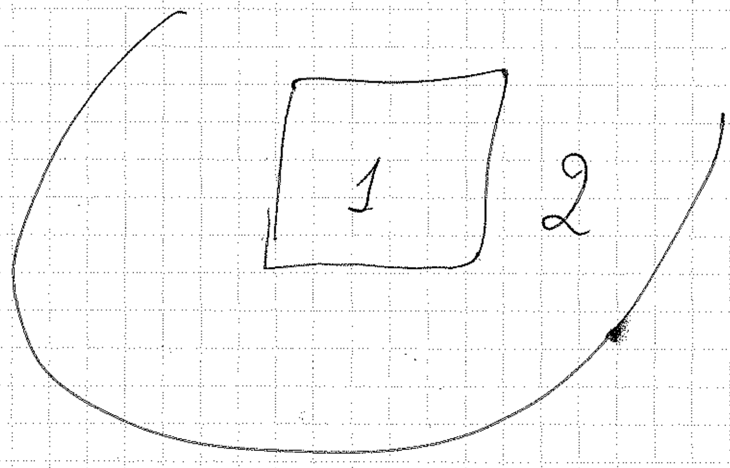
28 Marta 2008

Summary

§1. Equations of motion

1 - general
2 - harmonic



1. Hamiltonian:

$$\mathcal{H} = \underbrace{\mathcal{H}_1}_{\text{only within region 1}} + \underbrace{\sum_{j\in 2} h_j u_j}_{\text{interaction between two regions}} + \frac{1}{2}\sum_{jj'\in 2} u_j \Phi_{jj'} u_{j'} + \frac{1}{2}\sum_{j\in 2} m_j \dot{u}_j^2$$

2. EOM:

$$\begin{cases} m_1 \ddot{r}_1 = -\dfrac{\partial \mathcal{H}_1}{\partial r_1} - \sum\limits_{j\in 2} \dfrac{\partial h_j}{\partial r_1} u_j & , i\in 1 \\ m_j \ddot{u}_j = -h_j - \sum\limits_{j'\in 2} \Phi_{jj'} u_{j'} & , j\in 2 \end{cases}$$

New notation for region 2:

$$X_j = \sqrt{m_j}\, u_j \quad , \quad V_j = h_j / \sqrt{m_j}$$

Then EOM for $\{u_j, j\in 2\}$ reads:

$$\ddot{X}_j = -V_j - \sum_{j'\in 2} D_{jj'} X_{j'} \quad , \; j\in 2 \quad , \quad D_{jj'} = \frac{1}{\sqrt{m_j}} \Phi_{jj'} \frac{1}{\sqrt{m_{j'}}}$$

Its solution:

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

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

where $\quad D_{22} e_\lambda = \omega_\lambda^2 e_\lambda \quad , \quad D_{22} = \sum_\lambda \omega_\lambda^2 e_\lambda e_\lambda^+$

$\sum_\lambda e_\lambda e_\lambda^+ = \mathbb{1}$ and $e_\lambda^+ e_{\lambda'} = \delta_{\lambda\lambda'}$ (completeness & orthogonality)

ξ_λ - normal coordinates: $\quad X_2 = \sum_\lambda e_\lambda \xi_\lambda \quad (X_j = \sum_\lambda e_{j\lambda} \xi_\lambda)$

The part of $\mathcal{H}$, which depends on u_2, namely $\quad \xi_\lambda = e_\lambda^+ X_2$

$$\mathcal{H}_2 = h_2^+ u_2 + \frac{1}{2} u_2^+ \Phi_{22} u_2 + T_2 \quad ,$$

reads in normal coordinates:

$$\mathcal{H}_2 = \sum_\lambda \left(\frac{1}{2} \omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda + \frac{1}{2} \dot{\xi}_\lambda^2 \right) = \sum_\lambda \left(\frac{1}{2} \dot{\xi}_\lambda^2 + \mathcal{V}_\lambda \right)$$

$$V_\lambda(t) = e_\lambda^+ V_2(t) \qquad \left(V_\lambda = \sum_{j \in 2} e_{j\lambda} V_j(t) \right)$$

