Invariant molecular-dynamics approach to structural phase transitions

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Two fictitious Lagrangians to be used in molecular-dynamics simulations with variable cell shape and suitable to study problems like structural phase transitions are introduced. Because they are invariant with respect to the choice of the simulation cell edges and eliminate symmetry breaking associated with the fictitious part of the dynamics, they improve the physical content of numerical simulations that up to now have been done by using Parrinello-Rahman dynamics.

In the molecular-dynamics (MD) simulation method for statistical mechanics,[1] the equations of motion (EM) for a collection of particles are solved numerically. Because the number of particles is limited, periodic boundary conditions are used to eliminate unwanted surface effects. However, this suppresses fluctuations in volume and shape of the MD cell containing the particles under consideration. These (unharmonic) fluctuations are responsible for numerous phenomena of direct relevance to condensed matter physics, for instance, structural phase transitions.

In the past decade we have seen the extension of MD methods to deal with ensembles other than the traditional microcanonical,[2-4] and among these some allow for changes in the MD cell. The first of these methods was introduced by Andersen and aimed to simulate fluids subjected to constant pressure.[2] It allows us to obtain isenthalpic-isobaric ensemble averages by calculating averages over trajectories of particles evolving according to the following fictitious Lagrangian:

$$L=\Omega^{2/3}\sum_{i=1}^{N}\frac{m_i}{2}\dot{\mathbf{s}}_i\cdot\dot{\mathbf{s}}_i-\sum_{i=1}^{N}\sum_{j>i}\phi(r_{ij})+\frac{W}{2}\dot{\Omega}^2-P\Omega\ . \tag{1}$$

In Eq. (1) the particles coordinates $\mathbf{r}_i, i=1,\ldots,N$, were replaced by scaled coordinates $\mathbf{s}_i=\mathbf{r}_i/\Omega^{1/3}$, where Ω is the MD cell volume. The first term (K_I) is the kinetic energy (KE) of particles of mass m_i measured in a frame which "breathes" with the cell, the second is the potential energy (PE) of the interacting particles expressed in a pair potential form (U_I), where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$. The third term has a fictitious mass W and is the KE associated with volume fluctuations (K_L), and the last one represents the PE (U_L) due to an external pressure P.

A generalization of this idea led Parrinello and Rahman (PR) to propose a Lagrangian which has a time-dependent metric tensor.[3] Let h be the matrix formed by $\{\mathbf{a},\mathbf{b},\mathbf{c}\}$, where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, are the time-dependent edges of the MD cell, with the corresponding time-dependent metric tensor $g=h^Th$. The particles coordinates are then $\mathbf{r}_i=h\mathbf{s}_i$, where $\mathbf{s}_i$ are particles positions in lattice coordinates and consist of 3D vectors whose components vary from 0 to 1. The PR Lagrangian and the corresponding EM's then are

$$L=\sum_{i=1}^{N}\frac{m_i}{2}\dot{\mathbf{s}}_i^T\cdot g\dot{\mathbf{s}}_i-\sum_{i=1}^{N}\sum_{j>i}\phi(r_{ij})+\frac{W}{2}\mathrm{Tr}(\dot{h}^T\dot{h})-P\Omega\ , \tag{2}$$

$$\ddot{\mathbf{s}}_i=-\frac{1}{m_i}\sum_{j\neq i}\frac{\phi'(r_{ij})}{r_{ij}}(\mathbf{s}_i-\mathbf{s}_j)-g^{-1}\dot{g}\dot{\mathbf{s}}_i\ , \tag{3a}$$

$$\ddot{h}=\frac{1}{W}(\Pi-P)\sigma\ , \tag{3b}$$

where $\sigma=\{\mathbf{a}\times\mathbf{b},\ \mathbf{b}\times\mathbf{c},\ \mathbf{c}\times\mathbf{a}\}$ and Π is the symmetrized stress tensor:

$$\Pi=\frac{1}{\Omega}\sum_{i=1}^{N}m_i\mathbf{v}_i\mathbf{v}_i^T-\frac{1}{\Omega}\sum_{i=1}^{N}\sum_{j>i}\frac{\phi'(r_{ij})}{r_{ij}}\mathbf{r}_{ij}\cdot\mathbf{r}_{ij}^T \tag{4}$$

with $\mathbf{v}_i=h\dot{\mathbf{s}}_i$. In the limit of pure volume fluctuations, except for this third term, all the others coincide in both Lagrangians above.

