Langevin Dynamics from Microscopic Model [nln74]

Brownian particle harmonically coupled to N otherwise free particles that serve as a primitive form of heat bath. [Wilde and Singh 1998]

Classical Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2m} + \sum_{i=1}^{N} \left(\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \bar{x}_i^2 \right), \quad \bar{x}_i \doteq x_i - \frac{c_i x}{m_i \omega_i^2}, \tag{1}$$

where $m_i \omega_i^2$ is the stiffness of the harmonic coupling between the Brownian particle and one of the heat-bath particles. The c_i are conveniently scaled coupling constants.

Canonical equations:

$$\frac{dx}{dt} = \frac{\partial \mathcal{H}}{\partial p} = \frac{p}{m}, \quad \frac{dp}{dt} = -\frac{\partial \mathcal{H}}{\partial x} = \sum_{i=1}^{N} c_i \bar{x}_i, \tag{2a}$$

$$\frac{dx_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i} = \frac{p_i}{m_i}, \quad \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial x_i} = -m_i \omega_i^2 \bar{x}_i; \quad i = 1, \ldots, N. \tag{2b}$$

Elimination of momenta yields 2nd-order ODEs:

$$m \frac{d^2 x}{dt^2} = m \frac{d\dot{x}}{dt} = F(t), \quad F(t) \doteq \sum_{i=1}^{N} c_i \bar{x}_i, \tag{3a}$$

$$m_i \frac{d^2 x_i}{dt^2} = -m_i \omega_i^2 x_i + c_i x, \quad i = 1, \ldots, N. \tag{3b}$$

Formal solution of (3b):

$$x_i(t) = x_i(0) \cos(\omega_i t) + \frac{\dot{x}_i(0)}{\omega_i} \sin(\omega_i t) + \frac{c_i}{m_i \omega_i} \underbrace{\int_0^t dt' x(t') \sin\big(\omega_i (t - t')\big)}_{A(t)}. \tag{4}$$

Integrate by parts:

$$A(t) = \frac{1}{\omega_i} \left[x(t) - x(0) \cos(\omega_i t) - \int_0^t dt' \dot{x}(t') \cos\big(\omega_i (t - t')\big) \right]. \tag{5}$$

Assemble parts, then use (1) and (3a):

$$x_i(t) = \left(x_i(0) - \frac{c_i}{m_i \omega_i^2} x(0) \right) \cos(\omega_i t) + \frac{\dot{x}_i(0)}{\omega_i} \sin(\omega_i t) + \frac{c_i}{m_i \omega_i^2} \left[x(t) - \int_0^t dt' \dot{x}(t') \cos\big(\omega_i (t - t')\big) \right], \tag{6}$$

$$\bar{x}_i(t) = \bar{x}_i(0)\cos(\omega_i t) + \frac{\dot{x}_i(0)}{\omega_i}\sin(\omega_i t) - \frac{c_i}{m_i\omega_i^2}\int_0^t dt' \dot{x}(t')\cos\big(\omega_i(t-t')\big),$$

$$F(t) = \sum_{i=1}^N \Bigg[c_i\bar{x}_i(0)\cos(\omega_i t) + \frac{c_i}{\omega_i}\dot{x}_i(0)\sin(\omega_i t) - \frac{c_i^2}{m_i\omega_i^2}\int_0^t dt' \dot{x}(t')\cos\big(\omega_i(t-t')\big)\Bigg]. \tag{7}$$

Expectation values at thermal equilibrium:

$$\langle \bar{x}_i(0)\rangle = 0, \quad \langle \dot{x}_i(0)\rangle = 0, \quad \omega_i^2\langle \bar{x}_i(0)\bar{x}_j(0)\rangle = \langle \dot{x}_i(0)\dot{x}_j(0)\rangle = \frac{k_B T}{m_i}\delta_{ij}.$$

$$\langle F(t)\rangle = -\int_0^t dt' \dot{x}(t')\alpha_{\rm s}(t-t'), \quad \alpha_{\rm s}(t-t') = \underbrace{\sum_{i=1}^N \frac{c_i^2}{m_i\omega_i^2}\cos\big(\omega_i(t-t')\big)}_{\text{attenuation function}}.$$

Random force:

$$f(t) \doteq F(t) - \langle F(t)\rangle = \sum_{i=1}^N \left[c_i\bar{x}_i(0)\cos(\omega_i t) + \frac{c_i}{\omega_i}\dot{x}_i(0)\sin(\omega_i t)\right]. \tag{8}$$

Generalized Langevin equation:

$$m\frac{d\dot{x}}{dt} = -\int_0^t dt' \dot{x}(t')\alpha_{\rm s}(t-t') + f(t). \tag{9}$$

Fluctuation-dissipation relation:

$$\begin{aligned}\langle f(t)f(t')\rangle &= \sum_{i=1}^N \Bigg[c_i^2\cos(\omega_i t)\cos(\omega_i t')\underbrace{\langle \bar{x}_i(0)\bar{x}_i(0)\rangle}_{k_BT/m_i\omega_i^2} + \frac{c_i^2}{\omega_i^2}\sin(\omega_i t)\sin(\omega_i t')\underbrace{\langle \dot{x}_i(0)\dot{x}_i(0)\rangle}_{k_BT/m_i}\Bigg] \\ &= k_BT\sum_{i=1}^N \frac{c_i^2}{m_i\omega_i^2}\cos\big(\omega_i(t-t')\big) = k_BT\alpha_{\rm s}(t-t'). \end{aligned}\tag{10}$$