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Internal stress tensor in constant-pressure molecular dynamics of anisotropic molecular solids

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We introduce a new procedure to obtain the internal stress tensor in constant-pressure molecular dynamics (MD) simulations of molecular solids. We show that the internal stress tensor which governs the dynamics of the MD cell depends not only on the center-of-mass positions and velocities of the molecules, but also explicitly on the molecular orientations and angular velocities. The importance of these rotational contributions in a two-dimensional diatomic molecular monolayer system is discussed.

In recent years, constant-pressure (in general, constant external stress) molecular dynamics has been extremely useful in studying structural phase transitions in solids.[1] Such studies in molecular solids have elucidated the underlying physics of ferroelastic phase transitions which are usually accompanied by an orientational order-disorder transition.[2-5] In constant-pressure simulations,[6-9] the periodically repeating molecular dynamics (MD) cell is assigned a fictitious mass and the volume and the shape of the MD cell are allowed to change, this change being determined by the internally generated stress tensor and the externally applied pressure (stress).

In most of the early works on molecular solids,[7,8] the internal stress tensor is determined by the positions and the velocities of the molecular center of mass. The molecular orientations only appear indirectly in the calculation of the intermolecular forces. In the present work, we argue that there are additional important contributions to the stress tensor $P_{\mu\nu}$ which depend *explicitly* on the molecular *orientations* and *angular* velocities. We will discuss the significance of these new contributions in orientationally ordered molecular systems. Their effects on the ferroelastic phase transition temperature and the coupled translational-rotational dynamics will be discussed in a later publication.

In the isoenthalpic-isobaric molecular dynamics of a monoatomic system,[1,6] the essential idea behind the calculation of the internal stress tensor that determines the dynamics of the MD cell is to start from the Lagrangian $\mathcal{L}_1$ for the system given by

$$\mathcal{L}_1=\frac{1}{2}\sum_{i=1}^{N} m\dot{\mathbf{r}}_i^2-\sum_i\sum_{j(>i)} V(\mathbf{r}_{ij}) , \tag{1}$$

and scale the coordinate of the particles $\mathbf{r}_i$ by the vectors **a** and **b** [in two dimensions (2D), and **a**, **b**, and **c** in 3D] of the parallelogram (parallelepiped) MD cell, i.e.,

$$\mathbf{r}_i=\mathbf{h}\mathbf{s}_i , \tag{2}$$

where **h** is a transformation matrix given by

$$\mathbf{h}=(\mathbf{a},\mathbf{b}) \text{ in 2D } \text{ or } (\mathbf{a},\mathbf{b},\mathbf{c}) \text{ in 3D} . \tag{3}$$

Both the kinetic energy and the potential energy terms in $\mathcal{L}_1$ are now expressed in terms of the scaled coordinates and velocities $\mathbf{s}_i$ and $\dot{\mathbf{s}}_i$, respectively, and one usually neglects a term proportional to $\dot{\mathbf{h}}$ in the kinetic energy part.[6] The dynamics of the variables $\mathbf{s}_i$ and the matrix **h** are determined by the following Parrinello-Rahman Lagrangian:[6]

$$\mathcal{L}=\frac{1}{2}\sum_{i=1}^{N} m\dot{\mathbf{s}}_i\mathbf{G}\dot{\mathbf{s}}_i-\sum_i\sum_{j(>i)} V[\mathbf{h}(\mathbf{s}_i-\mathbf{s}_j)] -p_e\Omega+\frac{1}{2}W\,\mathrm{Tr}\,\dot{\mathbf{h}}^{+}\dot{\mathbf{h}} , \tag{4}$$

where the gauge matrix $\mathbf{G}=\mathbf{h}^{+}\mathbf{h}$ ($\mathbf{h}^{+}$ is transpose of the matrix **h**), $\Omega=\det(\mathbf{h})$ is the area (or volume in 3D) of the MD cell, p_e is the externally applied (constant) pressure, and W is the mass associated with the MD cell. The equations of motion (EOM's) for **h** which determine the dynamics of the MD cell can be obtained from the Lagrangian equation

