]^{1/2}$ is the frequency of harmonic oscillation of a particle in the row. If $d_0\sim\langle d\rangle$ the frequency of the radial oscillation becomes $\omega_R\sim v_s/R$, where v_s is the sound velocity.

It should be noted that the potential term in the value of σ in Eq. (3) is the interaction between neighboring halves of the ideal atomic chain cut in any place. The conventional Lagrangian formalism for an ideal infinite chain eliminates the interaction of this kind providing the equilibrium exists for any lattice period. The latter has to be obtained from the minimum of the total potential energy (or free energy for a finite temperature). The introduction of additional degree of freedom enables us to supplement the conventional condition of equilibrium that sets the forces acting on every atom to zero by the additional one of vanishing internal stress, and completes the problem of equilibrium in the frame of the unified Lagrangian formalism.

II. ISOSHAPE MOLECULAR DYNAMICS UNDER CONSTANT PRESSURE

The approach developed can be easily generalized to the 3D case when considering only isoshape fluctuations of the cell. The crystal is taken to lie on the surface of a 4D cylinder of radius R. Similarly to the one-dimensional case, an artificial curvature reveals an internal stress in the crystal. As a result the cell volume and coordinates fluctuate as the radius of the cylinder fluctuates. In full analogy with Eq. (3) we have

$$\dot{\mathbf{r}}_i = \mathbf{v}_i + \mathbf{r}_i \frac{\dot{R}}{R},$$

$$\dot{\mathbf{v}}_i = -\frac{1}{m} \sum_i \nabla_i \phi(r_{ij}) - \mathbf{v}_i \frac{\dot{R}}{R}, \tag{6}$$

$$Nm\ddot{R} = \frac{1}{R}(\sigma - 3p\Omega).$$

The expression

$$\sigma = m \sum_{i=1}^{N} v_i^2 - \sum_{i>j} \phi'(r_{ij}) r_{ij} \tag{7}$$

represents the kinetic and virial contribution to the internal pressure. In analogy with tension force f involved in the 1D case the hydrostatic external pressure p is introduced here.

The time evolution of a system governed by Eqs. (6) and (7) occurs in the $(6N+2)$-dimensional phase space on a surface corresponding to the constant energy H. The Hamiltonian H can be easily written from Eq. (5) by substitution 3D variables instead of 1D ones

$$H = \frac{m}{2} \sum_{i=1}^{N} (\dot{R}^2 + v_i^2) + \sum_{i>j}^{N} \phi(r_{ij}) + p\,\theta_N^{4D} R^3,$$

$$\mathbf{v}_i = \dot{\mathbf{r}}_i - \mathbf{r}_i \frac{\dot{R}}{R}, \tag{8}$$

θ_N^{4D} is the value of constant solid angle under which the cell is seen in 4D space during time evolution. Introducing the basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ defining the MD cell, this angle is equal to $\theta_N^{4D} = \Omega/R^3 = (\mathbf{a}_1[\mathbf{a}_2\mathbf{a}_3])/R^3$. The last term in Eq. (8), being equal to $p\Omega$, is written in a form displaying the direct dependence on R.

Since $\dot{R}/R = \dot{\Omega}/3\Omega$, the equations of motion, Eqs. (7) and (8), are almost the same as those obtained by Andersen [1]. The radius R, similar to the effective mass of the piston M in Ref. [1], is a free parameter determining the time scale of volume fluctuation. Of course, in equilibrium, the respective kinetic energies are equal: $\langle Nm\dot{R}^2 \rangle = \langle M\dot{\Omega}^2 \rangle = k_B T$ (k_B is the Boltzmann constant, and T is the temperature) regardless of the values of the both parameters. As above, the frequency of the volume fluctuation is determined by the value of the radius R: $\omega_R \sim v_s/R$. The comparison of this frequency with $\omega_\Omega \sim (Nmv_s^2/M\Omega^2)^{1/2}$ taken from Ref. [8] defines the relationship between the two free parameters: $M \sim Nm(R/\Omega)^2$. According to Ref. [1] the frequency value should be $\omega_\Omega \sim v_s/L$, $L = \Omega^{1/3}$, which reduces to $R \sim L$.

