Dynamics on a torus

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The dynamics of atoms on the surface of a torus is considered. The simple illustration of motion with regard to rotating and fixed space gives a model of a four-dimensional (4D) torus. Two different schemes including rotation and shear in angular frame are used to take into account shears of the surface. In general, a variable-cell-shape molecular dynamics method analogous to the Parrinello-Raman one is developed. The six dynamical variables, the three radiuses and the three angles, specifying the deformations of the surface describe the cell dynamics. The new equations of motion contain no vectors of translations of the cell making its shape irrelevant for the structural and thermodynamical description of the system. The new method was tested on two problems concerning structure transformations of two-dimensional lattices.

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In molecular dynamics (MD) the flexibility of a crystal under periodic boundary conditions is achieved by introducing additional degrees of freedom for the MD cell. Traditionally the dynamical variables associated with the MD cell are the Cartesian components of the three vectors defining the cell [1]. Since the number of the independent cell variables differs from the number of forces responsible for the cell deformation (the six components of the internal stress tensor) a correspondence between them is not direct producing a number of inconsistencies. At first, Nosé [2] has shown that three extraneous coordinates can be responsible for unphysical rotation of the cell. Further, one has to guarantee that equations of motion are invariant to the arbitrary choice of the lattice vectors [3]. Of course, all inconsistencies of prior Parrinello-Raman (PR) treatment founded have been successfully removed and further development of PR method has given a powerful means to study systems in the isoenthalpic-isobaric and isothermal-isobaric ensembles. One should note though that incorrect number of the variables is a consequence of the scaling model, which has not changed in process of all corrections and improvements. Originated with Andersen [4] and generalized later by PR [1] this model assumes the atomic coordinates and momenta to be scaled by the lattice coordinates. Because the scaling the equations of motion contain the direct dependence on the MD cell coordinates and the corresponding Lagrangian cannot be derivable from first principles. Evidently, this circumstance is likely not to be the serious one in view of numerous comparisons between the results of MD simulations and Monte Carlo calculations. The more especially as the rigor of the PR method arises from that fact that the trajectories sample the correct distribution function, assuming ergodicity. Still, it does not seem improbable that some features of dynamics may turn out to be sensitive to this dependence in a greater degree than to that implicitly contained in the potential of the lattice due to periodic boundary conditions. So the elimination of this dependence should be in accordance with the principle of material-frame indifference [5] and deserving motivation for a possible alternative.

A model of the ensemble of particles on the surface of a 6D torus proposed in Refs. [6,7] enables us to avoid in a natural way the problems mentioned above. This surface can be represented by the intersection of the three three-dimensional hypercylinder, given by parametric equations $\mathrm{s}_\alpha = R_\alpha \sin\theta_\alpha$, $\upsilon_\alpha = R_\alpha \cos\theta_\alpha$, and $\alpha = x,y,z$, where R_α is the radius of the cylinder. The closed and finite surface being isometric to 3D Euclidean space [8] is particularly suited to the consideration of the dynamics of a finite ensemble with periodic boundary conditions. Let $R_\alpha\theta_{i\alpha}$ be coordinates of ith particle on the surface of a 6D torus. Then the distance between the ith and jth particle on the surface is $s_{ij} = \sqrt{\Sigma_\alpha R_\alpha^2 \theta_{ij\alpha}^2}$. The motion of N particles of the mass m on the surface of torus can be evaluated with the help of the Lagrangian

$$L = \frac{m}{2}\sum_{i=1,\alpha}^{N}\left(R_\alpha^2\dot{\theta}_{i\alpha}^2 + \dot{R}_\alpha^2\right) - \phi, \tag{1}$$

which originates from the model of the curved chain [6].

