1.1.08 / 5.03.08

Exclusion of the outer region for arbitrary inner region

1. We do <u>not</u> assume here that the inner region is harmonic:

$$\mathcal{H} = \overbrace{\widetilde{\mathcal{H}}_1}^{T_1+V_1} + \sum_{j\in 2} h_j u_j + \frac{1}{2}\sum_{jj'\in 2} \Phi_{jj'} u_j u_{j'} + T_2$$

h_j – may depend on $\vec{r}_1$ in arbitrary way.

Eqs. of motion:

$$\begin{cases} M_i \ddot{r}_i = -\sum_{j\in 2} \frac{\partial h_j}{\partial r_i} u_j - \frac{\partial V_1}{\partial r_i} & \text{for any } i \in 1 \\ M_j \ddot{u}_j = -\underbrace{h_j}_{\substack{\text{depends on} \\ \{\vec{r}_i\}_{i\in 1} \equiv r_1}} - \sum_{j'\in 2} \Phi_{jj'} u_{j'} & , j \in 2 \end{cases}$$

Solution for the outer region: $\boxed{X_2 = M_2^{1/2} u_2}$

~~$X_2(t) = \dot{\Omega}_{22}(t) X_2(0) + \Omega_{22}(t)\dot{X}_2(0) + \int_0^t \Omega_{22}(t-\tau) D_2$~~

$\hookrightarrow$ $M_2 \ddot{u}_2 = -h_2 - \Phi_{22} u_2$

$M_2^{1/2} \ddot{X}_2 = -h_2 - \Phi_{22} M_2^{-1/2} X_2$

$\ddot{X}_2 = -M_2^{-1/2} h_2 - (M_2^{-1/2} \Phi_{22} M_2^{-1/2}) X_2$

$$\boxed{\ddot{X}_2 = -V_2 - D_{22} X_2} \qquad \boxed{V_2 = M_2^{-1/2} h_2}$$

depends on time t via $r_1(t)$

Solution:

$$\boxed{X_2(t) = \dot{\Omega}_{22}(t) X_2(0) + \Omega_{22}(t)\dot{X}_2(0) - \int_0^t \Omega_{22}(t-\tau) V_2(\tau)\, d\tau} \quad \oplus$$

Correct sign here!

Substitute into eq. for region 1:

$$M_i \ddot{r}_i = -\frac{\partial V_1}{\partial r_i} - \sum_{j\in 2} \frac{\partial h_j}{\partial r_i} M_j^{-1/2} X_j(t)$$

$$= -\frac{\partial V_1}{\partial r_i} - \sum_{j\in 2} \frac{\partial V_j(t)}{\partial r_i} X_j(t) \quad , \quad V_j(t) = M_j^{-1/2} h_j(t).$$

$$= -\frac{\partial V_1}{\partial r_i}$$

$$- \sum_{jj'\in 2} \frac{\partial V_j}{\partial r_i}\left[\dot{\Omega}_{jj'}(t) X_{j'}(0) + \Omega_{jj'}(t) \dot{X}_{j'}(0) \right]$$

$$+ \sum_{jj'\in 2} \int_0^t \frac{\partial V_j(t)}{\partial r_i} \Omega_{jj'}(t-\tau) \cdot V_{j'}(\tau)\, d\tau$$

so that:

$$\boxed{M_i \ddot{r}_i = \overset{-\partial V_1/\partial r_i}{f_i} + R_i(t) + \sum_{jj'\in 2} \frac{\partial V_j(t)}{\partial r_i} \int_0^t \Omega_{jj'}(t-\tau) V_{j'}(\tau)\, d\tau}$$

with the random force

$$\boxed{R_i(t) = -\sum_{jj'\in 2} \frac{\partial V_j}{\partial r_i}\left[\dot{\Omega}_{jj'}(t) X_{j'}(0) + \Omega_{jj'}(t) \dot{X}_{j'}(0) \right]}$$

2. Statistical averaging is performed only wrt region 2, i.e. for the current positions r_1 of atoms in region 1. This corresponds to the partial averaging. Averaging over r_1 is to be performed using MD means (doing many MD simulations).

Thus, our Hamiltonian

$$\mathcal{H} \to \mathcal{H}_2 = \sum_{j\in 2} h_2 u_2 + T_2 + V_2$$

$$T_2 = \sum_{j\in 2} \frac{1}{2} M_j \dot{u}_j^2 \quad , \quad V_2 = \frac{1}{2} \sum_{jj'\in 2} u_j \Phi_{jj'} u_{j'}$$

Changing ~~variables~~:

$$\hookrightarrow \boxed{\mathcal{H}_2 = \sum_{j\in 2} V_j x_j + \sum_{j\in 2} \frac{1}{2} \dot{x}_j^2 + \frac{1}{2} \sum_{jj'\in 2} x_j D_{jj'} x_{j'}} \quad \checkmark$$

We ~~need~~ introduce normal coordinates:

$$\cancel{D_{22}\xi_\lambda} = D_{22}\, e_\lambda = \omega_\lambda^2 e_\lambda \ , \quad D_{22} = \sum_\lambda \omega_\lambda^2 e_\lambda e_\lambda^\dagger \quad \checkmark$$

(a) $$\frac{1}{2} X_2^\dagger D_{22} X_2 = \frac{1}{2}\sum_\lambda \omega_\lambda^2 \underbrace{X_2^\dagger e_\lambda}_{\text{number}} \underbrace{e_\lambda^\dagger X_2}_{\text{number}} = \frac{1}{2}\sum_\lambda \omega_\lambda^2 (e_\lambda^\dagger X_2)^* e_\lambda^\dagger X_2$$

$$= \frac{1}{2} \sum_\lambda \omega_\lambda^2 \xi_\lambda^2 \ ,$$

assuming $\xi_\lambda = e_\lambda^\dagger X_2$ is real !

where $\boxed{\xi_\lambda = e_\lambda^\dagger X_2} \to \boxed{\xi_\lambda = \sum_{j\in 2} e_{\lambda j} x_j}$, $\cancel{x_j = \sum_\lambda}$ $\checkmark$

$$\boxed{\sum_\lambda e_\lambda e_\lambda^\dagger = \mathbb{1}} \ , \quad \underbrace{\sum_j e_{\lambda j} e_{\lambda' j} = \delta_{\lambda\lambda'}} \quad \checkmark$$

completeness

orthogonality $\longrightarrow \boxed{e_\lambda^\dagger e_{\lambda'} = \delta_{\lambda\lambda'}}$ $\checkmark$

which means that

$$\sum_\lambda e_\lambda \xi_\lambda = \sum_\lambda e_\lambda e_\lambda^\dagger X_2 = X_2 \ , \quad \text{i.e.} \ \boxed{X_2 = \sum_\lambda e_\lambda \xi_\lambda} \quad \checkmark$$

~~or~~, in detail, $\boxed{x_j = \sum_\lambda e_{\lambda j} \xi_\lambda}$, $j \in 2$ $\checkmark$

(b) $$\sum_{j\in 2} V_j x_j = \sum_{j\in 2} V_j \sum_\lambda e_{\lambda j} \xi_\lambda = \sum_\lambda \Big(\sum_{j\in 2} e_{\lambda j} V_j \Big) \xi_\lambda$$

$$= \sum_\lambda V_\lambda \xi_\lambda \ , \quad \boxed{V_\lambda = \sum_{j\in 2} e_{\lambda j} V_j} \quad \checkmark$$

(c) $T_2 = \sum_{j\in 2} \frac{1}{2} \dot{x}_j^2 = \boxed{\sum_{j\in 2}} \frac{1}{2} \sum_{\lambda\lambda'} \underbrace{\boxed{e_{\lambda j} e_{\lambda' j}}}_{\delta_{\lambda\lambda'}} \dot{\xi}_\lambda \dot{\xi}_{\lambda'}$ ✓