III. VARIABLE-CELL-SHAPE MOLECULAR DYNAMICS

Basically, the extra degrees of flexibility introduced by an independent curvature for the crystal with respect to every coordinate axis X, Y, and Z are insufficient to guarantee a proper trend to equilibrium. In particular, the vanishing of the radial forces due to the change of curvature related to every axis still leaves some residual stress. To resolve this, consider relaxation of an ideal 2D crystal with a mismatch in the lattice constants. Introducing independent curvatures along the axes X and Y, the crystal turns out to be stretched on the surface of the two hypercylinders in 4D configuration space of radius R_{xx} and R_{yy}, respectively. As before, curvatures reveal the radial forces $\sigma_{xx} = \Sigma_{i>j} \phi'(r_{ij}) x_{ij}^2 / r_{ij}$ and $\sigma_{yy} = \Sigma_{i>j} \phi'(r_{ij}) y_{ij}^2 / r_{ij}$ directed along respective radius. According to Eq. (3) each atom coordinate evolves as $\dot{x}_i/x_i = \dot{R}_{xx}/R_{xx}$ and $\dot{y}_i/y_i = \dot{R}_{yy}/R_{yy}$, while the both radii change independently. Assuming relaxation of the stress along both directions by means of radius decrease (or increase) until a state in which $\sigma_{xx} = \sigma_{yy} = 0$ is achieved, there are still possible equal but opposite stresses along axes X' and Y' rotated through the angle $\Delta\psi = \pi/4$ to the initial frame XY. Actually, within the new frame the tension $\sigma_{x'x'}$ along axis X', for instance, concurs with the same compression $\sigma_{y'y'}$ along the other axis Y'. The condition $\sigma_{xx} = \sigma_{yy} = 0$ is fulfilled whereas $\sigma_{xy} \neq 0$. To exclude this tension, consider the deformation process in the coordinate system $X'Y'$. Now, as before, we can introduce the curvatures along the new axes and consider independent deformation along X' and Y'. Since the deformations $\dot{x}_i'/x_i' = \dot{R}_{x'x'}/R_{x'x'}$ and $\dot{y}_i'/y_i' = \dot{R}_{y'y'}/R_{y'y'}$ along both axes differ only by sign, we can introduce $\dot{R}_{xy}/R_{xy} = \dot{R}_{x'x'}/R_{x'x'} = -\dot{R}_{y'y'}/R_{y'y'}$. The reverse rotation of coordinate frame $X'Y'$ to XY transforms the equations of deformation to $\dot{x}_i/y_i = \dot{R}_{xy}/R_{xy}$ and $\dot{y}_i/x_i = \dot{R}_{xy}/R_{xy}$. At the same time the components of tensor $\sigma_{x'x'} = -\sigma_{y'y'}$ and $\sigma_{x'y'} = 0$ transform to $\sigma_{xx} = -\sigma_{yy} = 0$ and $\sigma_{xy} = \Sigma_{i>j} \phi'(r_{ij}) x_{ij} y_{ij} / r_{ij}$.

This evaluation enables us to modify the initial equation of deformation by introducing an additional degree of freedom. Relaxation within the coordinate systems XY and $X'Y'$ could be introduced independently as operating in the different phase spaces. As a result, the velocities of the coordinate deformation due to the two kinds of curvature can be considered as additive and the final deformation for a 2D lattice can be defined as

$$\dot{x}_i = \frac{\dot{R}_{xx}}{R_{xx}} x_i + \frac{\dot{R}_{xy}}{R_{xy}} y_i,$$

$$\dot{y}_i = \frac{\dot{R}_{yy}}{R_{yy}} y_i + \frac{\dot{R}_{xy}}{R_{xy}} x_i. \tag{9}$$

Deformation of the basic cell vectors obeying Eq. (9) changes the cell volume. It is easy to show that the rate of this change is given by

$$\dot{\Omega} = \Omega \left(\frac{\dot{R}_{xx}}{R_{xx}} + \frac{\dot{R}_{yy}}{R_{yy}} \right), \tag{10}$$

containing only the diagonal component of the curvature radius.