In order to reduce a 6D dynamics on a torus to the real 3D atomic dynamics, the pair potential of interaction between atoms $\phi = \Sigma_{j>i=1}^{N} U(s_{ij})$ in Eq. (1) is assumed to be dependent on the arc length s_{ij} connecting atoms on the surface. Then the equations of motion from this Lagrangian are given by

$$\dot{s}_{i\alpha} = \mathrm{v}_{i\alpha} + \frac{\dot{R}_\alpha}{R_\alpha}s_{i\alpha},$$

$$m(R_\alpha \mathrm{v}_{i\alpha})^{\cdot} = R_\alpha F_{i\alpha},$$

$$m\ddot{R}_\alpha = \frac{\sigma_{\alpha\alpha}}{R_\alpha}, \tag{2}$$

where $\mathrm{v}_{i\alpha} = R_\alpha\dot{\theta}_{i\alpha}$ and the forces are defined by $F_{i\alpha} = -\Sigma_j \chi(s_{ij}) s_{ij\alpha}$ and $\chi(s) = s^{-1}\,\partial U(s)/\partial s$. The values of $\sigma_{\alpha\alpha}$ are the diagonal components of the tensor

$$N\sigma_{\alpha\beta} = m\sum_{i=1}^{N}\mathrm{v}_{i\alpha}\mathrm{v}_{i\beta} - \sum_{j>i=1}^{N}\chi(s_{ij})s_{ij\alpha}s_{ij\beta}. \tag{3}$$

Since the three-dimensional curvilinear coordinates on the surface have the Euclidean metrics, the transverse motion of atoms on the surface determining by tangent forces $F_{i\alpha}$ is

quite analogous to the Newtonian one in terms of three-dimensional Cartesian coordinates. The coupling of the atomic motion to the cell's motion is made through the radius of the curvature R_α. It is driven by the diagonal components of the internal stress tensor $\sigma_{\alpha\alpha}/V$, where V is the volume per atom. As a result, the system will evolve to a configuration with constant curvature, which corresponds to the stress-free state of the crystal in real space.

Basically, the equations of Eq. (2) account for only independent extensions in three directions. In particular, these equations with the same radius $R_\alpha = R$ generate the isoshape dynamics of Andersen's kind [5,6]. To include shears to the dynamics three other independent variables must be introduced. The trial to do that by means of nondiagonal elements of the curvature radius [7] failed since the motion equations obtained do not conserve energy. Below, the necessary deformation will be introduced through the use of new orders of freedom in an angular frame. In principle, there are two options available. Apart from a direct shear in angles it can be done by a rotation of angles with regard to a fixed reference frame orientated along directions of the main curvatures.

For illustrative purposes the application to the rotation of angular coordinates of a particle on the 4D torus will be considered first. Let the rotation of the vector $\boldsymbol{\theta}=(\theta_x,\theta_y)$ through the angle φ be accompanied by the displacement of the particle $\boldsymbol{\xi}$ along the axis of rotation. The Lagrangian associated with a rigid rotation can be obtained from that of Eq. (1) by the substitution $\dot{\boldsymbol{\theta}}\rightarrow\dot{\boldsymbol{\theta}}'=\dot{\boldsymbol{\theta}}+[\boldsymbol{\omega}\times\boldsymbol{\theta}]$ where $\boldsymbol{\omega}=\dot{\varphi}\boldsymbol{\xi}/\xi$ so that

$$L=\frac{m}{2}[\dot{\xi}+\dot{R}_x^2+\dot{R}_y^2+R_x^2(\dot{\theta}_x-\omega\theta_y)^2+R_x^2(\dot{\theta}_y+\omega\theta_x)^2]-\phi(\varphi). \tag{4}$$

The angles θ_x and θ_y in this expression are independent variables. If, in addition, we relate $\boldsymbol{\theta}$ and φ by the equations $\partial\theta_x/\partial\varphi=-\theta_y$ and $\partial\theta_y/\partial\varphi=\theta_x$, then the vector $\boldsymbol{\theta}$ can be defined in terms of its components θ^f_x and θ^f_y fixed in space. Introducing the matrix of rotation $\mathbf{A}$ through the angle φ, one substitutes $\theta_\alpha=A_{\alpha\beta}\theta^f_\beta$ to Eq. (4). Accordingly the velocity $\dot{\boldsymbol{\theta}}'$ in Eq. (4) becomes equal to the apparent velocity $\mathbf{A}\dot{\boldsymbol{\theta}}^f$ thus eliminating forces of reaction caused by rotation.

