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Submitted To:
Renata Wentzcovitch
Professor
APAM Department

Submitted By :
Qi Zhang
qz2280
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1 Some alogrithm for molecular dynamics

1.1 Closed methods

1.1.1 Euler's method

1.1.2 Modified Euler's method

1.1.3 Gear algorithm

1.2 Open methods

1.2.1 Verlet algorithm

1.2.2 Leap-frog algorithm

1.2.3 Beeman algorithm

2 Invariant molecular dynamics with variable cell shape

2.1 Andersen's approach

It was Anderson who first extends the molecular dynamics field to ensembles other than micro-canonical ensemble.[1] In his ground-breaking paper, he proposed ways to calculate properties average over isoenthalpic-isobaric (NPH) ensemble. In the article, he introduced a Lagrangian

$$\mathcal{L}(\boldsymbol{\rho}, \dot{\boldsymbol{\rho}}, Q, \dot{Q}) = \frac{1}{2} m Q^{\frac{2}{3}} \sum_{i=1}^{N} \dot{\boldsymbol{\rho}}_i \cdot \dot{\boldsymbol{\rho}}_i - \sum_{i<j=1}^{N} u\left(Q^{\frac{1}{3}} \rho_{ij}\right) + \frac{1}{2} M \dot{Q}^2 - \alpha Q, \tag{1}$$

where $\boldsymbol{\rho}_i = \boldsymbol{r}_i / V^{\frac{1}{3}}$, $i = 1, 2, \ldots, N$, is called scaled coordinates. Here α and M are constants, $\frac{1}{2} M \dot{Q}$ now is regarded as a kinetic energy with fictitious mass M, and αQ is regarded as a potential energy for the motion of Q. The generalized momentum conjugate to $\boldsymbol{\rho}$ is

$$\boldsymbol{\pi}_i = \frac{\partial \mathcal{L}_2}{\partial \dot{\boldsymbol{\rho}}_i} = m Q^{\frac{2}{3}} \boldsymbol{\rho}_i, \tag{2}$$

and which for Q is

$$\Pi = \frac{\partial \mathcal{L}_2}{\partial \dot{Q}} = M \dot{Q}. \tag{3}$$

The Hamiltonian is thus

$$\begin{aligned} \mathcal{H}(\boldsymbol{\rho}, \boldsymbol{\pi}, Q, \Pi) &= \sum_{i=1}^{N} \boldsymbol{\pi}_i \cdot \dot{\boldsymbol{\rho}}_i + \Pi \dot{Q} - \mathcal{L}_2(\boldsymbol{\rho}, \dot{\boldsymbol{\rho}}, Q, \dot{Q}) \\ &= \frac{1}{2 m Q^{\frac{2}{3}}} \sum_{i=1}^{N} \boldsymbol{\pi}_i \cdot \boldsymbol{\pi}_i + \sum_{i<j=1}^{N} u\left(Q^{\frac{1}{3}} \rho_{ij}\right) + \frac{1}{2M} \Pi^2 + \alpha Q. \end{aligned} \tag{4}$$

So the equations of motions are

$$\dot{\boldsymbol{\rho}}_i = \frac{\partial \mathcal{H}}{\partial \boldsymbol{\pi}_i} = \frac{\boldsymbol{\pi}_i}{m Q^{\frac{2}{3}}} \tag{5}$$

$$\dot{\boldsymbol{\pi}}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{\rho}_i} = -Q^{\frac{1}{3}} \sum_{\substack{j=1 \\ j \neq i}} \frac{u' \boldsymbol{\rho}_{ij}}{|\boldsymbol{\rho}_{ij}|} \tag{6}$$

$$\dot{Q} = \frac{\partial \mathcal{H}}{\partial \Pi} = \frac{\Pi}{M} \tag{7}$$

$$\dot{\Pi} = -\frac{\partial \mathcal{H}}{\partial Q} = -\frac{1}{3Q}\left(- \frac{1}{m Q^{\frac{2}{3}}} \sum_{i=1}^{N} \boldsymbol{\pi}_i \cdot \boldsymbol{\pi}_i + Q^{\frac{1}{3}} \sum_{i<j} \rho_{ij} u'\left(Q^{\frac{1}{3}} \rho_{ij}\right) + 3\alpha Q \right) \tag{8}$$

With these equations, the trajectory of the scaled system are given by $\boldsymbol{\rho}(t)$, $\boldsymbol{\pi}(t)$, $Q(t)$, and $\Pi(t)$.