With both relations of Eqs. (9) and (10), the final expression for the Hamiltonian in the 3D case can be constructed in the same way as the Hamiltonian Eq. (4) in the 1D case. We get

$$H = \frac{m}{2} \sum_{\alpha, j=1}^{N} \left[\sum_{\beta} \dot{R}_{\alpha\beta}^2 + \left(\dot{r}_{i\alpha} - \sum_{\beta} r_{\imath\gamma} \frac{\dot{R}_{\alpha\gamma}}{R_{\alpha\gamma}} \right)^2 \right] + \sum_{i>j}^{N} \phi(r_{ij})$$
$$+ p\,\theta_N^{4D} R_{xx} R_{yy} R_{zz},$$
$$\alpha, \beta, \gamma = x, y, z. \tag{11}$$

As above, the constant solid angle being equal to $\theta_N^{4D} = (\mathbf{a}_1[\mathbf{a}_2\mathbf{a}_3])/R_{xx}R_{yy}R_{zz}$ reduces the last term in Eq. (11) to the value $p\Omega$.

From the Hamiltonian, Eq. (11), the equations of motion can be easily found to be

$$v_{i\alpha} = \dot{r}_{i\alpha} - \sum_{\gamma} r_{i\gamma} \frac{\dot{R}_{\gamma\alpha}}{R_{\gamma\alpha}},$$

$$\dot{v}_{i\alpha} = -\frac{1}{m} \sum_{i>j} \nabla_{i\alpha} \phi(r_{ij}) - \sum_{\gamma} v_{i\gamma} \frac{\dot{R}_{\gamma\alpha}}{R_{\gamma\alpha}}, \tag{12}$$

$$Nm\ddot{R}_{\alpha\beta} = \frac{1}{R_{\alpha\beta}} \left[\sigma_{\alpha\beta} - p\Omega\,\delta_{\alpha\beta} + \frac{1}{2} \sum_{\gamma} \left(\frac{\dot{R}_{\alpha\gamma}}{R_{\alpha\gamma}} J_{\gamma\beta} + \frac{\dot{R}_{\beta\gamma}}{R_{\beta\gamma}} J_{\gamma\alpha} \right) \right].$$

Here $J_{\alpha\beta} = \Sigma_{i=1}^{N} (r_{i\alpha} v_{i\beta} - r_{i\beta} v_{i\alpha})$ are the components of the angular momentum. Six independent components of the curvature radius $R_{\alpha\beta} = R_{\beta\alpha}$ are driven by the symmetrical components of the internally generated stress tensor

$$\sigma_{\alpha\beta} = m \sum_{i=1}^{N} v_{i\alpha} v_{i\beta} - \sum_{i>j} \frac{\phi'(r_{ij})}{r_{ij}} r_{ij\alpha} r_{ij\beta}. \tag{13}$$

The coupling of the atomic motion to the cell motion is made through the last term of Eq. (11), which is independent of orientation and state of rotation of the cell. The components of vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ that span the edges of the MD cell evolve according to

$$\dot{a}_{k\alpha} = \sum_{\gamma} a_{k\gamma} \frac{\dot{R}_{\gamma\alpha}}{R_{\gamma\alpha}}, \quad k = 1,2,3. \tag{14}$$

Meanwhile, the cell volume is defined only by the diagonal components of the curvature radius. It is easy to see that the 3D analog of Eq. (10) still stands: $\dot{\Omega} = \Omega \Sigma_{\gamma} \dot{R}_{\gamma\gamma}/R_{\gamma\gamma}$. Therefore, only the diagonal components of radius of curvature contribute to the last term of the Hamiltonian of Eq. (11), proving the physical irrelevance of the orientation of the cell.

The temperature of the system is defined as the time average

$$k_B T = \left\langle \frac{1}{3N+6} \sum_{i=1}^{N} (2K_R + m v_i^2) \right\rangle, \tag{15}$$

where $K_R = m \Sigma_{\alpha\beta} \dot{R}_{\alpha\beta}^2 / 2$ is the kinetic energy related to the radial motion of a particle.