The extension to the case of the ensemble of particles on the surface of the 6D torus is straightforward. The Eulerian matrix $\mathbf{A}$ determines now the rotation of the vectors $\boldsymbol{\theta}_i$ with respect to a fixed frame so that the Lagrangian takes the form

$$L=\frac{m}{2}\sum_{i=1,\alpha}^{N}(\mathrm{v}_{i\alpha}^2+\dot{R}_\alpha^2+\dot{\varphi}_\alpha^2)-\phi-pV, \tag{5}$$

where $\mathrm{v}_{i\alpha}=R_\alpha A_{\alpha\beta}\dot{\theta}^f_{i\beta}$ and $\xi_\alpha=\varphi_\alpha$ is supposed. An external isotropic pressure p is introduced here additionally.

Following the usual procedure Eq. (5) gives the equations of motion. It is convenient to write them down not in terms of the independent variables but in terms of $\theta_{i\alpha}$ and furthermore make the substitution $\mathbf{s}_i\rightarrow\mathbf{r}_i$ taking into account the direct correspondence between the curvilinear and Cartesian coordinates in the 3D configuration space:

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

$$\dot{\mathbf{v}}_i=\frac{1}{m}\mathbf{F}_i-\mathbf{B}^t\mathbf{v}_i. \tag{6a}$$

The components of the matrix $\mathbf{B}$ can be written as

$$B_{\alpha\beta}=(\dot{R}_\alpha/R_\alpha)\delta_{\alpha\beta}+\varepsilon_{\alpha\gamma\beta}(R_\alpha/R_\beta)\omega_\gamma, \tag{6b}$$

where $\omega_\alpha=\dot{\varphi}_\alpha$ and $\varepsilon_{\alpha\beta\gamma}$ is the antisymmetric unit matrix in which $(\alpha\beta\gamma)$ is a cyclic rotation of (xyz). The equations for the curvature variables are

$$m\ddot{R}_\alpha=\frac{\sigma_{\alpha\alpha}-pV}{R_\alpha},$$

$$m\dot{\omega}_\alpha=\varepsilon_{\alpha\beta\gamma}(R_\beta/R_\gamma)\sigma_{\beta\gamma}. \tag{6c}$$

Since $dV/V=\Sigma_\alpha\, dR_\alpha/R_\alpha$, only the upper equation depends on the volume.

The second scheme is to work with a transformation of a pure shear $\dot{\theta}'_\alpha=\dot{\theta}_\alpha+\omega\theta_\beta$, $\alpha\neq\beta$ in Eq. (4) instead of rigid rotation. As before the relations $\partial\theta_x/\partial\varphi=\theta_y$ and $\partial\theta_y/\partial\varphi=\theta_x$ require that $\theta_\alpha=\mathcal{A}_{\alpha\beta}\theta^f_\beta$. The matrix $\boldsymbol{\mathcal{A}}$ with the components $\mathcal{A}_{\alpha\alpha}=\cosh(\varphi)$, $\mathcal{A}_{\alpha\beta}=\sinh(\varphi)$, $\alpha\neq\beta$ represents a pure shear whose principal axes are in the diagonal directions of the right angle $\theta^f_xO\theta^f_y$. The new transformation is seen as a rotation by an imaginary angle $i\varphi$ in the complex plane fixed in space. Hence a new Lagrangian differs from that of Eq. (4) only by the positive sign before $\omega\theta_y$. Therefore, in general, Eqs. (6a)–(6c) being implicitly dependent on the 3D matrix $\boldsymbol{\mathcal{A}}$ could be reduced to the new equations of motion by the substitution of the symmetric unit matrix $\varepsilon^s_{\alpha\beta\gamma}=1$, $\alpha\neq\beta\neq\gamma$ instead of the antisymmetric one $\varepsilon_{\alpha\beta\gamma}$. Use of either rotating or shear schemes is a matter of convenience. The second scheme allows one the same values of initial radiuses and it will be used below.