$$W\ddot{h}_{\mu\nu}=\left[\frac{\partial\mathcal{L}}{\partial h_{\mu\nu}}\right] , \tag{5}$$

which leads to

$$W\ddot{\mathbf{h}}=(\mathbf{P}-p_e\mathcal{I})\Lambda , \tag{6}$$

where $\mathcal{I}$ is the identity matrix and

$$\Lambda=\Omega(\mathbf{h}^{+})^{-1} . \tag{7}$$

In Eq. (6), **P** is the internally generated instantaneous stress tensor. For monoatomic systems, **P** is given by[6]

$$P_{\mu\nu}=\frac{1}{\Omega}\left[\sum_i m\dot{r}_i^{\mu}\dot{r}_i^{\nu}+\sum_i\sum_{j(>i)} F_{ij}^{\mu}(\mathbf{r}_i-\mathbf{r}_j)^{\nu}\right] , \tag{8}$$

where $\mu,\nu=x,y,z$, and $\mathbf{F}_{ij}=-\partial V(\mathbf{r}_{ij})/\partial\mathbf{r}_{ij}$ is the force between atoms i and j.

Now we consider a system of rigid polyatomic molecules described by the Lagrangian

$$\mathcal{L}_2=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{k} m_{ik}\dot{\mathbf{r}}_{ik}^{2}-\sum_{i,k}\sum_{j(>i)}\sum_{l}V(\mathbf{r}_{ik,jl})\ , \tag{9}$$

where i,j are the molecular and k,l are the atomic indices; $\mathbf{r}_{ik,jl}=\mathbf{r}_{jl}-\mathbf{r}_{ik}$. There are two ways of obtaining the internal stress tensor. In the first one, coordinates of each atom can be separated as

$$\mathbf{r}_{ik}=\mathbf{R}_i+\rho_{ik}\ , \tag{10}$$

where $\mathbf{R}_i$ is the center-of-mass coordinate and ρ_{ik} is the relative coordinate. Then conventional procedure[7,8] to handle the MD cell dynamics is to scale only the c.m. coordinates $\mathbf{R}_i$ by $\mathbf{h}$ and treat ρ_{ik} as a constant. In this case the internal stress tensor in Eq. (6) is given by

$$P_{\mu\nu}=\frac{1}{\Omega}\left[\sum_{i} M\dot{R}_i^{\mu}\dot{R}_i^{\nu}+\sum_{i}\sum_{j(>i)}F_{ij}^{\mu}(\mathbf{R}_i-\mathbf{R}_j)^{\nu}\right]\ , \tag{11}$$

where $M=\sum_k m_{ik}$ and

$$\mathbf{F}_{ij}=\sum_{k}\sum_{l}\mathbf{F}_{ik,jl}\ . \tag{12a}$$

Tbe Force between atoms ik and jl is

$$\mathbf{F}_{ik,jl}=-\frac{\partial V(\mathbf{r}_{ik,jl})}{\partial \mathbf{r}_{ik,jl}}\ . \tag{12b}$$

Note that $\mathbf{F}_{ij}$ and hence $P_{\mu\nu}$ do depend *implicitly* on the molecular orientations, although only the center-of-mass (c.m.) coordinates $\mathbf{R}_i$ and their velocities $\dot{\mathbf{R}}_i$ appear in the expression for $P_{\mu\nu}$ explicitly.

A second procedure for calculating the internal stress tensor which we propose here is to scale the position vectors ($\mathbf{r}_{ik}$) of *individual atoms* of the molecules by $\mathbf{h}$ and then use the rigid molecule conditions through the introduction of fictitious time-dependent forces. There will be additional terms in $P_{\mu\nu}$ coming from the kinetic energy term of the Lagrangian and these terms will depend upon the angular velocities (ω_i). The potential energy contribution to $P_{\mu\nu}$ now depends upon the forces acting on the individual atoms of each molecule. In addition to the external forces, one has to take into account the *constraint* forces acting on the atoms. The constraint forces fix the internuclear distance of the molecules. In systems where intra-atomic vibrations are important, one will have to replace the constraint forces by the actual forces acting between the atoms of a given molecule. The constraint force, which in general depends on the angular velocities, can be obtained from the equation of motion of the atomic coordinates. The dynamics of the MD system is described by the Lagrangian

$$\mathcal{L}_M=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{k} m_{ik}\dot{\mathbf{s}}_{ik}\mathbf{G}\dot{\mathbf{s}}_{ik}-\sum_{i,k}\sum_{j(>i)}\sum_{l}V(\mathbf{r}_{ik,jl})$$
$$-p_e\Omega+\tfrac{1}{2}W\,\mathrm{Tr}\dot{\mathbf{h}}^{+}\dot{\mathbf{h}}\ . \tag{13}$$