Despite the fact that this Lagrangian has not been obtained from first principles, many encouraging results have been obtained in MD simulations of structural phase transitions.[3,5,10] As a matter of principle, however, there are some objections one could raise regarding the K_L term. The most obvious is that its nominal value depends on the choice of cell edges. For instance, take a square lattice and consider volume fluctuations only. If the cell edges are chosen as $\mathbf{a}=(L,0)$, $\mathbf{b}=(0,L)$, at a particular time t_0, $\dot{\mathbf{a}}=(\delta,0)$, $\dot{\mathbf{b}}=(0,\delta)$, and $K_L=W\delta^2$. In contrast, if they are chosen as $\mathbf{a}'=\mathbf{a}$, and $\mathbf{b}'=\mathbf{a}+\mathbf{b}$, at t_0, $\dot{\mathbf{a}}=(\delta,0)$, $\dot{\mathbf{b}}=(\delta,\delta)$, and $K_L=\frac{3}{2}W\delta^2$. In MD simulations involving many ($\sim 10^2$) particles, this KE may be small and the above objection is likely not to be the most serious one. There are however further questionable dynamical effects which will be addressed below.

In this Brief Report two new Lagrangians which differ from the PR's by the choice of the K_L term and are invariant under modular transformations as described above are proposed. The first one uses a different scaling for the particles' coordinates, and the components of the strain tensor ϵ, instead of those of h, are chosen as dynamical variables. The second one, besides having all the properties of the first, coincides with Andersen's La-

grangian in the limit of isoshape fluctuations. The dynamics that the PR and the new invariant Lagrangians give rise to are compared under strict conditions and the superior (more physical) character of the invariant Lagrangians is demonstrated.

The lack of invariance in the PR dynamics refers to its behavior under a modular transformation, $h \rightarrow hm$, where m is a constant integer matrix with $\det(m)=1$. Because $\mathrm{Tr}(\dot{h}^T\dot{h}) \neq \mathrm{Tr}(m^T\dot{h}^T\dot{h}m)$, not only the nominal value of K_L, but also the forces and trajectories will depend on the choice of m. Instead if we choose $K_L=(W/2)\mathrm{Tr}(\dot{\epsilon}^T\dot{\epsilon})$, where ϵ is the strain, this problem is avoided because ϵ is invariant as is the rest of the Lagrangian. The relationship between ϵ and h is $h=(1+\epsilon)h_0$, where $h_0=\{\mathbf{a}_0,\mathbf{b}_0,\mathbf{c}_0\}$ corresponds to some reference structure, the initial one for example. The new scaling for the particles' coordinates then is, $\mathbf{r}_i=(1+\epsilon)\mathbf{q}_i$ and the new invariant Lagrangian becomes

$$L=\sum_{i=1}^{N}\dot{\mathbf{q}}_i^T\cdot d\,\dot{\mathbf{q}}_i-\sum_{i=1}^{N}\sum_{j>i}^{N}\phi(r_{ij})+\frac{W}{2}\mathrm{Tr}(\dot{\epsilon}\dot{\epsilon}^T)-P\Omega\ , \tag{5}$$

where $d=(1+\epsilon)^T(1+\epsilon)$. By applying Lagrange's equation we obtain the new EM's:

$$\ddot{\epsilon}=\frac{\Omega}{W}(\Pi-P)(1+\epsilon)^{T-1}\ , \tag{6a}$$

$$\ddot{\mathbf{q}}_i=-\frac{1}{m_i}\sum_{j\neq i=1}^{N}\frac{\phi' r_{ij})}{r_{ij}}(\mathbf{q}_i-\mathbf{q}_j)-d^{-1}\dot{d}\,\dot{\mathbf{q}}_i\ . \tag{6b}$$