The additional variables change as the response to the imbalance of the internal stress $\sigma_{\alpha\beta}/V$ and the external pressure p. Since $\partial V/\partial R_\alpha=V/R_\alpha$ the treatment of the motion equation of Eqs. (6a)–(6c) in the context of statistical mechanics is quite analogous to the one-dimensional case [9]. The average of the motion equation of Eq. (6c) over time comes to the relation $\langle(\sigma_{\alpha\alpha}-pV)/R_\alpha\rangle=0$. Besides, in equilibrium, $\langle\sigma_{\alpha\beta}/V\rangle=p\delta_{\alpha\beta}$. Detailed discussion of the virial theorems for a more general isothermic-isobaric ensemble will be made elsewhere.

The total energy, the momentum and the angular momentum are conserved in the usual constant volume dynamics. The equations of motion of Eqs. (6a)–(6c) conserve the energy

$$E=\frac{m}{2}\sum_{i=1,\alpha}^{N}[(\dot{r}_{i\alpha}-B_{\alpha\beta}r_{i\beta})^2+\dot{R}_\alpha^2+\dot{\varphi}_\alpha^2]+\phi+pV. \tag{7}$$

As it is seen from Eq. (6a) the momentum conservation law holds if the initial position of the center of mass $\mathbf{r}_{c.m}=\mathbf{0}$. However, as like as in the PR method, the full angular momentum $\mathbf{L}=m\Sigma_i[\mathbf{s}_i\times\dot{\mathbf{s}}_i]$ is not conserved. To see the reasons start with the relation $\Sigma_i[\mathbf{s}_i\times\mathbf{F}_i]=\mathbf{0}$ for the special case of 4D

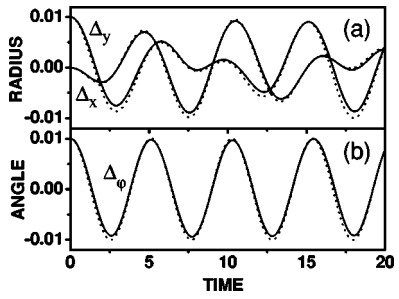

FIG. 1. The vibration of the triangular lattice. (a) The time evolution (in dimensionless units) of a change of radiuses of curvature from their initial values. (b) The change of shear strain. Analytical solutions are shown by the dots.

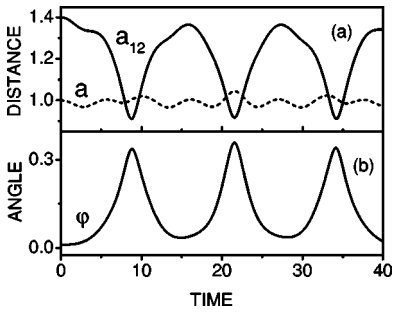

FIG. 2. Transition from the square to the triangular lattice. (a) The motion of the lattice vectors a and a_{12}. (b) The time evolution of the shear angle.

torus whose radiuses are $R_\alpha=1$. In view of Eq. (4) the rate of change of $L=L_v+\omega(J_{xx}-J_{yy})$ is given by $\dot{L}=\dot{\omega}(J_{xx}-J_{yy})$ where $L_v=m\Sigma_i[\mathbf{s}_i\times\mathbf{v}_i]$ and $J_{\alpha\beta}=m\Sigma_i s_{i\alpha}s_{i\beta}$. Hence, in an ideal lattice when $L_v=0$, the integration gives the conserved quantity L/ω. Only if one selects the initial value $J_{xx}=J_{yy}$, the cell angular momentum is zero. It corresponds to the shear diagonal being along a principal axis of inertia of the system.