$= \frac{1}{2} \sum_\lambda \dot{\xi}_\lambda^2$ ✓

Therefore,

$$\boxed{\begin{aligned} \mathcal{H}_2 &= \sum_\lambda V_\lambda \xi_\lambda + \frac{1}{2}\sum_\lambda \dot{\xi}_\lambda^2 + \frac{1}{2}\sum_\lambda \omega_\lambda^2 \xi_\lambda^2 \\ &= \sum_\lambda \left[\frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda + \frac{1}{2}\dot{\xi}_\lambda^2 \right] \end{aligned}}$$ ← the sum of "displaced" harmonic oscillators

⊕

Stat. function (for partial averaging over the phase space associated with region 2):

$$\boxed{\rho_2 = \frac{1}{Z_2} e^{-\beta \mathcal{H}_2}}$$

$Z_2 = \iint d u_2 \, d\underbrace{(\dot{u}_2 M_2)}_{P_2} e^{-\beta \mathcal{H}_2} = \iint d X_2 \, d\dot{X}_2 \, e^{-\beta \mathcal{H}_2}$ ✓

$= \iint \prod_\lambda d\xi_\lambda \, d\dot{\xi}_\lambda \, J \, e^{-\beta \mathcal{H}_2}$ ✓

$$J = (\text{Jacobian}) = \frac{\partial(x_j, \dot{x}_j)}{\partial(\xi_\lambda, \dot{\xi}_\lambda)} = \begin{vmatrix} \partial x_j/\partial \xi_\lambda & \partial \dot{x}_j/\partial \xi_\lambda \\ \partial x_j/\partial \dot{\xi}_\lambda & \partial \dot{x}_j/\partial \dot{\xi}_\lambda \end{vmatrix}$$

$$= \begin{vmatrix} (e_{\lambda j}) & 0 \\ 0 & (e_{\lambda j}) \end{vmatrix} = \det|e_{\lambda j}| \cdot \det|e_{\lambda j}| = 1 \cdot 1 = 1$$

Therefore,

$$\boxed{\begin{aligned} Z_2 &= \iint \prod_\lambda d\xi_\lambda d\dot{\xi}_\lambda \, e^{-\beta \mathcal{H}_2} = \prod_\lambda Z_\lambda \\ Z_\lambda &= \int d\xi_\lambda \int d\dot{\xi}_\lambda \, e^{-\beta\left(\frac{1}{2}\dot{\xi}_\lambda^2 + \frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda\right)} \end{aligned}}$$ ✓ ✓

It can be calculated:

$$\int d\dot{\xi}_\lambda \, e^{-\beta \frac{1}{2} \dot{\xi}_\lambda^2} = \boxed{Z_{\dot{\xi}_\lambda} = \sqrt{\frac{2\pi}{\beta}}}$$

$$Z_{\xi_\lambda} = \int d\xi_\lambda \, e^{-\beta\left(\frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda\right)}$$

$$= \cancel{\int d\xi \, e^{-\beta\left[\frac{1}{2}\omega^2 \xi^2 + 2 \cdot V \left(\frac{\xi \omega}{\sqrt{2}}\right) \cdot \frac{2}{\omega} + \left(\frac{2V}{\omega}\right)^2 - \left(\frac{2V}{\omega}\right)^2\right]}}$$

$$= \int d\xi \, e^{-\frac{\beta\omega^2}{2}\left(\xi^2 + \frac{2}{\omega^2} V \xi + \left(\frac{V}{\omega^2}\right)^2 - \left(\frac{V}{\omega^2}\right)^2\right)}$$

$$= e^{+\frac{\beta\omega^2}{2}\frac{V^2}{\omega^4}} \int d\xi \, e^{-\frac{\beta\omega^2}{2}\left(\xi + \frac{V}{\omega^2}\right)^2} = e^{+\frac{\beta V^2}{2\omega^2}} \int_{-\infty}^{\infty} d\eta \, e^{-\frac{\beta\omega^2}{2}\eta^2}$$

$$= e^{+\frac{\beta V^2}{2\omega^2}} \cdot \sqrt{\frac{\pi}{\frac{\beta\omega^2}{2}}} \Rightarrow \sqrt{\frac{2\pi}{\beta\omega_\lambda^2}} \, e^{+\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}$$

$$\boxed{Z_{\xi_\lambda} = \sqrt{\frac{2\pi}{\beta\omega_\lambda^2}} \, e^{+\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}}$$

Then, we can calculate the necessary averages.

~~We need~~: Eq. of motion for each oscillator:

$\cancel{\langle \xi_\lambda(0)\xi_{\lambda'}(0)\rangle =}$

$$\mathcal{L}_\lambda = \frac{1}{2}\dot{\xi}_\lambda^2 - \frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 - V_\lambda \xi_\lambda$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}_\lambda}{\partial \dot{\xi}_\lambda} = \frac{\partial \mathcal{L}_\lambda}{\partial \xi_\lambda} \rightarrow \frac{d}{dt}\dot{\xi}_\lambda = -\omega_\lambda^2 \xi_\lambda - V_\lambda, \quad \boxed{\ddot{\xi}_\lambda + \omega_\lambda^2 \xi_\lambda = -V_\lambda}$$

$$\xi_\lambda(t) = A_\lambda \cos\omega_\lambda t + B_\lambda \sin\omega_\lambda t - \frac{V_\lambda}{\omega_\lambda^2}$$

$$\xi_\lambda(0) = -\frac{V_\lambda(0)}{\omega_\lambda^2} + A_\lambda, \quad \dot{\xi}_\lambda(0) = B_\lambda\omega_\lambda - \frac{\dot{V}_\lambda(0)}{\omega_\lambda^2}$$

so that $A_\lambda = \frac{V_\lambda(0)}{\omega_\lambda^2} + \xi_\lambda(0)$, $B_\lambda = \frac{1}{\omega_\lambda}\left[\frac{\dot{V}_\lambda(0)}{\omega_\lambda^2} + \dot{\xi}_\lambda(0)\right]$

so that

$$\boxed{\xi_\lambda(t) = \left[\xi_\lambda(0) + \frac{V_\lambda(0)}{\omega_\lambda^2}\right]\cos\omega_\lambda t + \frac{1}{\omega_\lambda}\left[\frac{\dot V_\lambda(0)}{\omega_\lambda^2} + \dot\xi_\lambda(0)\right]\sin\omega_\lambda t - \frac{V_\lambda}{\omega_\lambda^2}}$$

Probably this is not needed.