Equation (6a) reveals that only under special conditions ($[\Pi,(1+\epsilon)^{T-1}]=0$, at all times) ϵ will remain symmetrical. In general there will be KE associated with free rotations of the cell. However, by symmetrizing the right-hand side of Eq. (6a),[11] which is equivalent to constraining the three antisymmetrical strain components, this superfluous rotation can be eliminated. Equation (6a) also indicates that in the absence of thermal fluctuations, in which case the first term on the right-hand side of Eq. (4) vanishes, the symmetry of the Bravais lattice will remain unchanged. This happens because initially $\epsilon=0$ and Π, as well as $\ddot{\epsilon}$, have the same point symmetry group of the lattice. In the following steps, ϵ, Π, and $\ddot{\epsilon}$ will again have the same original symmetry. Therefore, the fictitious dynamics associated with ϵ does not change the lattice symmetry. The same analysis applied to the strain resulting from the PR dynamics ($\ddot{\epsilon}=\ddot{h}h_0^{-1}$), indicates that the point symmetry group of ϵ, and therefore the Bravais lattices, should be that of the simulation cell, which in general is an invariant subgroup of the initial Bravais lattice's. This symmetry reduction associated with the noninvariant fictitious dynamics, will be demonstrated in the examples below. An alternative form for Eq. (5) is

$$L=\sum_{i=1}^{N}\frac{m_i}{2}\dot{\mathbf{s}}_i^T\cdot g\,\dot{\mathbf{s}}_i-\sum_{i=1}^{N}\sum_{j>i}\phi(r_{ij})+\frac{W}{2}\mathrm{Tr}(\dot{h}f_0\dot{h}^T)-P\Omega \tag{7}$$

with $f_0=(\sigma_0^T\sigma_0)$, where $\sigma_0=\{\mathbf{a}_0\times\mathbf{b}_0,\ \mathbf{b}_0\times\mathbf{c}_0,\ \mathbf{c}_0\times\mathbf{a}_0\}$. In this case the EM's for the particles' coordinates coincide with Eqs. (3a) and (6a) turns into

$$\ddot{h}=\frac{1}{W}(\Pi-P)\sigma f_0^{-1}\ . \tag{8}$$

This form is easier to implement in codes already performing PR dynamics.

In the following examples, the dynamics generated by Eqs. (2) and (7), as well as by another invariant modification of Eq. (7) (see below), are compared. The systems considered consist of lattices which are initially distorted and allowed to evolve along conservative trajectories. Zero temperature is chosen because thermal fluctuations would cover up the fluctuations addressed here and disguise the active role played by the noninvariant fictitious dynamics in breaking the systems' symmetry. Therefore the simulation of classical statistical systems is deferred to future work, until the basic aspect of interest here is unfolded.

First consider an fcc lattice with Ar atoms interacting through a Lennard-Jones pair potential. The MD cell is composed of two cubes, each one containing four atoms, stacked vertically, and placed initially away ($11.0a_0$, a_0 being the Bohr radius) from the equilibrium lattice constant ($\sim 9.91a_0$). Then, the system is allowed to move[12] through an ensemble of states along the trajectories generated by Eqs. (3b) and (8). Figures 1(a) and 1(b) show the evolution of cell dimensions according to Eqs. (3b) and (8), respectively. In Fig. 1(a) the ensemble of states generated has tetragonal symmetry, while in Fig. 1(b) the cubic symmetry is never reduced, with the vertical cell edge always twice longer than the horizontal ones. The point here is to show that fluctuations in the cell shape generated by Eq. (3b) are determined by the shape of the simulation cell, which is arbitrary, and not by the stresses which have the symmetry of the lattice. For instance, if a trigonal cell is chosen , the system will move through an ensemble of trigonal structures. Instead if Eq. (8) is used, a unique motion results, regardless of the simulation cell shape. As expected in this case, a pure volume fluctuation occurs.