4. Eq. of motion for 1:

$$m_i \ddot{r}_i = f_i - \sum_{j \in 2} \frac{\partial V_j}{\partial r_i} x_j \quad \left(\to m_1 \ddot{r}_1 = f_1 - V_{12} X_2 \right)$$

is worked into:

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

$$f_i = - \frac{\partial \mathcal{H}_1}{\partial r_i}$$

Take the integral by parts:

$$\Lambda_{22}(t) = \int_0^t \Omega_{22}(\tau) d\tau \quad \cancel{d\Lambda_{22} = \Omega_{22}(t) dt}$$

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

$$= \underbrace{-\Lambda(0)}_{=0} V(t) + \Lambda(t) V(0) + \int_0^t \Lambda(t-\tau) \dot{V}(\tau) d\tau$$

$$= + \Lambda(t) V(0) + \int_0^t \Lambda(t-\tau) \dot{V}(\tau) d\tau$$

resulting:

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

Here

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

$$= \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda t\Big|_t^0 = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2} - \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda t = D_{22}^{-1} - \Pi_{22}(t),$$

where $$\Pi_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda t .$$

This gives:

$$V_{12}\Lambda_{22}V_2(0) + \int_0^t V_{12}\Lambda_{22}(t-\tau)\dot V_2(\tau)\,d\tau = V_{12}(\cancel{D_{22}^{-1}} - \Pi_{22})V_2(0) +$$

$$+ V_{12}D_{22}^{-1}\underbrace{\int_0^t \dot V_2(\tau)\,d\tau}_{V_2(t) - \cancel{V_2(0)}} - V_{12}\int_0^t \Pi_{22}(t-\tau)\dot V_2(\tau)\,d\tau$$

$$= -V_{12}\Pi_{22}(t)V_2(0) + V_{12}D_{22}^{-1}V_2(t) - V_{12}\int_0^t \Pi_{22}(t-\tau)\dot V_2(\tau)\,d\tau$$

This finally yields:

$$m_1\ddot r_1 = f_1 - \left[V_{12}\left(\dot\Omega_{22}(t)X_2(0) + \Omega_{22}(t)\dot X_2(0)\right) + V_{12}\Pi_{22}(t)V_2(0)\right]$$

$$+ V_{12}D_{22}^{-1}V_2(t) - V_{12}\int_0^t \Pi_{22}(t-\tau)\dot V_2(\tau)\,d\tau$$

5. Introduce the <u>random force</u>:

$$\boxed{R_1(t) = -V_{12}\left[\dot\Omega_{22}(t)X_2(0) + \Omega_{22}(t)\dot X_2(0) + \Pi_{22}(t)V_2(0)\right]}$$

EOM:

$$\boxed{m_1\ddot r_1 = \tilde f_1 + R_1(t) - \int_0^t V_{12}(t)\Pi_{22}(t-\tau)\dot V_2(\tau)\,d\tau}$$

$$\boxed{\tilde f_1 = f_1 + V_{12}(t)D_{22}^{-1}V_2(t)}$$

§2. Statistical averaging over region 2

1. Statistical distribution function corresponding to region 2:

$$\rho_2 = \frac{1}{Z_2} e^{-\beta \mathcal{H}_2}, \quad Z_2 = \sum_\lambda Z_{\xi_\lambda} Z_{\dot\xi_\lambda},$$

$$Z_{\xi_\lambda} = \sqrt{\frac{2\pi}{\beta\omega_\lambda^2}}\, e^{\frac{\beta V_\lambda^2(t)}{2\omega_\lambda^2}}, \quad Z_{\dot\xi_\lambda} = \sqrt{\frac{2\pi}{\beta}}$$