We have:

$$\cancel{\langle \xi_\lambda(0)\xi_{\lambda'}(0)\rangle = \frac{1}{Z_{\xi_\lambda\xi_{\lambda'}}}\int d\xi_\lambda d\xi_{\lambda'}\, \xi_\lambda \xi_{\lambda'} e^{-\beta(\mathcal{H}_\lambda + \mathcal{H}_{\lambda'})}}$$

$$\langle X_j(0) X_{j'}(0)\rangle = \sum_{\lambda\lambda'} e_{\lambda j} e_{\lambda' j'} \langle \xi_\lambda(0)\xi_{\lambda'}(0)\rangle$$

$$\bar\xi_\lambda = \langle \xi_\lambda(0)\rangle = \frac{1}{Z_{\xi_\lambda}}\int d\xi_\lambda\, e^{-\beta\left(\frac{1}{2}\omega_\lambda^2\xi_\lambda^2 + V_\lambda\xi_\lambda\right)}\cdot\xi_\lambda$$

$$= \frac{1}{Z_{\xi_\lambda}}\int d\xi_\lambda \left(\xi_\lambda + \frac{V_\lambda}{\omega_\lambda^2} - \frac{V_\lambda}{\omega_\lambda^2}\right) e^{-\frac{\beta\omega_\lambda^2}{2}\left(\underbrace{\xi_\lambda + \frac{V_\lambda}{\omega_\lambda^2}}_{y_\lambda}\right)^2} e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}$$

$$= \frac{1}{Z_{\xi_\lambda}} e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}\int dy_\lambda\, e^{-\frac{\beta\omega_\lambda^2}{2}y_\lambda^2}\left(y_\lambda - \frac{V_\lambda}{\omega_\lambda^2}\right)$$

$$= \frac{1}{Z_{\xi_\lambda}} e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}\left(-\frac{V_\lambda}{\omega_\lambda^2}\right)\sqrt{\frac{\pi}{\frac{\beta\omega_\lambda^2}{2}}} = -\frac{V_\lambda(0)}{\omega_\lambda^2}.$$

$$\boxed{\bar\xi_\lambda(0) = -\frac{V_\lambda(0)}{\omega_\lambda^2}}$$

atoms in region 2 are displaced due to interaction with region 1.

Therefore,

$$\langle \xi_\lambda(0)\xi_{\lambda'}(0)\rangle = \left\langle\left(\xi_\lambda(0) - \bar\xi_\lambda(0)\right)\left(\xi_{\lambda'}(0) - \bar\xi_{\lambda'}(0)\right)\right\rangle + \bar\xi_\lambda(0)\,\bar\xi_{\lambda'}(0)$$

where

$$\left\langle\left(\xi_\lambda - \bar\xi_\lambda\right)\left(\xi_{\lambda'} - \bar\xi_{\lambda'}\right)\right\rangle = 0 \text{ for } \lambda \neq \lambda', \text{ and}$$

for $\lambda = \lambda'$:

$$\langle (\xi_\lambda - \bar{\xi}_\lambda)^2 \rangle = \frac{1}{Z_{\xi_\lambda}} \int d\xi_\lambda \, (\xi_\lambda - \bar{\xi}_\lambda)^2 \, e^{-\frac{\beta\omega_\lambda^2}{2}(\xi_\lambda - \bar{\xi}_\lambda)^2} \, e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}$$

$$= \sqrt{\frac{\beta\omega_\lambda^2}{2\pi}} \int dy \, y^2 \, e^{-\frac{\beta\omega_\lambda^2}{2} y^2} = \sqrt{\frac{\beta\omega_\lambda^2}{2\pi}} \sqrt{\pi} \, \frac{1}{2 \cdot \frac{\beta\omega_\lambda^2}{2} \sqrt{\frac{\beta\omega_\lambda^2}{2}}}$$

$$= \frac{1}{\beta\omega_\lambda^2}.$$

Thus,

$$\boxed{\langle \xi_\lambda(0)\, \xi_{\lambda'}(0) \rangle = \frac{\delta_{\lambda\lambda'}}{\beta\omega_\lambda^2} + \underbrace{\frac{V_\lambda(0)}{\omega_\lambda^2} \frac{V_{\lambda'}(0)}{\omega_{\lambda'}^2}}_{\text{due to interaction with region 1}}}$$

Also,

$$\boxed{\langle \mathring{\xi}_\lambda(0)\, \mathring{\xi}_{\lambda'}(0) \rangle = \frac{\delta_{\lambda\lambda'}}{\beta}}$$

as before. Cross correl. functions, $\langle \mathring{\xi}_\lambda(0)\, \xi_{\lambda'}(0) \rangle = 0$.

3. Statistical description of the random force I

$$R_i(t) = -\sum_{jj' \in 2} \frac{\partial V_j}{\partial r_i} \left[\mathring{\Omega}_{jj'}(t) X_{j'}(0) + \Omega_{jj'}(t) \mathring{X}_{j'}(0) \right]$$

$$\langle R_i(t) R_{i'}(t') \rangle = \sum_{jj'} \sum_{kk'} \frac{\partial V_j}{\partial r_i} \frac{\partial V_k}{\partial r_{i'}} \Big\{ \mathring{\Omega}_{jj'}(t) \langle X_{j'}(0) X_{k'}(0) \rangle \times$$

$$\times \mathring{\Omega}_{kk'}(t') + \Omega_{jj'}(t) \langle \mathring{X}_{j'}(0) \mathring{X}_{k'}(0) \rangle \Omega_{kk'}(t') \Big\}$$

Since

$$\langle \mathring{X}_{j'}(0)\, \mathring{X}_{k'}(0) \rangle = \sum_{\lambda\lambda'} e_{\lambda j'} e_{\lambda' k'} \overbrace{\langle \mathring{\xi}_\lambda(0)\, \mathring{\xi}_{\lambda'}(0) \rangle}^{= \delta_{\lambda\lambda'}/\beta}$$

$$= \sum_\lambda e_{\lambda j'} e_{\lambda k'} \frac{1}{\beta} = \frac{1}{\beta} \delta_{j'k'}$$

$$\boxed{\langle \mathring{X}_2(0)\, \mathring{X}_2^T(0) \rangle = \frac{1}{\beta} \mathbb{1}}$$

$$\langle X_{j'}(0) X_{k'}(0)\rangle = \sum_{\lambda\lambda'} e_{\lambda j'} e_{\lambda' k'} \left[\frac{\delta_{\lambda\lambda'}}{\beta\omega_\lambda^2} + \frac{V_\lambda(0)V_{\lambda'}(0)}{\omega_\lambda^2 \omega_{\lambda'}^2}\right]$$ ✓

$$= \frac{1}{\beta}\sum_\lambda \frac{e_{\lambda j'} e_{\lambda k'}}{\omega_\lambda^2} + \sum_{\lambda\lambda'} e_{\lambda j'} e_{\lambda' k'} \frac{1}{\omega_\lambda^2\omega_{\lambda'}^2} \sum_{\ell\ell'} e_{\lambda\ell} e_{\lambda'\ell'} V_\ell V_{\ell'}$$ ✓

$$= \frac{1}{\beta}\sum_\lambda \frac{e_{\lambda j'} e_{\lambda k'}}{\omega_{\lambda}^2} + \sum_{\ell\ell'}\left(\sum_\lambda \frac{e_{\lambda j'} e_{\lambda \ell}}{\omega_\lambda^2}\right)\left(\sum_{\lambda'} \frac{e_{\lambda' k'} e_{\lambda'\ell'}}{\omega_{\lambda'}^2}\right) V_\ell V_{\ell'}$$ ✓