The first term in Eq. (11) is an analog of the kinetic energy with effective mass W in the PR method [2]. Although the "effective" mass of each radius vibration mode is equal to Nm, in equilibrium, at temperature $T, 3k_BT$ is contributed to H by the first term and $3N/2k_BT$ by the second kinetic term. Hence, the enthalpy is conserved within the range of the fluctuation of the K_R term. The average over the time evolution of the system corresponds to an average in the isobaric-isoenthalpic ensemble to which can be associated a canonical isothermal-isobaric ensemble [1]. Starting from initial conditions $\mathbf{r}_i(0), \dot{\mathbf{r}}_i(0), R_{\alpha\beta}(0)$ with respect to the given energy and pressure the evolution of the system occurs in $(6N+12)D$ phase space on the surface corresponding to constant energy. The relaxation time for recovery from imbalance between the external pressure and the internal stress is determined now by the values of curvature radius. The comparison of the frequency of cell parameter fluctuation $\omega^{PR} \sim (Nmv_s^2/WL^2)^{1/2}$ taken from Ref. [8] with $\omega_R \sim v_s/R_{\alpha\beta}$ defines the relationship between the two free parameters: $R_{\alpha\beta} \sim L(W/Nm)^{1/2}$.

IV. MD COMPUTATIONS

The solid-solid transitions in ^{4}He at high temperature studied in Ref. [11] by the PR method have been employed here to illustrate the proposed MD technique. It is not the intention to make detailed comparison with the results of Ref. [11], but two examples of fcc-bcc transitions are explored to check the validity of the results summarized above.

The simulation cell for bcc→fcc transition contained $N = 686$ atoms initially disposed in a bcc structure, with the lattice constant $d_0 = 2.4$ Å and nonzero components $a_{1,x}$, $a_{2,y}$, and $a_{3,z}$. Small random displacement of the particles from the lattice sites and zero velocities provided the initial conditions for the ensuing dynamics. After some time to establish equilibrium, an MD run with curvature was made.

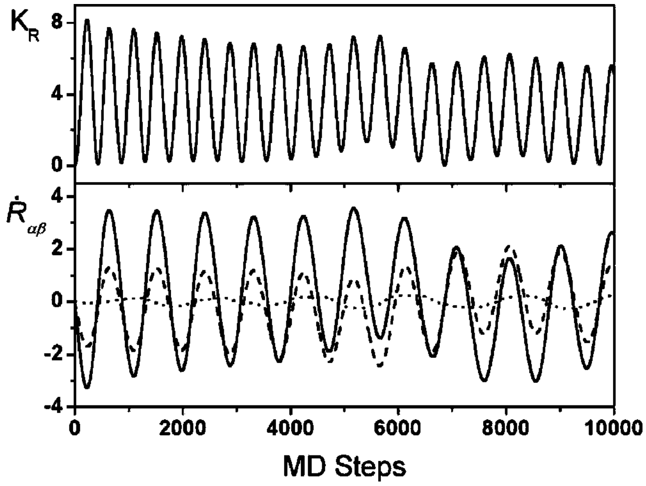

FIG. 2. Fluctuation in the curvature radius velocities of a bcc crystal of He. (a) The kinetic energy along the additive degrees of freedom K_R. (b) The velocities of curvature radius contributed to K_R. Solid line is $\dot{R}_{xx}$ (the component $\dot{a}_{1x}$ behaves in an equivalent manner). Since the evolution of the component $\dot{R}_{yy}$ and $\dot{R}_{zz}$ looks similar (like that of nondiagonal components $\dot{R}_{\alpha\beta}, \alpha \neq \beta$), there only two components $\dot{R}_{yy}$ (dashed curve) and $\dot{R}_{xy}$ (dotted curve) are shown.