Other reason of the quantity L not being conserved can be understood by the example of extending cylinder with a screw. A ratio of a screw pitch and the radius decreases with radius thus making a screw (as well as the MD cell as a whole) rotate in the development of the cylinder in spite of no torque acted. (Of course, radial forces of reactions are responsible for this kind of the rotation in 3-space). One should try to combine both schemes to deal with varying direction of the shear diagonal thus avoiding the cell rotation. However such complication is hardly justified, since the cell rotation itself does not influence the dynamics of the system [2] and troubles in the analysis of the molecular orientations and crystal structures mentioned in Ref. [2] are mainly a consequence of non-Euclidean metrics used in the PR method [10].

Two 2D model problems were used to test the new method proposed herein: the oscillations of the period of the triangular lattice and the distortion of a square lattice. Particles of the mass $m=1$ are assumed to interact via a Lennard-Jones 6-12 pair potential with the force constant at the minimum of the potential taken to be unity: $c(r)=r^{-1}\,\partial\chi(r)/\partial r|_{r=1}=1$. The potential was truncated to take into account the six nearest (and the eight in the next example) neighbors. Zero temperature is assumed because the basic aspect of interest here is the structural transformation.

The perfect triangular structure is characterized by the lattice translation vectors $\mathbf{a}_1=(1,0)$, $\mathbf{a}_2=(1/2,\sqrt{3}/2)$ and the curvature variables $R_\alpha=1$ and $\varphi=0$. The initial extension $R_y-1=\Delta_y^0=0.01$ in the Y direction and the distortion $\varphi=\Delta_\varphi^0=0.01$ make the structure transform along the trajectory generated by Eqs. (6a)–(6c). Periodic uniform deformation near equilibrium shown in Fig. 1 occurs with small amplitude. Therefore, adequate treatment of these results and appropriate test of calculation procedure, which was analogous to that developed in Ref. [11], can be given with the help of harmonic approximation to the total potential in terms of displacements of the curvatures from their equilibrium values Δ_k, $k=x,y,\varphi$. Retaining the second-order term in the expression of the total energy

$$\phi=(N/2)\sum_{kl} g_{kl}\Delta_k\Delta_l, \tag{8}$$

we obtain the coefficients $g_{\alpha\beta}=S^{22}_{\alpha\beta}$, $g_{\alpha\varphi}=2S^{31}_{\alpha\varphi}$, and $g_{\varphi\varphi}=4S^{22}_{\alpha\varphi}$ where $S^{mn}_{\alpha\beta}=(1/N)\Sigma_{i>j}c(r_{ij})r^m_{ij\alpha}r^n_{ij\beta}$. Calculation of the lattice sum gives the values $g_{xx}=g_{yy}=9/8$, $g_{xy}=3/4$, $g_{\alpha\varphi}=0$, and $g_{\varphi\varphi}=3/2$.

The reduction of the quadratic form of Eq. (8) to a sum of squares gives the solution $\Delta_\alpha(t)$ as a superposition of two normal modes Δ_1 and Δ_2 with the frequencies $\omega_1=\sqrt{3/2}$ and $\omega_2=\sqrt{3/4}$ correspondingly: $\Delta_x=\Delta_1+\Delta_2$; $\Delta_y=\Delta_1-\Delta_2$. The expressions for the amplitudes $\Delta_1=(\Delta_y^0/2)\cos(\omega_1 t)$ and $\Delta_2=(\Delta_y^0/2)\cos(\omega_2 t)$ follow from the initial conditions. Similarly the shear strain is $\Delta_\varphi=\Delta_\varphi^0\cos(\omega_s t)$, where the frequency $\omega_s=\sqrt{3/2}$. The difference between the exact and analytical results (dot curves) in Fig. 1 vanishes when $\Delta\to 0$.