~~If~~ Since

$$\boxed{\sum_\lambda \frac{e_{\lambda j} e_{\lambda j'}}{\omega_\lambda^2} = \left(D_{22}^{-1}\right)_{jj'}},$$ ✓

then

$$\langle X_j(0) X_{j'}(0)\rangle = \frac{1}{\beta}\left(D_{22}^{-1}\right)_{jj'} + \sum_{\ell\ell'\in 2} V_\ell \left(D_{22}^{-1}\right)_{\ell j} \left(D_{22}^{-1}\right)_{\ell' j'} V_{\ell'}$$ ✓

$$\boxed{\langle X_2(0) X_2^\dagger(0)\rangle = \frac{1}{\beta} D_{22}^{-1} + \cancel{\left(D_{22}^{-1} V_2\right)\left(D_{22}^{-1} V_2\right)^\dagger}}$$

$$\left(V_2(0) D_{22}^{-1}\right)\left(V_2(0) D_{22}^{-1}\right)^\dagger$$

} Both forms OK as D_{22} symmetric

Therefore, if

$$\cancel{\langle R_1(t) R_1^\dagger(t')\rangle} = \boxed{R_1(t) = -\overbrace{V_{12}}^{\|\partial V_j/\partial r_i\|}\left(\dot{\Omega}_{22}(t) X_2(0) + \Omega_{22}(t)\dot{X}_2(0)\right)}$$

then

$$\langle R_1(t) R_1^\dagger(t')\rangle = V_{12}\left\{\dot{\Omega}_{22}(t)\langle X_2(0) X_2^\dagger(0)\rangle \dot{\Omega}_{22}(t') + \right.$$

$$\left. + \Omega_{22}(t)\langle \dot{X}_2(0)\dot{X}_2^\dagger(0)\rangle \Omega_{22}(t')\right\} V_{21}$$ ✓

$$= V_{12}\left\{\dot{\Omega}_{22}(t)\left(\frac{1}{\beta} D_{22}^{-1} + \left(D_{22}^{-1} V_2\right)\left(D_{22}^{-1} V_2\right)^\dagger\right)\dot{\Omega}_{22}(t') + \right.$$ ✓

$$\left. + \Omega_{22}(t)\frac{1}{\beta}\Omega_{22}(t')\right\} V_{21}$$ ✓

Here:

$$\Omega_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda} \sin\omega_\lambda t$$

$$\dot{\Omega}_{22}(t) = \sum_\lambda e_\lambda e_\lambda^+ \cos\omega_\lambda t \;;\; \ddot{\Omega}_{22}(t) = -\sum_\lambda \omega_\lambda e_\lambda e_\lambda^+ \sin\omega_\lambda t$$

$$D_{22}^{-1} = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}$$

so that:

$\delta_{\lambda\lambda'}$ $\delta_{\lambda'\lambda''}$

$$\text{(a)}\quad \dot{\Omega}_{22}(t)\, D_{22}^{-1}\, \dot{\Omega}_{22}(t') = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda} \sin\omega_\lambda t \sum_{\lambda'} \frac{e_{\lambda'} e_{\lambda'}^+}{\omega_{\lambda'}^2} \sum_{\lambda''} \frac{e_{\lambda''} e_{\lambda''}^+}{\omega_{\lambda''}} \sin\omega_{\lambda''} t'$$

$$= \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^4} \sin^2\omega_\lambda t$$

$\delta_{\lambda\lambda'}$

$$\text{(b)}\quad \dot{\Omega}_{22}(t)\, D_{22}^{-1} V_2 = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda} \sin\omega_\lambda t \sum_{\lambda'} \frac{e_{\lambda'} e_{\lambda'}^+}{\omega_{\lambda'}^2} V_2$$

$$= \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^3} \sin\omega_\lambda t \cdot V_2 \rightarrow \sum_{j'} \sum_\lambda \frac{e_{\lambda j} e_{\lambda j'}^+}{\omega_\lambda^3} \sin\omega_\lambda t \cdot V_{j'}$$

(this is a vector).

If we denote

$$\boxed{\Pi_{22}(t) = \sum_\lambda \frac{\sin\omega_\lambda t}{\omega_\lambda^3}\, e_\lambda e_\lambda^+}$$

~~then~~ so that

$$\ddot{\Pi}_{22}(t) = -\sum_\lambda \frac{\sin\omega_\lambda t}{\omega_\lambda}\, e_\lambda e_\lambda^+ \equiv -\Omega_{22}(t),$$

then

$$\dot{\Omega}_{22}(t)\, D_{22}^{-1} V_2 = \Pi_{22}(t)\, V_2 .$$

and thus

$\dot{\Omega}_{22}(t)$

so that, term by term:

(a) $$\mathring{\Omega}_{22}(t)\, D_{22}^{-1}\, \mathring{\Omega}_{22}(t') = \sum_\lambda e_\lambda \underbrace{e_\lambda^\dagger \cos\omega_\lambda t \cdot \sum_{\lambda'} \frac{e_{\lambda'}}{}}_{\delta_{\lambda\lambda'}} \underbrace{\frac{e_{\lambda'}^\dagger}{\omega_{\lambda'}^2} \sum_{\lambda''} e_{\lambda''}}_{\delta_{\lambda'\lambda''}} e_{\lambda''}^\dagger \cos\omega_{\lambda''} t'$$

$$= \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos\omega_\lambda t \cos\omega_\lambda t' \quad \cancel{\equiv C_{22}(t,t')}$$ ✓

(b) $$\mathring{\Omega}_{22}(t)\, D_{22}^{-1} V_2 = \sum_\lambda e_\lambda \underbrace{e_\lambda^\dagger \cos\omega_\lambda t \cdot \sum_{\lambda'} e_{\lambda'}}_{\delta_{\lambda\lambda'}} \frac{e_{\lambda'}^\dagger}{\omega_{\lambda'}^2} \cdot V_2$$

$$= \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos\omega_\lambda t \cdot V_2 \equiv \Pi_{22}(t) V_2 ,$$ ✓

where

$$\cancel{\int_0^t \Omega_{22}(\tau)\,d\tau = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \int_0^t \sin\omega_\lambda \tau\, d\tau}$$

✓ $$\boxed{\Pi_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos\omega_\lambda t} \qquad \boxed{\mathring{\Pi}_{22}(t) = -\Omega_{22}(t)} \oplus$$

symmetric matrix

$$\mathring{\Pi}_{22}(t) = -\sum_\lambda \frac{e_\lambda \cdot e_\lambda^\dagger}{\omega_\lambda} \sin\omega_\lambda t \equiv -\Omega_{22}(t)$$ ✓

(c) $$\Omega_{22}(t)\,\Omega_{22}(t') = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \sin\omega_\lambda t \sum_{\lambda'} \frac{e_{\lambda'} e_{\lambda'}^\dagger}{\omega_{\lambda'}} \sin\omega_{\lambda'} t$$

$$= \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \sin\omega_\lambda t \sin\omega_\lambda t'$$ ✓

Collecting all terms,

$$\langle R_1(t) R_1(t')\rangle = V_{12} \left\{ \frac{1}{\beta} \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \overbrace{(\cos\omega_\lambda t \cos\omega_\lambda t' + \sin\omega_\lambda t \sin\omega_\lambda t')}^{\cos[\omega_\lambda (t-t')]} \right.$$

$$\left. + \cancel{\beta}\left(\Pi_{22}(t) V_2\right)\left(\Pi_{22}(t') V_2\right)^\dagger \right\} V_{21}$$ ✓

$$\boxed{\langle R_1(t) R_1^\dagger(t')\rangle = V_{12}^{(t)} \left\{ \frac{1}{\beta} \underbrace{\left[\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos\omega_\lambda (t-t') \right]}_{\Pi(t-t')} + \left(\Pi_{22}(t) V_2^{(0)}\right)\left(V_2^{(0)} \Pi_{22}(t')\right) \right\} V_{21}^{(t)}}$$

- We also consider $\langle \mathring{R}_1(t) R_1(t') \rangle$.