Averages (at $t=0$):

$$\overline{\xi_\lambda(0)} = \frac{1}{Z_{\xi\lambda}} \int \xi_\lambda e^{-\beta v_\lambda} d\xi_\lambda = -\frac{V_\lambda(0)}{\omega_\lambda^2} \equiv \langle \xi_\lambda(0)\rangle$$

$$\langle \xi_\lambda(0)\, \xi_{\lambda'}(0)\rangle = \frac{\delta_{\lambda\lambda'}}{\beta\omega_\lambda^2} + \frac{V_\lambda(0)}{\omega_\lambda^2} \cdot \frac{V_{\lambda'}(0)}{\omega_{\lambda'}^2}$$

$$\langle \dot\xi_\lambda(0)\, \xi_{\lambda'}(0)\rangle = 0, \quad \langle \dot\xi_\lambda(0)\, \dot\xi_{\lambda'}(0)\rangle = \delta_{\lambda\lambda'} \frac{1}{\beta}$$

2. Statistical averages of X_2:

$$\langle X_2(0) X_2^\dagger(0)\rangle = \sum_{\lambda\lambda'} e_\lambda e_{\lambda'}^\dagger \langle \xi_\lambda(0)\, \xi_{\lambda'}(0)\rangle =$$

$$= \frac{1}{\beta}\sum_\lambda \frac{e_\lambda e_{\lambda'}^\dagger}{\omega_\lambda^2} + \sum_\lambda \frac{e_\lambda V_\lambda(0)}{\omega_\lambda^2} \cdot \sum_{\lambda'} \frac{V_{\lambda'}(0) e_{\lambda'}^\dagger}{\omega_{\lambda'}^2}$$

$$= \frac{1}{\beta} D_{22}^{-1} + \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} V_2(0) \cdot \sum_{\lambda'} \frac{V_2^\dagger(0) e_{\lambda'} e_{\lambda'}^\dagger}{\omega_{\lambda'}^2}$$

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

$$\langle \dot X_2(0) X_2^\dagger(0)\rangle = 0;$$

$$\langle \dot X_2(0) \dot X_2^\dagger(0)\rangle = \sum_{\lambda\lambda'} e_\lambda e_{\lambda'}^\dagger \langle \dot\xi_\lambda(0)\, \dot\xi_{\lambda'}(0)\rangle = \frac{1}{\beta}\sum_\lambda e_\lambda e_\lambda^\dagger = \frac{1}{\beta}\mathbb{1}.$$

Average of $X_2(0)$:

$$\langle X_2(0)\rangle = \sum_\lambda e_\lambda \langle \xi_\lambda(0)\rangle = -\sum_\lambda e_\lambda \frac{V_\lambda(0)}{\omega_\lambda^2} = -\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} V_2(0) = -D_{22}^{-1} V_2(0)$$

$$\langle \dot X(0)\rangle = 0$$

§ 3. Random force

1. Average of the random force is zero:

$$\langle R_1(t)\rangle = -V_{12}\Big(\dot\Omega_{22}(t)\,\langle X_2(0)\rangle + \Omega_{22}(t)\,\underbrace{\langle \dot X_2(0)\rangle}_{=0} + \Pi_{22}(t)V_2(0)\Big)$$

$$= +V_{12}\Big[\dot\Omega_{22}(t)D_{22}^{-1}\Big]V_2(0) - V_{12}\Pi_{22}(t)V_2(0)$$

Here:

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

$$= \sum_\lambda \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda t \equiv \Pi_{22}(t)$$

hence:

$$\langle R_1(t)\rangle = 0$$

2. Correlation function:

$$\langle R_1(t)R_1^\dagger(t')\rangle = V_{12}(t)\dot\Omega_{22}(t)\langle X_2(0)X_2^\dagger(0)\rangle\dot\Omega_{22}(t')V_{21}$$

$$+V_{12}(t)\dot\Omega_{22}(t)\langle X_2(0)\rangle V_2^\dagger(0)\Pi_{22}(t')V_{21}(t') + V_{12}(t)\Omega_{22}(t)\langle \dot X_2(0)\dot X_2^\dagger(0)\rangle\Omega_{22}(t')V_{21}(t')$$

$$+V_{12}(t)\Pi_{22}(t)V_2(0)\langle X_2^\dagger(0)\rangle\dot\Omega_{22}(t')V_{21}(t') + \big(V_{12}\Pi_{22}(t)V_2(0)\big)\big(V_2^\dagger(0)\Pi_{22}(t')V_{21}\big)$$

$$= V_{12}\dot\Omega_{22}\Big[\frac{1}{\beta}D_{22}^{-1} + \big(D_{22}^{-1}V_2(0)\big)\big(V_2^\dagger(0)D_{22}^{-1}\big)\Big]\dot\Omega_{22}V_{21}$$

