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Molecular

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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

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

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 $\{\boldsymbol{r}_i\}$ and $\{\boldsymbol{p}_i\}$. 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.

References

[1] H C Andersen. Molecular dynamics simulations at constant pressure and/or temperature. *The Journal of chemical physics*, 1980.

[2] JW Dufty, JJ Brey, A Santos, G Ciccotti, and WG Hoover. Molecular dynamics simulation of statistical mechanical systems. In *Proc. Int. School of Physics Enrico Fermi, North-Holland, Amsterdam*, 1986.