$$\mathring{R}_1(t) = -V_{12}\left[\ddot{\Omega}_{22}(t)\, X_2(0) + \mathring{\Omega}_{22}(t)\, \mathring{X}_2(0)\right]$$

$$- \mathring{V}_{12}\left[\mathring{\Omega}_{22}(t)\, X_2(0) + \Omega_{22}(t)\, \mathring{X}_2(0)\right], \text{ so that}$$

$$\langle \mathring{R}_1(t) R_1^\dagger(t') \rangle = V_{12}\left\{ \ddot{\Omega}_{22}(t) \langle X_2(0) X_2^\dagger(0) \rangle \mathring{\Omega}_{22}(t') + \right.$$

$$\left. + \mathring{\Omega}_{22}(t) \langle \mathring{X}_2(0) \mathring{X}_2^\dagger(0) \rangle \Omega_{22}(t') \right\} V_{21}$$

$$+ \mathring{V}_{12}\left[\mathring{\Omega}_{22}(t) \langle X_2(0) X_2^\dagger(0) \rangle \mathring{\Omega}_{22}(t') + \Omega_{22}(t) \langle \mathring{X}_2(0) \mathring{X}_2^\dagger(0) \rangle \Omega_{22}(t')\right] V_{21}$$

$$= V_{12}\left\{ \ddot{\Omega}_{22}(t)\left[\frac{1}{\beta} D_{22}^{-1} + (D_{22}^{-1} V_2)(D_{22}^{-1} V_2)^\dagger\right] \mathring{\Omega}_{22}(t') + \right.$$

$$\left. + \frac{1}{\beta} \mathring{\Omega}_{22}(t)\, \Omega_{22}(t') \right\} V_{21} + \mathring{V}_{12}\left\{ \mathring{\Omega}_{22}(t)\left[\frac{1}{\beta} D_{22}^{-1} + (D_{22}^{-1} V_2)(V_2 D_{22}^{-1})\right] \mathring{\Omega}_{22}(t') \right.$$

$$\left. + \frac{1}{\beta} \Omega_{22}(t)\, \Omega_{22}(t') \right\} V_{21}$$

$$= \left(V_{12} \ddot{\Omega}_{22}(t) + \mathring{V}_{12} \mathring{\Omega}_{22}(t)\right)\left[\frac{1}{\beta} D_{22}^{-1} + (D_{22}^{-1} V_2)(V_2 D_{22}^{-1})\right] \mathring{\Omega}_{22}(t')\, V_{21} +$$

$$+ \frac{1}{\beta}\left[\left(V_{12} \mathring{\Omega}_{22}(t) + \mathring{V}_{12} \Omega_{22}(t)\right) \Omega_{22}(t')\right] V_{21}$$

Can be still simplified, but not clear what else we achieve with this corr. f.

- <u>Weak region 1 – region 2 interaction</u>

In this approximation:

$$\langle R_1(t) R_1^\dagger(t') \rangle \simeq \frac{1}{\beta} V_{12}(t)\left[\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos \omega_\lambda (t-t')\right] V_{21}(t')$$

and

$$\langle \dot{R}_1(t) R_1^\dagger(t')\rangle \simeq \frac{1}{\beta}\left(V_{12}\ddot{\Omega}_{22}(t) + \dot{V}_{12}\dot{\Omega}_{22}(t)\right) D_{22}^{-1}\dot{\Omega}_{22}(t')\, V_{21}$$

$$+ \frac{1}{\beta}\left(V_{12}\dot{\Omega}_{22}(t) + \dot{V}_{12}\Omega_{22}(t)\right)\Omega_{22}(t')\, V_{21}$$

~~Both depend on the time difference;~~

(a) $\ddot{\Omega}_{22}(t) D_{22}^{-1}\dot{\Omega}_{22}(t') = -\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\cancel{\omega_\lambda}}\,\omega_\lambda \sin\omega_\lambda t \cdot \sum_{\lambda'} \frac{e_{\lambda'} e_{\lambda'}^\dagger}{\omega_{\lambda'}^2} \times$

$\times \sum_{\lambda''} e_{\lambda''} e_{\lambda''}^\dagger \cos\omega_{\lambda''} t' = -\sum_\lambda e_\lambda e_\lambda^\dagger \frac{\sin\omega_\lambda t \cos\omega_\lambda t'}{\omega_\lambda}$;

(b) $\dot{\Omega}_{22}(t)\, D_{22}^{-1}\, \dot{\Omega}_{22}(t') = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos\omega_\lambda t \cos\omega_\lambda t'$

(c) $\dot{\Omega}_{22}(t)\,\Omega_{22}(t') = \sum_\lambda e_\lambda e_\lambda^\dagger \cos\omega_\lambda t \cdot \sum_{\lambda'} \frac{e_{\lambda'} e_{\lambda'}^\dagger}{\omega_{\lambda'}} \sin\omega_{\lambda'} t'$

$= \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \cos\omega_\lambda t \sin\omega_\lambda t'$

(d) $\Omega_{22}(t)\,\Omega_{22}(t') = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \sin\omega_\lambda t \sin\omega_\lambda t'$

so that:

$$\langle \dot{R}_1(t) R_1^\dagger(t')\rangle \simeq \frac{1}{\beta} V_{12}\Big[\overbrace{-\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \sin\omega_\lambda(t-t')}^{-\Omega_{22}(t-t')}\Big] V_{21}$$

$$+ \frac{1}{\beta}\dot{V}_{12}\Big[\underbrace{\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos\omega_\lambda(t-t')}_{\Pi_{22}(t-t')}\Big] V_{21} \qquad \oplus$$

Note that both do <u>not</u> depend on just $t-t'$, as V_{12} and V_{21} depend on t, t', respectively (!).

- The kernel term ("friction") in the eq. of motion for $\vec{P}_1$ is:

$$V_{12} \int_0^t \Omega_{22}(t-\tau)\, V_2(\tau)\, d\tau$$

← it is not yet "friction" as we have to take it by pa[rts]

Relationship to the correlation functions is unclear.

§4. Probability distribution

The random force $R_1(t)$:

$$R_1(t) = -V_{12}(t)\left[\dot{\Omega}_{22}(t)\, X_2(0) + \Omega_{22}(t)\, \dot{X}_2(0)\right] \quad ✓$$

is a random function due to the linear dependence on stochastic variables $X_2(0)$ and $\dot{X}_2(0)$:

$$X_2(0) = \sum_\lambda e_\lambda \underbrace{\xi_\lambda(0)}_{\text{random, distributed via}} \quad ✓$$

$$\boxed{\rho_{\xi_\lambda}(\xi_\lambda) = \frac{1}{Z_{\xi_\lambda}}\, e^{-\beta\left(\frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda\right)}} \quad ✓$$

$$\dot{X}_2(0) = \sum_\lambda e_\lambda \dot{\xi}_\lambda(0) \quad ✓$$

$$\boxed{\rho_{\dot{\xi}_\lambda}(\dot{\xi}_\lambda) = \frac{1}{Z_{\dot{\xi}_\lambda}}\, e^{-\beta\frac{1}{2}\dot{\xi}_\lambda^2}} \qquad Z_{\dot{\xi}_\lambda} = \sqrt{\frac{2\pi}{\beta}} \quad ✓$$

2nd is purely Gaussian. The 1st is as well:

$$Z_{\xi_\lambda} = \sqrt{\frac{2\pi}{\beta\omega_\lambda^2}}\; e^{\beta V_\lambda^2/2\omega_\lambda^2} \quad ✓$$

$$\bar{\xi}_\lambda = -\frac{V_\lambda}{\omega_\lambda^2}, \qquad \frac{1}{2}\omega_\lambda^2\xi_\lambda^2 + V_\lambda \xi_\lambda = \frac{1}{2}\omega_\lambda^2\left[\left(\xi_\lambda + \frac{V_\lambda}{\omega_\lambda^2}\right)^2 - \left(\frac{V_\lambda}{\omega_\lambda^2}\right)^2\right] \quad ✓$$

that

$$\mathcal{P}_{\xi_\lambda}(\xi_\lambda) = \sqrt{\frac{\beta\omega_\lambda^2}{2\pi}}\, e^{-\beta V_\lambda^2/2\omega_\lambda^2}\, e^{-\frac{\beta\omega_\lambda^2}{2}\left(\xi_\lambda + \frac{V_\lambda}{\omega_\lambda^2}\right)^2} \cdot e^{+\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}$$

$$\boxed{\mathcal{P}_{\xi_\lambda}(\xi_\lambda) = \sqrt{\frac{\beta\omega_\lambda^2}{2\pi}}\, e^{-\frac{\beta\omega_\lambda^2}{2}\left(\xi_\lambda + \frac{V_\lambda}{\omega_\lambda^2}\right)^2}}$$ is also (a "displaced") Gaussian