Use this trajectory, any function's time average are given by

$$\overline{G} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt G(\boldsymbol{\rho}(t), \boldsymbol{\pi}(t), Q(t), \Pi(t)), \tag{9}$$

and this can be given by the average of an NE ensemble. That is,

$$G_{NE}(N,E) = \frac{1}{N!\Omega(N,E)} \int d\boldsymbol{\rho} \int d\boldsymbol{\pi} \int dQ \int d\Pi \\ \delta\big(\mathcal{H}(\boldsymbol{\rho},\boldsymbol{\pi},Q,\Pi) - E\big) G(\boldsymbol{\rho}(t), \boldsymbol{\pi}(t), Q(t), \Pi(t)), \tag{10}$$

where

$$\Omega(N,E) = \frac{1}{N!} \int d\boldsymbol{\rho} \int d\boldsymbol{\pi} \int dQ \int d\Pi\, \delta\big(\mathcal{H}(\boldsymbol{\rho},\boldsymbol{\pi},Q,\Pi) - E\big). \tag{11}$$

The scaled system has a correspondence

$$V = Q, \tag{12}$$

$$\boldsymbol{r}_i = Q^{\frac{1}{3}} \boldsymbol{\rho}_i, \tag{13}$$

$$\boldsymbol{p}_i = \boldsymbol{\pi}_i / Q^{\frac{1}{3}} \tag{14}$$

to the phase space of a system spanned by $\boldsymbol{r}_i, i = 1, \ldots, N$ and $\boldsymbol{p}_i, i = 1, \ldots, N$, where $\boldsymbol{r}_i$ is the particle coordinate, $\boldsymbol{p}_i$ is its momentum. Thus the trajectory $\boldsymbol{\rho}(t)$, $\boldsymbol{\pi}(t)$, $Q(t)$, and $\Pi(t)$ have its correspondence $V(t)$, $\boldsymbol{r}_i(t)$ and $\boldsymbol{p}_i(t)$ by (12). Since the time average $\overline{F}$ of any function F derived by this trajectory is the same as an isoentahlpic-isobaric ensemble average of F_{NPH}, and $\overline{G} = \overline{F}$, thus we get the NPH ensemble average. The ensemble pressure P is α in (1) indeed.

2.2 Rahman and Parrinello's approach

Rahman and Parrinello then proposed a method to perform MD simulations which allows volume and shape of the MD cell to change with time.[2] If the MD cell edges are $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$, which are time dependent. Stack them to form a matrix $h = \{\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}\}$, and the volume of a cell is then $\Omega = \boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}$, the metric tensor is $g = h^{\mathsf{T}} h$. Let $\boldsymbol{r}_i = \xi_i \boldsymbol{a} + \eta_i \boldsymbol{b} + \zeta_i \boldsymbol{c} = h \boldsymbol{s}_i$, where $\boldsymbol{s}_i$ store its coordinates ξ_i, η_i, and ζ_i, each from 0 to 1. Then they introduced a Lagrangian

$$\mathcal{L} = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{\boldsymbol{s}}_i^{\mathsf{T}} g \dot{\boldsymbol{s}}_i - \sum_{i=1}^{N} \sum_{i<j} \phi(r_{ij}) + \frac{1}{2} W \operatorname{Tr}(\dot{h}^{\mathsf{T}} \dot{h}) - P\Omega, \tag{15}$$

where $r_{ij}^2 = (\boldsymbol{s}_i - \boldsymbol{s}_j)^{\mathsf{T}} g (\boldsymbol{s}_i - \boldsymbol{s}_j)$, P is the external hydrostatic pressure, $\phi(r_{ij})$ is the pair potential, W is the fictitious mass.