From Eq. (5) with $\mathcal{L}$ replaced by $\mathcal{L}_M$ and adding the constraint force, we obtain Eq. (6) for the dynamics of the MD cell with the internal stress tensor given by

$$P_{\mu\nu}=\frac{1}{\Omega}\sum_{i,k} m_{ik}(\mathbf{h}\dot{\mathbf{s}}_{ik})^{\mu}(\mathbf{h}\dot{\mathbf{s}}_{ik})^{\nu}$$
$$+\frac{1}{\Omega}\sum_{i,k}\sum_{j(>i)}\sum_{l}F_{ik,jl}^{\mu}r_{ik,jl}^{\nu}+\frac{1}{\Omega}\sum_{i,k}f_{ik}^{\mu}\rho_{ik}^{\nu}\ , \tag{14}$$

where $\mathbf{f}_{ik}$ is the constraint force acting on the atom ik with the condition $\sum_k \mathbf{f}_{ik}=0$. We can write Eq. (14) in a more transparent form as

$$P_{\mu\nu}=P_{\mu\nu}^{\text{c.m.}}+\frac{1}{\Omega}\sum_{i,k} m_{ik}\dot{\rho}_{ik}^{\mu}\dot{\rho}_{ik}^{\nu}+\frac{1}{\Omega}\sum_{i,k}(F_{ik}^{\mu}+f_{ik}^{\mu})\rho_{ik}^{\nu}\ , \tag{15}$$

where $P_{\mu\nu}^{\text{c.m.}}$ is the stress tensor given in Eq. (11); $\mathbf{F}_{ik}=\sum_{j(\neq i)}\sum_l \mathbf{F}_{ik,jl}$ is the force acting on the atom ik. The stress tensor given in (15) has translational and rotational contributions from both the kinetic (kin) and potential (pot) energy parts of $\mathcal{L}_M$. Equation (15) is the central result of this paper. We can formally write

$$\mathbf{P}=\mathbf{P}^{\text{kin}}+\mathbf{P}^{\text{pot}}\ , \tag{16a}$$

with

$$\mathbf{P}^{\text{kin}}=\mathbf{P}^{\text{kin,c.m.}}+\mathbf{P}^{\text{kin,rot}}\ , \tag{16b}$$

$$\mathbf{P}^{\text{pot}}=\mathbf{P}^{\text{pot,c.m.}}+\mathbf{P}^{\text{pot,rot}}\ , \tag{16c}$$

where

$$\mathbf{P}^{\text{kin,c.m.}}+\mathbf{P}^{\text{pot,c.m.}}=\mathbf{P}^{\text{c.m.}}\ . \tag{16d}$$

To illustrate the significance of the above results in MD simulations, we consider a system of homonuclear (rigid) diatomic molecules for simplicity. Assume that the molecules are confined to move in a two-dimensional plane with their rotational motion confined to the same plane (see Fig. 1). The rigid rotor condition yields

$$\dot{\rho}_{ik}=\tfrac{1}{2}d\dot{\theta}_i\hat{\mathbf{n}}_{ik}\ , \tag{17}$$

$$\mathbf{f}_{i1}=-\mathbf{f}_{i2}=-[\tfrac{1}{4}Md\dot{\theta}_i^{2}+\tfrac{1}{2}(\mathbf{F}_{i1}-\mathbf{F}_{i2})\cdot\hat{\mathbf{r}}_{i1}]\hat{\mathbf{r}}_{i1}\ , \tag{18}$$