Therefore, at any time t (will be omitted):

$$\mathcal{P}(R_1) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(R_1 - \overline{R}_1)^2}{2\sigma^2}\right]$$

is also random, with:

(a) <u>average</u>

$$\overline{R_1} = -V_{12}\left[\dot{\Omega}_{22}\,\overline{X_2}(0) + \Omega_{22}\cdot \underbrace{\overline{\dot{X}_2}(0)}_{=0}\right]$$

$$\overline{X_2}(0) = \langle X_2\rangle = \sum_\lambda e_\lambda \langle \xi_\lambda\rangle = -\sum_\lambda e_\lambda \frac{V_\lambda}{\omega_\lambda^2}$$

$\hookrightarrow$ $\cancel{= -\sum_\lambda \frac{e_\lambda}{\omega_\lambda^2} \sum_{j\in 2} e_{\lambda j} V_j = -\sum}$ for $j \in 2$:

$$\overline{X_j} = -\sum_\lambda \frac{e_{\lambda j}}{\omega_\lambda^2} V_\lambda = -\sum_\lambda \frac{e_{\lambda j}}{\omega_\lambda^2} \sum_{j'\in 2} e_{\lambda j'} V_{j'}$$

$$= -\left[\sum_{j'\in 2}\sum_\lambda \frac{e_{\lambda j}\, e_{\lambda j'}}{\omega_\lambda^2}\right] V_{j'} \equiv -\sum_{j'\in 2} (D_{22}^{-1})_{jj'} V_{j'},$$

$$\boxed{\overline{X}_2(0) = -D_{22}^{-1} V_2(0)} \rightarrow \boxed{\overline{R_1} = +V_{12}\,\dot{\Omega}_{22}(t)\, D_{22}^{-1} V_2(0)}$$

~~dispersion (for the given atom j)~~

$\cancel{S_j^2 = \langle R_j^2\rangle = V_{j2}\left[\dot{\Omega}_{22}\right.}$

Here:

$\Omega_{22}(t)\, D_{22}^{-1} = \sum e_\lambda e_\lambda^t \cos\omega t \quad \sum e_\lambda e_\lambda^t \ldots \quad \Omega_{22}(t)$

so that

$$\boxed{\overline{R}_1(t) = +V_{12}\left[\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos\omega_\lambda t\right] V_2(0) \equiv +V_{12}\,\Pi_{22}(t)\,V_2(0)} \oplus$$

(b) ~~Redefinition of the random force~~. **Some algebra**

Consider the integral term in the EOM for $\vec{r}_1$ (see p. 2):

$$V_{12}\int_0^t \Omega_{22}(t-\tau)\,V_2(\tau)\,d\tau = \text{Integral term}$$

We shall integrate it by parts. There are 2 possibilities:

(a) $\Pi_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos\omega_\lambda t$, $\Pi_{22}(0) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} = D_{22}^{-1}$

$$\dot\Pi_{22}(t) = -\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda}\sin\omega_\lambda t \equiv -\Omega_{22}(t).$$

(i) By parts:

$$dv(\tau) = \Omega_{22}(t-\tau)\,d\tau, \quad u(\tau) = V_2(\tau),$$

$$v(\tau) = \int_t^\tau \Omega_{22}(t-\tau')\,d\tau' = \left|x = t-\tau'\right| = \int_0^{t-\tau}\Omega_{22}(x)(-dx)$$

$$= \int_{t-\tau}^{0}\Omega_{22}(x)\,dx = -\int_0^{t-\tau}\Omega_{22}(x)\,dx$$

On the other hand, $\dot\Pi_{22}(t) = -\Omega_{22}(t)$,

$$\int_0^t \dot\Pi_{22}(\tau')\,d\tau' = -\int_0^t \Omega_{22}(\tau')\,d\tau'$$

$\downarrow$

$\Pi_{22}(t) - \Pi_{22}(0)$, ~~so~~

So that:

$$\boxed{\int_0^t \Omega_{22}(\tau')\,d\tau' = +D_{22}^{-1} - \Pi_{22}(t) \equiv \Lambda_{22}(t)} \oplus$$

Thus,

$$\int_0^t \Omega(t-\tau)V(\tau)\,d\tau = +\left(-\int_0^{t-\tau}\Omega(x)\,dx\right)V(\tau)\Big|_0^t -$$

$$-\int_0^t\left(-\int_0^{t-\tau}\Omega(x)\,dx\right)\dot V(\tau)\,d\tau = +\left(\int_0^t \Omega(x)\,dX\right)V(0)$$

$$+\int_0^t\left(\int_0^{t-\tau}\Omega(x)\,dx\right)\dot V(\tau)\,d\tau$$

$$= \Lambda_{22}(t)\,V_2(0) + \int_0^t \Lambda_{22}(t-\tau)\,\dot V_2(\tau)\,d\tau \qquad \checkmark$$

(ii) Another possibility is to define (as in Adelman & Doll)

$$\Lambda_{22}(t) = \int_t^\infty \Omega_{22}(\tau)\,d\tau \quad ; \quad \Lambda_{22}(\infty) = 0$$

$$\Lambda_{22}(0) = \Pi_{22}(\infty) - D_{22}^{-1} \quad \checkmark$$

Then $\dot\Lambda_{22}(t) = -\Omega_{22}(t)$

and

$$\cancel{\int_0^t \Omega(t-\tau)V(\tau)\,d\tau \Rightarrow} \quad \frac{d}{d\tau}\Lambda(t-\tau) = \frac{d}{d\tau}\int_{t-\tau}^\infty \Omega(\tau')\,d\tau' = +\Omega(t-\tau).$$

so that

$$\int_0^t \Omega(t-\tau)V(\tau)\,d\tau = \Lambda(t-\tau)V(\tau)\Big|_0^t - \int_0^t \Lambda(t-\tau)\,\dot V(\tau)\,d\tau$$

$$= \Lambda(0)V(t) - \Lambda(t)V(0) - \int_0^t \Lambda(t-\tau)\,\dot V(\tau)\,d\tau$$

~~I'd prefer the 1st definition:~~

$$\cancel{\boxed{\Lambda_{22}(t) = \int_0^t \Omega_{22}(\tau)\,d\tau \equiv D_{22}^{-1} - \Pi_{22}(t)}}$$

~~Note that $\Pi_{22}(\infty)$ is finite since $\left|\Pi_{22}(\infty)\right| = \left|\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos\omega_\lambda t\right| \leq$~~

~~$\leq \sum_\lambda \left|\frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\right| = \sum_\lambda \frac{1}{\omega_\lambda^2}\left|e_\lambda e_\lambda^\dagger\right|$~~

Note that

$$\Lambda_{22}(t) = -\Pi_{22}(\infty) + \Pi_{22}(t)$$

in this case is also well defined, since ~~$\Pi_{22}(\infty)$~~

$$\Pi_{22}(\infty) = \lim_{t\to\infty} \sum_\lambda \frac{e_\lambda e_\lambda^t}{\omega_\lambda^2} \cos\omega_\lambda t$$

is finite.