Despite Eq. (7) describing more properly the behavior of systems with isoshape fluctuations, it does not coincide with Eq. (1) in the isoshape limit. It is possible however to modify slightly the third term (K_L) to obtain the desired limit while still keeping the invariance property. This mapping is advantageous since in the isoshape case the averages over the trajectories correspond to isenthalpic-isobaric ensemble averages,[2] and also the virial theorem is obeyed.[2,13] Consider $K_L=(W/2)\mathrm{Tr}(\dot{h}\sigma^T\sigma\dot{h}^T)$. Recall that the components of h are proportional to $\Omega^{1/3}$ and $\sigma^T=\Omega h^{-1}$. Then $\dot{h}\sigma^T\simeq\dot{\Omega}$ and $K_L\simeq\dot{\Omega}^2$, which is the isoshape limit. The EM's for the particles' coordinates obtained from this invariant Lagrangian remain unchanged [Eq. (3a)] while those for the components of h become

$$\ddot{h}=\frac{1}{W}(\Pi-P)\sigma f^{-1}+\tfrac{1}{2}\mathrm{Tr}(ef'^{(h)})f^{-1}-\dot{h}\dot{f}f^{-1} \tag{9}$$

with $f=(\sigma^T\sigma)$, $e=\dot{h}^T\dot{h}$ and $f'^{(h_{ij})}=\partial f/\partial h_{ij}$.

This is the EM used in the next example, which deals

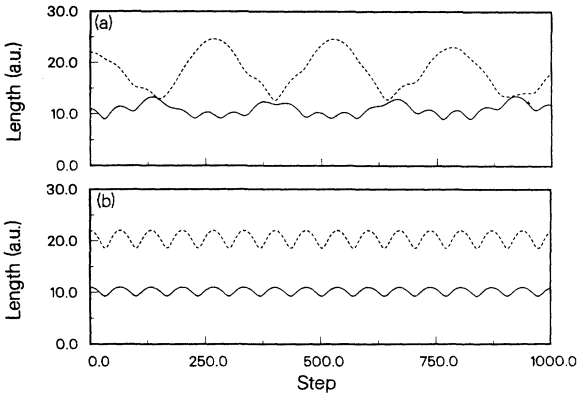

FIG. 1. Fluctuations in the cell edges lengths of an fcc crystal of Ar initially displaced from the equilibrium lattice constant (see text). The simulation cell contains two cubes stacked vertically. In (a) Eq. (3b) is used while in (b) Eq. (7). The time step is $dt \approx 10$ fmt sec, $m_i = 39m_p$ (m_p being the proton mass), and in (a) $W = 35m_p$ while in (b) $W = 0.0007 m_p / a_0^4$. The cutoff radius for the pair interactions is $50.0a_0$.

with the dynamical effects caused by the lack of invariance of the PR Lagrangian during a cell relaxation or a sudden quench. Figure 2(a) shows the contour plot of the energy surface associated with the set of trigonal Bravais lattices with one Ar per cell. The structures are characterized by a nearest-neighbor distance d and by the angle θ. The global minimum is located at the fcc structure ($E = -6.566$ mRy/atom, $d = 7.006a_0$, and $\theta = 60°$). There is also a local minimum at the bcc ($E = -6.282$ mRy/atom, $d = 6.866a_0$, $\theta = 109.47°$) and a saddle point at the simple cubic (sc) ($E = -4.339$ mRy/atom, $d = 6.858a_0$, $\theta = 90°$) along the energy barrier (dashed line) separating the fcc and the bcc minima. Figure 2(b) represents the basins of attraction of Bravais lattices after relaxations by means of "downhill" trajectories[14] generated by Eq. (9). These basins faithfully portray the shape of the total energy surface, with the fcc (bcc or sc) lattice being the end structure if the starting point is at the left (right or top) of the energy barrier. The symmetry is not broken along the invariant trajectories and the basins are unique regardless of the choice of the simulation cell. In contrast if the PR dynamics is used, then the basins of attraction will depend of the choice of the MD cell. For example, if the cell edges $\{\mathbf{a},\mathbf{b},\mathbf{c}\}$ have the same length and angle between them, Fig. 2(b) still holds, but if they are chosen differently, as $\{\mathbf{a}'=\mathbf{a},\ \mathbf{b}'-\mathbf{b},\ \mathbf{c}'=\mathbf{a}+\mathbf{b}+\mathbf{c}\}$, then the original symmetry reduces along the trajectories and a larger set of end structures is possible [Fig. 2(c)].[15]