Then the equations of motion are

$$\ddot{s}_i = \frac{1}{m_i} \sum_{j\neq i} \frac{\phi'(r_{ij})}{r_{ij}} (\boldsymbol{s}_i - \boldsymbol{s}_j) - g^{-1} \dot{g} \dot{\boldsymbol{s}}_i, \quad i, j = 1, 2, \ldots, N, \tag{16}$$

$$\ddot{h} = \frac{1}{W} (\Pi - P)\sigma, \tag{17}$$

where $\sigma = \{\boldsymbol{b}\times\boldsymbol{c}, \boldsymbol{c}\times\boldsymbol{a}, \boldsymbol{a}\times\boldsymbol{b}\}$, matrix Π is given by

$$\Omega\Pi = \sum_{i=1}^{N} m_i \boldsymbol{v}_i \otimes \boldsymbol{v}_i + \sum_{i=1}^{N}\sum_{i<j} \frac{\phi'(r_{ij})}{r_{ij}}(\boldsymbol{r}_i - \boldsymbol{r}_j)\otimes(\boldsymbol{r}_i - \boldsymbol{r}_j), \tag{18}$$

with $\boldsymbol{v}_i = h\boldsymbol{s}_i$. Then Andersen's case is a special one of (16), where $h = \mathrm{diag}(\Omega^{\frac{1}{3}}, \ldots, \Omega^{\frac{1}{3}})$ and $g^{-1}\dot{g} = \frac{2\dot{\Omega}}{3\Omega}$. Though his equation for $\ddot{V}$ cannot be obtained from (17). But this Lagrangian also results in a isoenthalpic, isobaric ensemble, though with a small correction from the third term.

2.3 Wentzcovitch's approach

Wentzcovitch stated that R and P's method is dependent on the choice of cell edges.[3] For different $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, the fictitious kinetic energy K_L term could be different. For MD simulation of $\sim 10^2$ particles the problem may not be too serious. But if the cell experience a modular transformation, the nominal value of K_L, and the resulted forces and trajectories will be dependent on the choice of h. Then she proposed a new Lagrangian

$$\mathcal{L} = \sum_{i=1}^{N} \dot{\boldsymbol{q}}_i^{\mathsf{T}} d\, \dot{\boldsymbol{q}}_i - \sum_{i=1}^{N}\sum_{i<j}\phi(r_{ij}) + \frac{W}{2}\,\mathrm{Tr}\left(\dot{\epsilon}\dot{\epsilon}^{\mathsf{T}}\right) - P\Omega, \tag{19}$$

where ϵ is the strain, $\boldsymbol{q}_i$ is the defined as $\boldsymbol{r}_i = (1+\epsilon)\boldsymbol{q}_i$, thus $d = (1+\epsilon)^{\mathsf{T}}(1+\epsilon)$. The equations of motion are

$$\ddot{\epsilon} = \frac{\Omega}{W}(\Pi - P)\left((1+\epsilon)^{\mathsf{T}}\right)^{-1}, \tag{20}$$

$$\ddot{q}_i = -\frac{1}{m_i}\sum_{\substack{i,j=1\\ j\neq i}}^{N} \frac{\phi'(r_{ij})}{r_{ij}}(\boldsymbol{q}_i - \boldsymbol{q}_j) - d^{-1}\dot{d}\,\dot{\boldsymbol{q}}_i. \tag{21}$$

An equivalent form of (19) is

$$\mathcal{L} = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\boldsymbol{s}}_i^{\mathsf{T}} g\, \dot{\boldsymbol{s}}_i - \sum_{i=1}^{N}\sum_{i<j}\phi(r_{ij}) + \frac{1}{2}W\,\mathrm{Tr}(\dot{h} f_0 \dot{h}^{\mathsf{T}}) - P\Omega, \tag{22}$$

with $f_0 = \sigma_0^{\mathsf{T}}\sigma_0$, where $\sigma_0 = \{\boldsymbol{a}_0\times\boldsymbol{b}_0, \boldsymbol{b}_0\times\boldsymbol{c}_0, \boldsymbol{c}_0\times\boldsymbol{a}_0\}$.

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