Formal proof

$A_{22}(\omega) = \sum_\lambda e_\lambda^* e_\lambda^t \, \delta(\omega - \omega_\lambda)$ – spectral function

$|A_{22}(\omega)| \leq A_m$ (bound from above & below)

then

$$\Pi_{22}(t) = \int_0^{\omega_m} A_{22}(\omega) \frac{\cos\omega t}{\omega^2} d\omega$$

ω_m – max phonon frequency

We split the integral into two parts:

$$\int_0^{\omega_1} A_{22}(\omega) \frac{\cos\omega t}{\omega^2} d\omega + \int_{\omega_1}^{\omega_m} A_{22}(\omega) \frac{\cos\omega t}{\omega^2} d\omega = I_< + I_>$$

where ω_1 is a small freq., so that only acoustic modes contribute. For acoustic modes $\lambda = x, y, z$ and

$$e_{\lambda j} / \sqrt{m_j} = u_\lambda \quad \text{and} \quad \omega_\lambda = v_\lambda |\vec{k}|$$

$$A_{jj'}(\omega) = \sum_{\lambda=1}^{3} e_{\lambda j} e_{\lambda j'} \delta(\omega - \omega_\lambda) = \sqrt{m_j m_{j'}} \sum_{\lambda=1}^{3} u_\lambda^2 \delta(\omega - \omega_\lambda)$$

On the other hand, from normalisation:

$$\sum_\lambda \sum_j e_{\lambda j} e_{\lambda j} = 1 \to u_\lambda^2 \sum_j m_j = 1,$$

$$u_\lambda^2 = 1 \Big/ \sum_j m_j \quad \to \text{does not depend on } \lambda,$$

so that

$$A_{jj'}(\omega) = \frac{\sqrt{m_j m_{j'}}}{\sum_j m_j} \left[\sum_{\lambda=1}^{3} \delta(\omega - \omega_\lambda) \right] \sim \text{phonon DOS at small } \omega \,!$$

so that, using the Debye model argument, we find that $A_{jj'}(\omega) \sim \omega^2$.

Hence,

$$I_< = \int_0^{\omega_1} \alpha \omega^2 \frac{\cos \omega t}{\omega^2} d\omega = \alpha \int_0^{\omega_1} \cos \omega t \, d\omega = \frac{\alpha}{t} \sin \omega_1 t$$

and tends to zero as $t \to \infty$.

The other integral can be bound ~~as well~~:

$$|I_>| = \left| \int_{\omega_1}^{\omega_m} A_{22}(\omega) \frac{\cos \omega t}{\omega^2} d\omega \right| \leq \int_{\omega_1}^{\omega_m} \left| A_{22}(\omega) \frac{\cos \omega t}{\omega^2} \right| d\omega$$

$$\leq A_m \int_{\omega_1}^{\omega_m} \frac{d\omega}{\omega^2} = A_m \left(-\frac{1}{\omega} \right) \Big|_{\omega_1}^{\omega_m} = A_m \left(\frac{1}{\omega_1} - \frac{1}{\omega_m} \right)$$

and does not depend on t.

~~Therefore,~~

$$\left| t\int_0^{\omega_m t} A_{22}\left(\frac{v}{t}\right)\frac{\cos v}{v^2}\,dv\right| \le \left| t\int_0^{v_1} A_{22}\left(\frac{v}{t}\right)\frac{\cos v}{v^2}\,dv\right| + \left| t\int_{v_1}^{\omega_m t}\cdots\right|$$

$$\le t\,\frac{\alpha}{t^2}\sin v_1 + A_m\left(\frac{t}{v_1}-\frac{1}{\omega_m}\right)$$

$$= \frac{\alpha}{t}\sin v_1 - \frac{A_m}{\omega_m} + \frac{A_m}{v_1}\cdot t$$

~~and thus tends to ∞ as $t\to\infty$. This is why the 2nd definition cannot be accepted.~~

- We use the first:

$$\Lambda_{22}(t) = \int_0^t \Omega_{22}(t-\tau)\,d\tau = D_{22}^{-1} - \Pi_{22}(t)$$

and the eom for the $\vec{r}_1$ is:

$$\boxed{m_1\ddot{r}_1 = f_1 + V_{12}\left(\dot{\Omega}_{22}(t)X_2(0) + \Omega_{22}(t)\dot{X}_2(0)\right) + V_{12}(t)\Lambda_{22}(t)V_2(0) + V_{12}(t)\int_0^t \Lambda_{22}(t-\tau)\dot{V}_2(\tau)\,d\tau}$$

The last two terms [~~before~~ after $V_{12}(t)$]:

$$\Lambda_{22}(t)V_2(0) + \int_0^t \Lambda_{22}(t-\tau)\dot{V}_2(\tau)\,d\tau$$

$$= \left(D_{22}^{-1}-\Pi_{22}(t)\right)V_2(0) + D_{22}^{-1}\int_0^t \dot{V}_2(\tau)\,d\tau - \int_0^t \Pi_{22}(t-\tau)\dot{V}_2(\tau)\,d\tau$$

$$= \left(\cancel{D_{22}^{-1}}-\Pi_{22}(t)\right)V_2(0) + D_{22}^{-1}V_2(t) - \cancel{D_{22}^{-1}V_2(0)} - \int_0^t \Pi_{22}(t-\tau)\dot{V}_2(\tau)\,d\tau$$

$$= D_{22}^{-1}V_2(t) - \Pi_{22}(t)V_2(0) - \int_0^t \Pi_{22}(t-\tau)\dot{V}_2(\tau)\,d\tau$$

So:

$$\boxed{m_1\ddot{r}_1 = f_1 + V_{12}(t)\left[D_{22}^{-1}V_2(t) - \Pi_{22}(t)V_2(0)\right] + R_1(t) - V_{12}(t)\int_0^t \Pi_{22}(t-\tau)\dot{V}_2(\tau)\,d\tau} \quad (+)$$

We shall <u>redefine the random</u> force to have its average to be zero:

$$\boxed{m_1 \ddot{r}_1 = f_1 + V_{12}(t)\left[D_{22}^{-1} V_2(t) \right] + R_1'(t) - V_{12}(t)\int_0^t \Pi_{22}(t-\tau)\, \dot{V}_2(\tau)\, d\tau}$$

where

$$\boxed{\begin{aligned} R_1'(t) &= R_1(t) - V_{12}(t)\,\Pi_{22}(t)\,V_2(0) \\ \overline{R}_1'(t) &= 0 \end{aligned}}$$

<u>Dispersion</u> $\quad R_1(t) = -V_{12}(t)\left[\dot{\Omega}_{22}(t) X_2(0) + \Omega_{22}(t) \dot{X}_2(0) \right]$

$$\sigma^2 = \left\langle \left(R_1'(t) - \overline{R}_1'(t) \right)^2 \right\rangle = \left\langle R_1'(t)^2 \right\rangle$$

$$= \left\langle V\left(\dot{\Omega}(t) X(0) + \Omega(t) \dot{X}(0) + \Pi(t) V(0) \right)\left(X^\dagger(0)\, \dot{\Omega}(t) + \dot{X}^\dagger(0)\, \Omega(t) + V^\dagger(0)\, \Pi(t) \right) V^\dagger \right\rangle$$

$$= V \dot{\Omega}(t) \langle X(0) X^\dagger(0) \rangle \dot{\Omega}(t) V^\dagger + V \Omega(t) \langle \dot{X}(0) \dot{X}^\dagger(0) \rangle \Omega(t) V^\dagger$$
$$+ V \dot{\Omega}(t) \langle X(0) \rangle V^\dagger(0)\, \Pi(t) V^\dagger + V \Pi(t) V(0) \langle X^\dagger(0) \rangle \dot{\Omega}(t) V^\dagger$$
$$+ V \Pi(t) V(0) V^\dagger(0) \Pi(t) V^\dagger$$