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

$$-V_{12}\Pi_{22}V_2(0)V_2^\dagger(0)D_{22}^{-1}\dot\Omega_{22}V_{21} + \big(V_{12}\Pi_{22}(t)V_2(0)\big)\big(V_2^\dagger(0)\Pi_{22}(t')V_{21}\big)$$

$$= \frac{1}{\beta}V_{12}\dot\Omega_{22}D_{22}^{-1}\dot\Omega_{22}V_{21} + \big(V_{12}\dot\Omega_{22}D_{22}^{-1}V_2(0)\big)\big(V_2^\dagger(0)D_{22}^{-1}\dot\Omega_{22}V_{21}\big)$$

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

$$-\big(V_{12}\Pi_{22}V_2(0)\big)\big(V_2^\dagger(0)D_{22}^{-1}\dot\Omega_{22}V_{21}\big) + \big(V_{12}\Pi_{22}V_2(0)\big)\big(V_2^\dagger(0)\Pi_{22}V_{21}\big)$$

Here we need some identities:

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

$$\Pi_{22}(t)\,\dot{\Omega}_{22}(t') = \sum_{\lambda} \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2}\cos\omega_\lambda t \sum_{\lambda'} \frac{e_{\lambda'} e_{\lambda'}^+}{\cancel{\omega_{\lambda'}^2}} \cos\omega_{\lambda'} t'$$

$$= \sum_{\lambda} \frac{e_\lambda e_\lambda^+}{\omega_\lambda^2} \cos\omega_\lambda t \cos\omega_{\lambda'} t' \quad ;$$

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

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

These yield:

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

$$+ \cancel{\left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^+(0)\Pi_{22}(t')V_{21}\right) - \left(V_{12}\Pi_{22}(t)V_2(0)\right)\left(V_2^+(0)\Pi_{22}(t')V_{21}\right)}$$

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

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

~~4/ Therefore, the EOM now can be rewritten as follows:~~

$$\cancel{m_1\ddot{r}_1 = \tilde{f}_1 + R_1(t) - \beta\int_0^t \langle R_1(t) R_1^+(\tau)\rangle \dot{V}_2(\tau)\,d\tau}$$

5. Dispersion of the random force:

$$\sigma_1^2 = \langle R_1^2(t)\rangle = \frac{1}{\beta} V_{12}(t)\Pi_{22}(0)V_{21}(t) = \frac{1}{\beta}V_{12}(t) D_{22}^{-1} V_{21}(t)$$

~~This is a Gaussian!~~

~~6. If we assume that the correlation function decays as $|t-t'| \to \infty$,~~

~~then~~ $\cancel{\langle R_1(t) R_1^+(t')\rangle \to 0 \text{ as } |t-t'| \to \infty}$

~~Then we can use the Markovian approximation:~~

$\cancel{\int_0^{t_0} f(t,\tau)\,d\tau}$ if $\Pi(t-t') \to 0$ when $|t-t'| \to \infty$,

5. This is a Gaussian random force, since it is given as a linear combination of $X_2(0)$ and $\dot{X}_2(0)$, which are Gaussian stochastic variables.

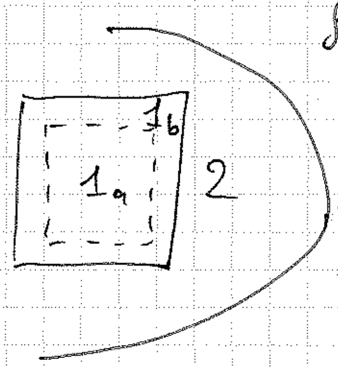
$$\boxed{\mathcal{S}(R_i) = \frac{1}{\sqrt{2\pi}\,\sigma_i} \exp\left[-\frac{R_i^2}{2\sigma_i^2}\right]}$$

In principle, we can formulate

$$\mathcal{S}(\{R_i\}_{i\in 1_b})$$

as a joint probability function (multidimensional), but practically this is not convenient. By i it is meant an atom in 1_b <u>and</u> one of its components (x, y, z).

