Research Notes
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Absorption Spectra from Langevinic Analysis of RPMD

In generalized Langevin equation description of the RPMD system, the equation of motion of the centroid can be written as described in previous research notes

$$m\ddot{u}(t) = \bar{F}(t) + R(t) - \beta_P \int_0^t dt' C_F(t-t')\dot{u}(t) \tag{1}$$

where $\beta_P = \frac{\beta}{P}$, $\bar{F}$ is the PMF of the centroid, R is the random force on the centroid, and C_F is the force autocorrelation function.

Then, using harmonic approximation for the centroid potential such that

$$V(u) = \frac{m{\omega_0}^2}{2}u^2 \tag{2}$$

the PMF for the centroid can be written as

$$\bar{F}(t) = -\left(m{\omega_0}^2 - \beta_P C_F(0)\right)u(t). \tag{3}$$

Using the PMF from equation 3, multiply equation 1 on the left by $u(0)$ and take the ensemble average with respect to the total Hamiltonian to have

$$\frac{d^2}{dt^2}C(t) = -\bar{\omega}^2 C(t) - \int_0^t dt' B(t-t')\frac{d}{dt'}C(t') \tag{4}$$

where

$$\langle u(0)u(t)\rangle = C(t)$$

$$B(t) = \frac{\beta_P}{m}C_F(t)$$

$$\bar{\omega}^2 = {\omega_0}^2 - B(0). \tag{5}$$

Take Laplace transform of both sides of equation 4 and express the Laplace transform of the position correlation function to have

$$\tilde{C}(s) = \frac{sC(0) + \dot{C}(0) + \tilde{B}(s)C(0)}{s^2 + \bar{\omega}^2 + s\tilde{B}(s)} \tag{6}$$

where

$$\mathcal{L}[C(t)] = \tilde{C}(s)$$

$$\mathcal{L}[B(t)] = \tilde{B}(s).$$

Equation 6 can be simplified further since

$$\dot{C}(0) = 0$$

because position and velocity of centroid at zero time is uncorrelated.

Then, we write

$$\tilde{C}(s) = C(0)\frac{s + \tilde{B}(s)}{s^2 + \varpi^2 + s\tilde{B}(s)}. \tag{7}$$

The absorption spectra is related to the position correlation function by relation

$$Abs(\omega) \propto \omega^2 Re\left[\tilde{C}(i\omega)\right]. \tag{8}$$

Then, we calculate the real part of the Fourier transform of the position correlation function. First, let

$$\tilde{B}(i\omega) = \gamma'(\omega) + i\gamma''(\omega) \tag{9}$$

to write

$$\tilde{C}(i\omega) = C(0)\frac{i\omega + \gamma' + i\gamma''}{\Delta + i\omega(\gamma' + i\gamma'')} = C(0)\frac{\gamma' + i(\omega + \gamma'')}{(\Delta - \omega\gamma'') + i(\omega\gamma')}$$
$$= C(0)\frac{\big(\gamma' + i(\omega + \gamma'')\big)\big((\Delta - \omega\gamma'') - (\omega\gamma')\big)}{(\Delta - \omega\gamma'')^2 + (\omega\gamma')^2} \tag{10}$$

where

$$\Delta = \varpi^2 - \omega^2.$$

Then, we have

$$Re\left[\tilde{C}(i\omega)\right] = C(0)\frac{\gamma'(\Delta - \omega\gamma'') + (\omega + \gamma'')(\omega\gamma')}{(\Delta - \omega\gamma'')^2 + (\omega\gamma')^2}$$

$$= C(0)\frac{\overline{\omega}^2\gamma'}{(\overline{\omega}^2 - \omega^2 - \omega\gamma'')^2 + (\omega\gamma')^2}. \tag{11}$$

Using the force ACF from different potentials, one can then calculate the absorption spectrum of the centroid with equation

$$Abs(\omega) \propto \frac{\overline{\omega}^2\omega^2\gamma'}{(\overline{\omega}^2 - \omega^2 - \omega\gamma'')^2 + (\omega\gamma')^2}. \tag{12}$$