In conclusion, because of the lack of invariance under modular transformations of the PR Lagrangian, the cell and particles dynamics it generates depend on the choice of the simulation cell. This creates questionable dynamical effects related to symmetry breaking. In classical physical systems, symmetry is broken by internal stresses caused by thermal fluctuations of the atoms. The fictitious dynamics associated with the lattice should not play any active role in this regard. By making the Lagrangian invariant, the arbitrariness of the cell shape and the "fictitious" symmetry breaking are eliminated, and constraints on the strain tensor, other than symmetrization, become unnecessary and undesirable. This is a relevant point in addressing dynamical processes behind reconstructive structural phase transitions, where distortions of the cell are unavoidable.

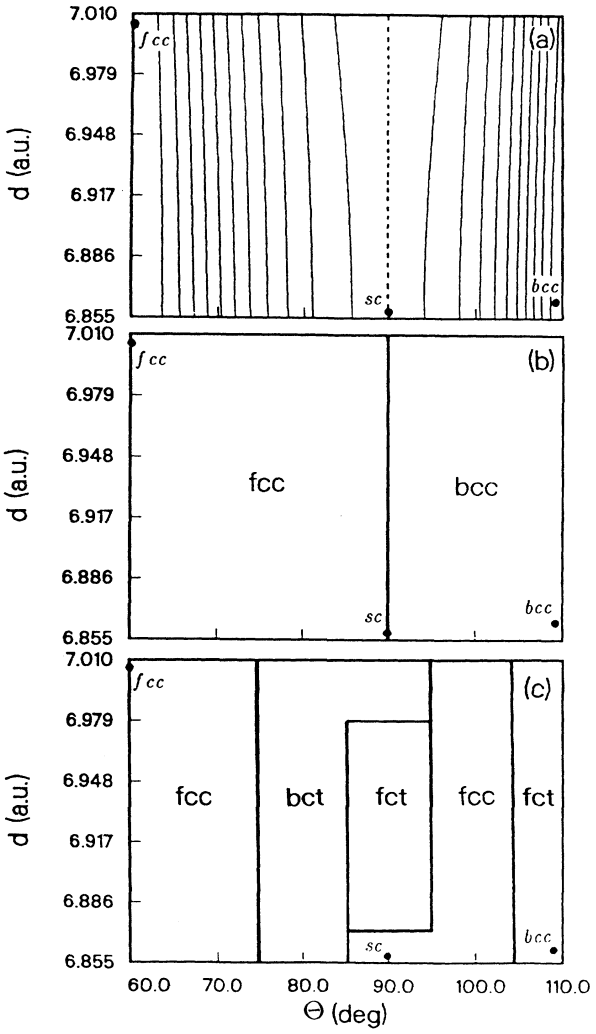

FIG. 2. (a) Contour plot of the energy per atom associated with trigonal lattices characterized by the nearest-neighbor distance d and angle θ. There is a global minimum at the fcc structure, a local one at the bcc, and a saddle point at the sc along the energy barrier (dashed line) separating the fcc and the bcc minima (see text). The contour lines are separated by 0.2 mRy. Basins of attraction of the final structures which have initially been placed in trigonal phase characterized by d and θ and allowed to relax by means of the (b) Eq. (9) and (c) by Eq. (3b) (see text). The 2D mesh used is $\theta = 60° + 10°i$, with $i = 0, \ldots, 5$ and $d = (6.855 + 0.0155j)a_0$, with $j = 0, \ldots, 10$.

Note added in proof. It was recently brought to my attention that C. Cleveland had proposed an invariant Lagrangian [J. Chem. Phys. **89**, 4987 (1988)] that is equivalent to the second one proposed in this paper.

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[15]The new found structures are bct, $E = -6.565$ mRy/atom, $\Omega = 245.13 a_0^3$/atom, $c/a = 1.426$; fct, $E = -6.300$ mRy/atom, $249.09 a_0^3$/atom, $c/a = 0.629$.