Introduction to Molecular Dynamics IV

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A one-dimensional example

Full problem,

$$m\ddot{u}_j = \phi'(u_{j+1} - u_j) - \phi'(u_j - u_{j-1}).$$

Linearized model

$$\begin{aligned} m\ddot{u}_j &= K(u_{j+1} - 2u_j + u_{j-1}), j \leq 0. \\ m\ddot{u}_1 &= \phi'(u_2 - u_1) - K(u_1 - u_0) \\ m\ddot{u}_j &= \phi'(u_{j+1} - u_j) - \phi'(u_j - u_{j-1}), j > 1. \end{aligned}$$

Assume that,

$$u_j(0) = \dot{u}_j(0) = 0.$$

Exact boundary condition.

Laplace transform,

$$KU_{j+1} - (s^2 + 2K)U_j + U_{j-1} = 0, U_1 \text{given}.$$

Solution of U_0,

$$U_0 = \alpha(s)U_1.$$

Inverse Laplace transform,

$$u_0(t) = \int_0^t \alpha(s)u_1(t-s)ds, \alpha(t) = \frac{J_2(2\omega t)}{\omega t}, \omega = \sqrt{K/m}.$$

Define,

$$\theta(t) = \int_t^{+\infty} \alpha(s)ds.$$

Then,

$$m\ddot{u}_1 = -\int_0^t \theta(s)\dot{u}_1(t-s)ds + \phi'(u_2 - u_1).$$

Analysis of the boundary condition

Most existing boundary conditions can be written as (Li 2008),

$$u_0(t) = \sum_{j\geq 1} \int_0^{t_0} \alpha_j(s) u_j(t-s) ds.$$

Dispersion relation,

$$\omega^2 = \frac{K}{m}\big(2 - 2\cos(k)\big), \quad k \in (-\pi, \pi).$$

Incidence wave and reflection,

$$u_j = e^{i(jk-\omega t)} + Re^{i(-jk-\omega t)},\ k \in (\pi, 0).$$

Reflection coefficients

$$R(k) = \frac{1 - \sum_j e^{ijk} \int_0^{t_0} a_j(\tau) e^{i\omega\tau} d\tau}{1 - \sum_j e^{-ijk} \int_0^{t_0} a_j(\tau) e^{i\omega\tau} d\tau}.$$

A model for the heat bath

A toy model

$$\begin{cases} \dot{x} &= v, \\ \dot{v} &= -U'(x) + q - x, \\ \dot{q} &= p, \\ \dot{p} &= x - q. \end{cases}$$

- (q, p): heat bath variables,
- (x, v): retained variables.
- initial distribution,

$$(q(0), p(0)) \sim \frac{1}{Z} e^{-\beta(\frac{1}{2}p^2 + \frac{1}{2}(q-x)^2)}.$$

Modeling the heat bath

The solution of the heat bath variables,

$$q(t) - x(t) = (q(0) - x(0)) \cos t + p(0) \sin t - \int_0^t \cos(t-s) v(s) ds.$$

The equation for the retained variables,

$$\ddot{x} = -U'(x) - \int_0^t \cos(t-s) v(s) ds + F(t).$$

The random noise,

$$F(t) = (q(0) - x(0)) \cos t + p(0) \sin t.$$

The time correlation,

$$\langle F(t_1) F(t_2) \rangle = k_B T \cos(t_1 - t_2).$$

Equilibrium distribution

The generalized Langevin equation

$$\ddot{x} = -U'(x) - \int_0^t \cos(t-s)v(s)ds + F(t).$$

We expect that,

$$\rho \sim \frac{1}{Z} e^{-\beta(U+\frac{1}{2}v^2)}.$$

In addition, we assume that, $\langle F(t)v(0)\rangle = 0$.

Define the correlation functions,

- $\phi(t) = \langle v(t)v(0)\rangle$
- $a(t) = \langle U'(x(t))x(0)\rangle$
- $b(t) = \langle x(t)U'(x(0))\rangle = a(-t)$
- $c(t) = \langle V(x(t)), V(x(0))\rangle$.

The fluctuation-dissipation theorem

Multiply the equation by $v(0)$, $V(x(0))$ and $F(0)$, and compute the correlation functions.

Two useful formulae,

$$\frac{d}{dt}\langle x(t)y(0)\rangle = \langle \dot{x}(t)y(0)\rangle = -\langle x(t)\dot{y}(0)\rangle.$$

Correlation of the noise,

$$\langle F(t)F(0)\rangle = \phi(0)\theta(t).$$

At equilibrium, $\phi(0) = k_B T$.

More general derivation

Applying a projection operator,

$$\frac{d}{dt}\varphi(t) = e^{t\mathcal{L}}\mathcal{L}\varphi(0) = e^{t\mathcal{L}}\mathcal{P}\mathcal{L}\varphi(0) + e^{t\mathcal{L}}\mathcal{Q}\mathcal{L}\varphi(0).$$

Dyson's formula,

$$e^{t\mathcal{L}} = e^{t\mathcal{Q}\mathcal{L}} + \int_0^t e^{(t-s)\mathcal{L}}\mathcal{P}\mathcal{L}e^{s\mathcal{Q}\mathcal{L}}ds.$$

The generalized Langevin equation

$$\begin{aligned} \tfrac{d}{dt}\varphi(t) &= e^{t\mathcal{L}}\mathcal{P}\mathcal{L}\varphi(0) + \int_0^t e^{(t-s)\mathcal{L}}K(s)ds + F(t). \\ F(t) &= e^{t\mathcal{Q}\mathcal{L}}\mathcal{Q}\mathcal{L}\varphi(0), \quad K(t) = \mathcal{P}\mathcal{L}F(t). \end{aligned}$$

Projection operator

Mori's projection operator,

$$\mathcal{P}f = \frac{\langle f \cdot \phi(0) \rangle}{\langle \phi(0) \cdot \phi(0) \rangle} \phi(0).$$

Conditional average

$$\mathcal{P}f = \frac{\displaystyle\int f(x,v,q,p) e^{-\beta(\frac{1}{2}p^2 + \frac{1}{2}(q-x)^2)} dqdp}{\displaystyle\int e^{-\beta(\frac{1}{2}p^2 + \frac{1}{2}(q-x)^2)} dqdp}$$

Dynamical variables $\phi = (x, v)$. $Lx = v, Lv = -U'(x) + q - x$.

The first term: $e^{t\mathcal{L}} \mathcal{P} \mathcal{L} v(0) = -U'(x(t))$.

Random noise and memory term

The random noise $F(t) = e^{t\mathcal{QL}}\mathcal{QL}v(0)$.

Assume that, $F(t) = c(t)(x(0) - q(0)) + s(t)p(0)$.

The memory term $K(t) = -c(t)v(0)$.

Therefore:

$$\int_0^t e^{(t-s)\mathcal{L}} K(s)ds = -\int_0^t c(s)v(t-s)ds.$$

Application to the one-dimensional chain model

The generalized Langevin equation

$$\begin{aligned} m\ddot{u}_1 &= -\int_0^t \theta(s)\dot{u}_1(t-s)ds + \phi'(u_2 - u_1) + F(t) \\ m\ddot{u}_j &= \phi'(u_{j+1} - u_j) - \phi'(u_j - u_{j-1}), j > 1. \end{aligned}$$

The time correlation,

$$\langle F(t)F(0)\rangle = k_B T\theta(t).$$