$$\tfrac{1}{2}Md\ddot{\theta}_i=F_i^{(\theta)}\ , \tag{19}$$

where d is the internuclear separation and

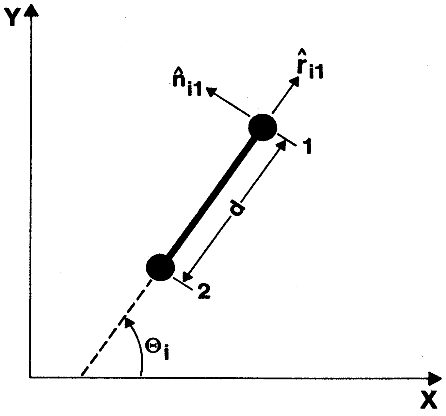

FIG. 1. A diatomic molecule confined to the XY plane.

$F_i^{(\theta)}=(\mathbf{F}_{i1}-\mathbf{F}_{i2})\cdot\hat{\mathbf{n}}_{i1}$ is the total force acting on the molecule i in the direction perpendicular to the internuclear axis. Equation (19) is simply the equation of motion for the orientational variable θ_i. From Eqs. (15), (17), and (18), we then have

$$P_{\mu\nu}=P_{\mu\nu}^{\text{c.m.}}+\frac{1}{\Omega}\sum_i I\dot{\theta}_i^2(\hat{n}_{i1}^{\mu}\hat{n}_{i1}^{\nu}-\hat{r}_{i1}^{\mu}\hat{r}_{i1}^{\nu}) +\frac{1}{\Omega}\sum_i \tfrac{1}{2}dF_i^{(\theta)}\hat{n}_{i1}^{\mu}\hat{r}_{i1}^{\nu}\,, \tag{20}$$

where $I=Md^2/4$ is the moment of inertia of the molecule. We find that the rotational kinetic energy contribution to the stress tensor [the second sum on the right-hand side of Eq. (20)] is

$$\mathbf{P}^{\text{kin,rot}}=\frac{1}{\Omega}\sum_i I\dot{\theta}_i^2\begin{bmatrix}-\cos2\theta_i & -\sin2\theta_i\\ -\sin2\theta_i & \cos2\theta_i\end{bmatrix}, \tag{21}$$

and the rotational potential energy contribution [the third sum on the right-hand side of Eq. (20)] is

$$\mathbf{P}^{\text{pot,rot}}=\frac{1}{\Omega}\sum_i \tfrac{1}{4}dF_i^{(\theta)}\begin{bmatrix}-\sin2\theta_i & \cos2\theta_i-1\\ \cos2\theta_i+1 & \sin2\theta_i\end{bmatrix}. \tag{22}$$

The internal pressure is defined by $p=\text{Tr}\mathbf{P}$. From Eqs. (21) and (22), it is interesting to note that p depends only on $\mathbf{P}^{\text{c.m.}}$, i.e., $p=\text{Tr}\mathbf{P}^{\text{c.m.}}$. However, the antisymmetric component $\mathcal{A}=\frac{1}{2}(P_{xy}-P_{yx})$ has important θ_i-dependent terms, i.e.,

$$\mathcal{A}=\tfrac{1}{2}(P_{xy}^{\text{c.m.}}-P_{yx}^{\text{c.m.}})-\frac{1}{\Omega}\sum_i \tfrac{1}{2}dF_i^{(\theta)}\,. \tag{23}$$

The last term is extremely important in MD simulation as it makes a significant contribution towards keeping the total angular momentum conserved.[9]

Next we consider the strength and the temperature dependence of the rotational contributions to the stress tensor in Eq. (20). To do so, we calculate the *ensemble average* of $\mathbf{P}-\mathbf{P}^{\text{c.m.}}$ and for simplicity we consider the low-temperature ferroelastic phase[3] (see Fig. 2). In this phase, at low temperatures, the rotational motion is dominated by the libron spectrum.[10] Let the rotational Hamiltonian be $H_{\text{rot}}=\frac{1}{2}\sum_i I\dot{\theta}_i^2+\frac{1}{2}\sum_{i,j}D(\mathbf{R}_i-\mathbf{R}_j)\tilde{\theta}_i\tilde{\theta}_j$ with $\tilde{\theta}_i=\theta_i-90°$. Defining $D(\mathbf{q})=\sum_{\mathbf{R}}e^{i\mathbf{q}\cdot\mathbf{R}}D(\mathbf{R})$, we obtain the thermal-averaged values of $\mathbf{P}^{\text{kin,rot}}$ and $\mathbf{P}^{\text{pot,rot}}$ as