§4. Stochastic layer approximation



$$V_2 = \| V_j \|, \quad V_j = \frac{1}{\sqrt{m_j}} h_j = \frac{1}{\sqrt{m_j}} \sum_{i \in 1_b} \varphi_{ji} u_i$$

$$V_{12} = \left\| \frac{\partial V_j}{\partial u_i} \right\|, \quad \frac{\partial V_j}{\partial u_i} = \begin{cases} \frac{1}{\sqrt{m_j}} \varphi_{ji}, & i \in 1_b \\ 0, & i \in 1_a \end{cases}$$

1. EOM for atoms in 1_a:

$\boxed{m_i \ddot{u}_i = f_i}$, $i \in 1_a$ since $V_{12} = 0$ for $i \in 1_a$.

EOM for atoms in 1_b:

$$m_i \ddot{u}_i = f_i + \left(V_{12} D_{22}^{-1} V_2 \right)_i - \int_0^t \left(V_{12} \Pi_{22}(t-\tau) \dot{V}_2(\tau) \right)_i d\tau$$

where

$$\left(V_{12} D_{22}^{-1} V_2 \right)_i = \sum_{jj' \in 2} \frac{1}{\sqrt{m_j}} \varphi_{ij} D^{-1}_{jj'} \frac{1}{\sqrt{m_{j'}}} \sum_{i' \in 1_b} \varphi_{j'i'} u_{i'}$$

$$= \sum_{i' \in 1_b} \sqrt{m_i m_{i'}} \sum_{jj' \in 2} \left(D_{ij} D^{-1}_{jj'} D_{j'i'} \right) u_{i'} ;$$

$$f_i = \underbrace{f_i^{(a)}}_{\text{from atoms in } 1_a} - \underbrace{\sum_{i' \in 1_b} \varphi_{ii'} u_{i'}}_{\text{due to atoms in } 1_B} = f_i^{(a)} - \sum_{i' \in 1_b} \sqrt{m_i m_{i'}} D_{ii'} u_{i'} ;$$

$$\dot{V}_2(\tau) \to \dot{V}_j(\tau) = \frac{1}{\sqrt{m_j}} \sum_{i' \in 1_b} \varphi_{ji'} \dot{u}_{i'}$$

and

$$\left(V_{12}(t) \Pi_{22}(t-\tau) \dot{V}_2(\tau) \right)_i = \sum_{jj' \in 2} \frac{1}{\sqrt{m_j}} \varphi_{ij} \Pi_{jj'}(t-\tau) \frac{1}{\sqrt{m_{j'}}} \sum_{i' \in 1_b} \varphi_{j'i'} \dot{u}_{i'}$$

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

so that we obtain ($i \in 1_b$):

$$\boxed{m_i \ddot{u}_i = f_i^{(a)} - \sum_{i' \in 1_b} \sqrt{m_i m_{i'}} \left(D_{11} - D_{12} D_{22}^{-1} D_{21} \right)_{ii'} u_{i'} + R_i - \sum \sqrt{m_i m_{i'}} \int_0^t \left(D_{12} \Pi_{22}(t-\tau) D_{21} \right)_{ii'} \dot{u}_{i'}(\tau) \, d\tau}$$