where

$$\langle X_2(0) \rangle = -D_{22}^{-1} V_2(0)$$

$$\langle X_2(0) X_2^\dagger(0) \rangle = \frac{1}{\beta} D_{22}^{-1} + \left(D_{22}^{-1} V_2(0) \right)\left(V_2^\dagger(0)\, D_{22}^{-1} \right)$$

$$\langle \dot{X}_2(0) \dot{X}_2^\dagger(0) \rangle = \frac{1}{\beta} \mathbb{1}$$

so that:

$$\sigma^2 = V_{12}\,\dot\Omega_{22}(t)\left[\frac{1}{\beta}D_{22}^{-1} + \left(D_{22}^{-1}V_2(0)\right)\left(V_2^\dagger(0)D_{22}^{-1}\right)\right]\dot\Omega_{22}(t)\,V_{21}$$ ✓

$$+\frac{1}{\beta}V_{12}\,\Omega_{22}(t)\,\Omega_{22}(t)V_{21} - V_{12}\,\dot\Omega_{22}(t)\,D_{22}^{-1}V_2(0)V_2^\dagger(0)\,\Pi_{22}(t)V_{21}$$ ✓

$$- V_{12}\Pi_{22}(t)V_2(0)\,\cancel{D_{22}^{-1}}\,V_2^\dagger(0)\,D_{22}^{-1}\,\dot\Omega_{22}(t)V_{21}$$ ✓

$$+\left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^\dagger(0)\Pi_{22}(t)V_{21}\right)$$ ✓

Here:

$$\dot\Omega_{22}(t)D_{22}^{-1} = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\cancel{\omega}}\cos\omega_\lambda t\ \sum_{\lambda'}\frac{e_{\lambda'}e_{\lambda'}^\dagger}{\omega_{\lambda'}^2} = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos\omega_\lambda t$$

$$= \Pi_{22}(t)\,;$$ ✓

$$\Omega_{22}(t)\Omega_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\sin^2\omega_\lambda t$$ ✓

~~so that~~ $\cancel{\sigma^2 = \frac{1}{\beta}V_{12}}$

$$\dot\Omega_{22}(t)D_{22}^{-1}\dot\Omega_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos^2\omega_\lambda t$$ ✓

so that:

$$\sigma^2 = \frac{1}{\beta}V_{12}\underbrace{\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\left(\sin^2\omega_\lambda t + \cos^2\omega_\lambda t\right)}_{D_{22}^{-1}}V_{21} + \cancel{\left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^\dagger(0)\Pi_{22}(t)V_{21}\right)}$$ ✓

$$- \cancel{\left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^\dagger(0)\Pi_{22}(t)V_{21}\right)}$$ ✓

$$-\cancel{\left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^\dagger(0)\Pi_{22}(t)V_{21}\right)} + \cancel{\left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^\dagger(0)\Pi_{22}(t)V_{21}\right)}$$

$$= \frac{1}{\beta}V_{12}D_{22}^{-1}V_{21}\,,$$ ✓

so that

$$\boxed{\sigma^2 = \frac{1}{\beta}V_{12}(t)\,D_{22}^{-1}\,V_{21}(t)}$$ ⊕

Correlation function

$$R_1'(t) = -V_{12}\left[\dot{\Omega}_{22}(t)X_2(0) + \Omega_{22}(t)\dot{X}_2(0)\right] + V_{12}\Pi_{22}(t)V_2(0)$$

the random force. Then,

$$\langle R_1'(t)R_1'(t')^+\rangle = V_{12}\langle(\dot{\Omega}X(0) + \Omega\dot{X}(0) + \Pi V(0))(X^+(0)\dot{\Omega} + \dot{X}^+\Omega +$$

$$+ V^+(0)\Pi)\rangle V_{21} =$$

$$= V_h\{\dot{\Omega}\langle X(0)X^+(0)\rangle\dot{\Omega} + \dot{\Omega}\langle X(0)\rangle V^+(0)\Pi + \Omega\langle\dot{X}(0)\dot{X}^+(0)\rangle\Omega$$

$$+ \Pi V(0)\langle X^+(0)\rangle\dot{\Omega} + \Pi V(0)V^+(0)\Pi\}V_{21}$$

$$= V_h\{\dot{\Omega}(\tfrac{1}{\beta}\Delta^{-1} + \Delta^{-1}V(0)V^+(0)\Delta^{-1})\dot{\Omega} - \dot{\Omega}\Delta^{-1}VV^+\Pi + \tfrac{1}{\beta}\Omega\Omega$$

$$-\Pi VV^+\Delta^{-1}\dot{\Omega} + \Pi VV^+\Pi\}V_{21}$$

$$= V_h\{\tfrac{1}{\beta}(\dot{\Omega}\Delta^{-1}\dot{\Omega} + \Omega\Omega) + (\dot{\Omega}\Delta^{-1}V_0)(V_0^+\Delta^{-1}\dot{\Omega}) - (\dot{\Omega}\Delta^{-1}V_0)(V_0^+\Pi)$$

$$-(\Pi V_0)(V_0^+\Delta^{-1}\dot{\Omega}) + (\Pi V_0)(V_0^+\Pi)\}V_{21}$$

Here:

$$\dot{\Omega}_t\Delta^{-1}\dot{\Omega}_{t'} = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda t\cos\omega_\lambda t'$$

$$\Omega_t\Omega_t = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\sin\omega_\lambda t\sin\omega_\lambda t'$$

$$\dot{\Omega}_t\Delta^{-1} = \Pi_t, \quad \Delta^{-1}\dot{\Omega}_{t'} = \Pi_{t'}$$

Therefore,

$$\langle R_1'(t)R_1'(t')^+\rangle = \frac{1}{\beta}V\left[\sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda(t-t')\right]V^+ + \cancel{(V\Pi_t V_0)(V_0^+\Pi_{t'}V^+)}$$

$$-\cancel{(V\Pi_t V_0)(V_0^+\Pi_{t'}V^+)} - \cancel{(V\Pi_t V_0)(V_0^+\Pi_{t'}V^+)} + \cancel{(V\Pi_t V_0)(V_0^+\Pi_{t'}V^+)},$$

so that

$$\boxed{\langle R_1'(t)\, R_1'(t')^{+}\rangle = \frac{1}{\beta} V_{12}(t)\, \Pi_{22}(t-t')\, V_{21}(t')}$$

which is nearly the kernel of the integral-friction term.
In the approximation of region 1_b being stochastic,

$$V_{h} \to V_{ij} = \frac{1}{\sqrt{m_j}}\, \varphi_{ij} = \sqrt{m_i}\, D_{ij}$$

and

$$\boxed{\langle R_i'(t)\, R_{i'}'(t')\rangle = \frac{1}{\beta} \sqrt{m_i m_{i'}} \sum_{jj'\in 2} D_{ij}\, \Pi_{jj'}(t-t')\, D_{j'i'} \qquad i,i'\in 1_b}$$

The integral term:

$$-\sum_{i'\in 1_b} \int_0^t \left(\sqrt{m_i m_{i'}} \sum_{jj'\in 2} D_{ij}\, \Pi_{jj'}(t-\tau)\, D_{j'i'} \right) \dot{u}_{i'}(\tau)\, d\tau$$

$$\equiv -\beta \sum_{i'\in 1_b} \int_0^t \langle R_i'(t)\, R_{i'}'(\tau)\rangle\, \dot{u}_{i'}(\tau)\, d\tau .$$

i.e. the friction is indeed given by the correlation function of the random force.