$$\langle\mathbf{P}^{\text{kin,rot}}\rangle\approx\langle n\rangle k_BT[1-2g_1k_BT +2(g_2+g_1^2)(k_BT)^2+\cdots]\Sigma_z\,, \tag{24a}$$

$$\langle\mathbf{P}^{\text{pot,rot}}\rangle\approx\langle n\rangle k_BT[-1+4g_1k_BT+\cdots]\Sigma_z\,, \tag{24b}$$

with

$$\Sigma_z=\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}, \tag{24c}$$

where $\langle n\rangle$ is the average molecular surface density and $g_n=1/(2\pi)^2\int d\mathbf{q}[D(\mathbf{q})]^{-n}$ $(n=1,2,3,\ldots)$, the integral being over the first Brillioun zone. As can be seen from Eqs. (24), the off-diagonal contributions to the stress tensor coming from the rotational part vanish in the harmonic theory. This is also true if one includes the effects of linear rotation-translation coupling on the libron dynamics. However, near the ferroelastic structural phase transition where the harmonic theory breaks down, these off-diagonal terms were found to be significant in our molecular dynamics simulations.[3,5]

Coming back to the diagonal terms, we give in Fig. 3 the temperature dependence of the xx components of the internal stress tensor. It is interesting to note that the linear term in T of $\langle P_{xx}-P_{xx}^{\text{c.m.}}\rangle$ is identically zero due to a cancellation between the kinetic and potential contributions and the net result is a quadratic (T^2) increase. The increase in P_{xx}^{rot} and the corresponding decrease in P_{yy}^{rot} with increasing T make physical sense since in the ordered state the molecules are orientated along the y direc-

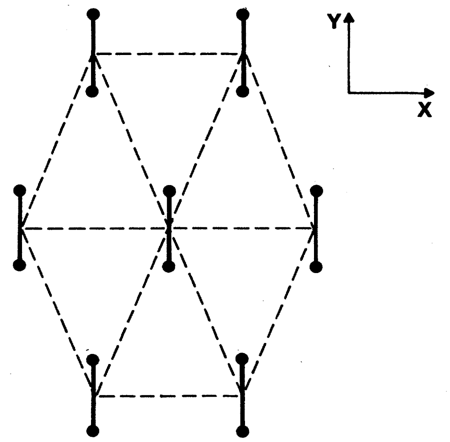

FIG. 2. Ferroelastic phase of a two-dimensional diatomic molecular solid with a centered rectangular lattice structure.

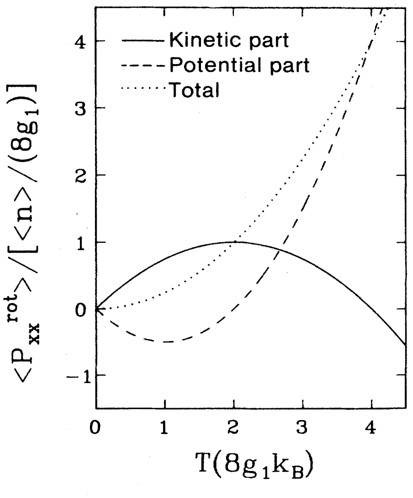

FIG. 3. Temperature (T) dependence of the thermal-averaged rotational contributions to the internal stress tensor P_{xx}^{rot} in the ferroelastic phase. T is measured in units of $8g_1k_B$, where g_1 has the dimension of inverse energy.

tion at $T=0$.

In summary, we have proposed that both the center-of-mass and the rotational contributions to the stress tensor should be considered in a proper treatment in the molecular dynamics simulations of a molecular system. In particular, the latter can be quite important near a structural phase transition involving orientational degrees of freedom.

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