The equations of the motion, Eq. (12), were solved using a Verlet-type integration and the potential of Aziz *et al.* [12], truncated at a distance $r_c = 5.67$ Å. A conservation of H of 10^{-4} in relative value was obtained over integration times of $10^4 \Delta t$ with the time step $\Delta t = 10^{-3}(ml^2/\varepsilon)^{1/2}$, $l = 2.553$ Å. The reduced units (r.u.) of energy and time are $\varepsilon = k_B(10.22\ \text{K})$ and $(ml^2/\varepsilon)^{1/2}$, respectively.

Unlike the PR method with only one free parameter (effective mass), here are six. The initial curvature radius $R_{xx} = 10.0$ Å with respect to the X axis, being unequal to $R_{\alpha\beta} = 20.0$ Å, $\alpha, \beta \neq x, x$ enables us to emphasize the preferred direction of cell deformation (c axis). The time history of the radius velocities for energy $H^* = H/\varepsilon N = 1128.9$, pressure $p^* = pl^3/\varepsilon = 2200$ and temperature $T^* = k_B T/\varepsilon = 28.7$ is shown in the lower part of Fig. 2. Initially, in each simulation the diagonal elements of internal virial pressure fluctuate about the same values $\sim p\Omega$, the off-diagonal elements of the pressure tensor fluctuate about zero. When the structure transformation occurs, one diagonal element of the internal stress becomes responsible for cell deformation, while maintaining the dynamical balance. It is better seen in oscillations of the velocity $\dot{R}_{xx}$ along the c axis, whose values (averaged over a limited number of MD steps ~ 10) distinctly diverge from other ones just after ~ 2000 MD steps. It results in successive deformation of the initial cubic MD cell to a rectangular parallelepiped with quadratic section in the plain YZ. The final ratio a_{1x}/a_{2y} and a_{1x}/a_{3z} vary from 1 to $\sim 1/\sqrt{2}$ while $a_{2y}/a_{2y}(0)$ and $a_{3z}/a_{3z}(0)$ vary from 1 to 0.89. The angular distortion of the cell was negligible. The calculations [11] exhibited the same kind of transformation.

The upper part of Fig. 2 shows the curve of the radial kinetic energy K_R. Oscillations of K_R near the mean value $\langle K_R \rangle = T_R^* \sim 2.0$ attenuate too slowly to achieve the equilibrium value $T_{RE}^* = 3k_B T/\varepsilon N \sim 0.1$ after 10^4 MD steps because of the large initial radius. The effective mass $W = 20m$ used in Ref. [11] corresponds to $R_{\alpha\beta}(0) \sim L(W/Nm)^{1/2} \sim 3$ Å. The transition bcc→fcc also occurs for the same $R_{\alpha\beta}(0) = 3.0$ Å but in much more time.

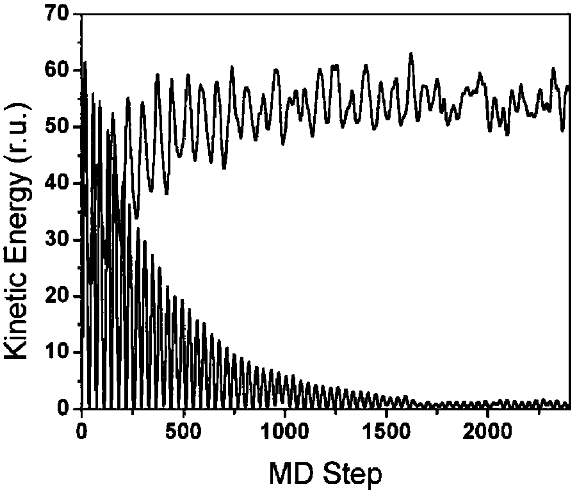

FIG. 3. Time histories of NPH simulation during fcc→bcc transition in He crystal. The component a_{1x} of the cell vector $\mathbf{a}_1$ evolves similarly to R_{xx}. The cell components a_{2y} and a_{3z} evolve as R_{yy} (dashed curve). Evolution of all nondiagonal components looks similar, therefore only R_{xy} (dotted curve) is shown here.