It should be noted that small curvatures are equal to their correspondent components of a plane strain $e_{\alpha\alpha}=\Delta_\alpha$ and $e_{xy}=\Delta_\varphi$ thus producing the conventional linear stress-strain relations in a lattice [12].

In the next example, the atoms were arranged initially in a square structure, whose basis vectors are $\mathbf{a}_1=(1,0)$ and $\mathbf{a}_2=(0,1)$. Being unstable to a small initial shear $\Delta_\varphi^0=0.01$ the lattice undergoes a uniform deformation to a triangular structure while holding the same values of the period $a_i=a$ [see Fig. 2(a)]. Therefore, the instantaneous structure could be monitored by the length of the diagonal $\mathbf{a}_{12}=\mathbf{a}_2-\mathbf{a}_1$. Since $a\approx 1$ the oscillations of a_{12} correlate with those of φ [Fig. 2(b)]. The transition is reversible in spite of strong anharmonic effect caused by a large amplitude.

The initial part of the time evolution is determined by a saddle point configuration. For the perfect square lattice and the next-nearest neighbors taken into account, the coefficients of the expansion of Eq. (9) are $g_{xy}=2e$, $g_{xx}=g_{yy}=b+2e$, $g_{kl}=0, k\neq l$, and $g_{\varphi\varphi}=8e<0$, where $b=c(R_e)R_e^4$ and $e=c(\sqrt{2}R_e)R_e^4$. The equilibrium value of the radius $R_e=0.9831$ follows from relation $\chi(R_e)=-2\chi(\sqrt{2}R_e)$. Therefore, the period of isoshape oscillations due to a misfit between the equilibrium and initial lattice parameter is close $T_V\approx 2\pi/\sqrt{b}=5.34$. Naturally results of all calculations depend

on neither a number of particles nor a shape of the MD cell. Evidently also that the condition of a positive definite quadratic form of Eq. (8) coincides with the Born-Karman condition of the lattice stability [12].

The result of this work is a set of dynamical equations governing the structure of the lattice. Formally, the equations of motion of Eqs. (6) and (7) are similar to the modified version of the PR equations using Cartesian (not scaled) coordinates [11,13]. However, the method outlined above has two principal differences. First, only six dynamical variables describe the cell motion. Basically, these are the three radiuses and the three angles determining the deformation of the torus surface. In fact, the correct number of the cell dynamical variables was suggested earlier by Souza and Martins [10]. The six components of the dot product between the cell vectors were used there instead of their components thus leaving the scaling model unchanged. Therefore this metric-based formulation appears to be the one of the possible improvement of the conventional PR scheme. The second difference is in the form of the cell box. The matrix **B** does not depend on the lattice vectors making the orientation and the shape of the MD cell irrelevant for the structural and thermodynamical description of the system. In particular, the molecular dynamics apart, the new method can be useful to reconsider well-known relations obtained for infinite crystal with the internal stress of the system taken into account.

[1] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).
[2] S. Nosé and M. L. Klein, Mol. Phys. **50**, 1055 (1983).
[3] R. M. Wentzcovitch, Phys. Rev. B **44**, 2358 (1991).
[4] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[5] J. V. Lill and J. Q. Broughton, Phys. Rev. B **49**, 11619 (1994).
[6] V. A. Ryabov, Phys. Lett. A **220**, 258 (1996).
[7] V. A. Ryabov, Phys. Rev. E **64**, 026112 (2001).
[8] D. Gilbert and S. Fon-Kossen, *Visible Geometry* (GIS, Moskow, 1954).
[9] J. R. Ray, J. Chem. Phys. **79**, 5128 (1983).
[10] I. Souza and J. L. Martins, Phys. Rev. B **55**, 8733 (1997).
[11] G. J. Martina, D. J. Tobias, and M. L. Klein, J. Chem. Phys. **101**, 4177 (1994).
[12] M. Born and H. Kun, *Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
[13] G. Ciccotti and J. P. Ryckaert, Comput. Phys. Rep. **4**, 345 (1986).