To consider more rapid evolution of the cell parameters the next example of reverse fcc→bcc transition started from the radius $R_{\alpha\beta}(0) = 1.0$ Å. Furthermore, the initial lattice constant $d_0 = 2.8$ Å for the pressure $p^* = pd^3/\varepsilon = 1800$ in this example was far from the equilibrium value (~ 3.0 Å), thus giving a large amplitude of oscillations of all cell parameters. After ~ 2400 MD steps the cubic cell of $N = 256$ atoms in the initial *bcc* structure with $H^* = 1002.7$ transforms also to a rectangular parallelepiped of fcc phase with

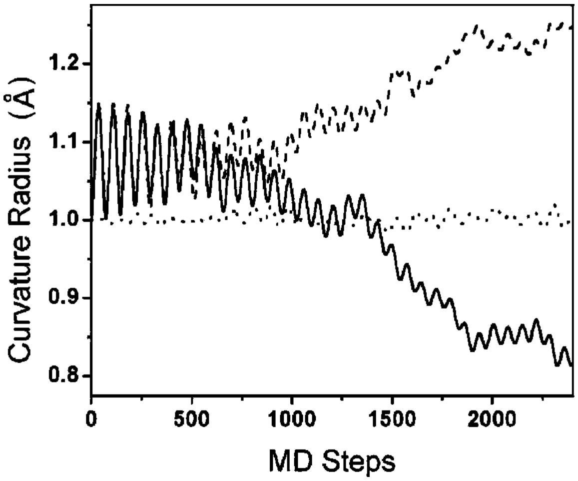

FIG. 4. Kinetic energy fluctuations during fcc→bcc transition in He crystal. The contributions of the curvature radius vibration K_R and the transverse kinetic energy [the second term in triangular brackets of Eq. (15)] are shown separately by the upper and lower curve.

respect to the ratio $a_{1x}/a_{3z}\sim\sqrt{2}$ and $a_{2y}/a_{2y}(0)\sim 0.89$ (Fig. 3). Because the pressure is isotropic and all components of $R_{\alpha\beta}(0)$ are equal to each other, which element of the pressure is mainly responsible for the transformation is purely a matter of chance. In this example it depends on initial atomic displacements. Unlike the previous example, the kinetic energy K_R drops considerably during the evolution up to an equilibrium value of $T_R^*\sim 0.01$, as the temperature tends to the value $T^*=k_BT/\varepsilon=36.2$ (Fig. 4).

CONCLUSIONS

A constant pressure method has been developed from first principles and tested. The equations of motion, Eq. (12), provide essential simplification of calculation for variable-cell-shape MD since the distance between atoms is not the metric tensor. No special metric formula is required for the calculation of the total distance traveled by a particle which can be misleading in the PR formalism [7].

The Hamiltonian, Eq. (11), eliminates the cell orientation from dynamics and fluctuation in the cell shape generated by Eq. (12) is not determined by the shape of the simulation cell, which is arbitrary. Accordingly the motion equations are invariant with respect to the interchange between equivalent cells and one can conclude that the Hamiltonian, Eq. (11), is invariant under modular transformation [5].

The general treatment reduces to the Andersen case of isoshape cell fluctuation within the same approach. Because of its physical transparency, the extension to anisotropic external stress and constant-temperature condition is straightforward. Corresponding results will be discussed elsewhere.

The principal difference of the present method with respect to the PR one is the number of extended degrees of freedom. In the PR formalism, nine independent components of the scaling matrix, viz., the components of basic cell vectors, determine the dynamics of the system. Only six of them are necessary to define the shape of the MD cell. The three remaining parameters describing the orientation of the MD cell in space are responsible for the physically irrelevant cell rotation [8]. Six extended degrees of freedom exploited by the proposed method avoid this problem regardless of the symmetry condition for the components of the pressure tensor. The motion equations are driven by the six free parameters related to the additional degrees of freedom. The vanishing of each stress tensor component by means of an appropriate curvature provides quite independently the equilibrium value of one of the six cell parameters. Hence, the problem of lattice equilibrium can be solved in full in terms of the unified approach.

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