2. Correlation function:

$$\langle R_i(t) R_{i'}(t') \rangle = \frac{1}{\beta} \sum_{jj' \in 2} \frac{1}{\sqrt{m_j}} \Phi_{ij} \Pi_{jj'}(t-t') \frac{1}{\sqrt{m_{j'}}} \Phi_{j'i'}$$

$$= \frac{\sqrt{m_i m_{i'}}}{\beta} \sum_{jj'} D_{ij} \Pi_{jj'}(t-t') D_{j'i'} = \frac{\sqrt{m_i m_{i'}}}{\beta} \left(D_{12} \Pi_{22}(t-t') D_{21} \right)_{ii'}$$

so that the EOM for $i \in 1_b$ becomes:

$$m_i \ddot{u}_i = f_i^{(a)} - \sum_{i' \in 1_b} \sqrt{m_i m_{i'}} \left(D_{11} - D_{12} D_{22}^{-1} D_{21} \right)_{ii'} u_{i'}$$

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

$$\boxed{\begin{aligned} m_i \ddot{u}_i = & \left[f_i^{(a)} - \sum_{i' \in 1_b} \left(\Phi_{11} - \Phi_{12} \Phi_{22}^{-1} \Phi_{21} \right)_{ii'} u_{i'} \right] \\ & + R_i - \sum_{i' \in 1_b} \beta \int_0^t \underbrace{\langle R_i(t) R_{i'}(\tau) \rangle}_{\text{depends on } t-\tau} \dot{u}_{i'}(\tau)\, d\tau \end{aligned}}$$

3. The random force:

$$\boxed{\begin{aligned} & \langle R_i(t) \rangle = 0 \\ & \sigma_i^2 = \langle R_i^2(t) \rangle = \frac{m_i}{\beta} \left(D_{12} \Pi_{22}(0) D_{21} \right)_{ii} \end{aligned}}$$

Gaussian stochastic variable.

4. Markovian approximation + diagonal approximation (kernel):

$$m_i \ddot{u}_i = f_i^{(a)} + \tilde{f}_i^{(b)} - \gamma_i (\dot{u}_i m_i) + R_i \Rightarrow \dot{p}_i = f_i^{(a)} + f_i^{(b)} \underbrace{- \gamma_i p_i}_{\text{friction}} + R_i$$

with the friction coefficient

$$\boxed{\gamma_i = \int_0^\infty \left(D_{12} \Pi_{22}(\tau) D_{21} \right)_{ii} d\tau}$$

where $f_i^{(b)} = - \sum \left(\Phi_{11} - \Phi_{12} \Phi_{22}^{-1} \Phi_{21} \right)_{ii'} u_{i'}$ is the force from 1_b on $i \in 1_b$.

If $\Pi_{22}(\tau) \to 0$ very quickly as $\tau \to \infty$, then

$$\int_0^\infty \Pi_{22}(\tau)\,d\tau \simeq \Pi_{22}(0)\,(\delta\tau)\cdot\eta, \quad \eta - \text{numerical factor}$$

where $\delta\tau$ is the relaxation time. Then,

$$\boxed{\gamma_i = \left(D_{12}\Pi_{22}(0)D_{21}\right)_{ii}\,\delta\tau\cdot\eta}$$

The relationship with dispersion:

$$\sigma_i^2 = \frac{m_i}{\beta}\,\frac{\gamma_i}{\delta\tau\cdot\eta} = \frac{m_i}{\beta}\gamma_i/\eta\delta\tau = \frac{k_B T\,\gamma_i m_i}{\eta\cdot\delta\tau} \equiv \mathbb{C}\,\frac{k_B T m_i \gamma_i}{\delta\tau},$$

wher $\mathbb{C}$ – numerical factor to be determined from the condition that the system would become canonical at equilibrium.

§ 5. Another kernel (as in Adelman-Doll)

- Another way of representing an EOM for 1:

$$\Lambda'_{22}(t) = \int_t^\infty \Omega_{22}(\tau)\, d\tau$$

would guarantee to go to 0 as $t \to \infty$. With this choice:

$$\int_0^t \Omega(t-\tau) V(\tau)\, d\tau = \Lambda'(0) V(t) - \Lambda'(t) V(0) - \int_0^t \Lambda'(t-\tau) \dot{V}(\tau)\, d\tau$$

and the EOM reads:

$$m_1 \ddot{r}_1 = f_1 - V_{12}\left(\dot{\Omega}_{22}(t) X_2(0) + \Omega_{22}(t) \dot{X}_2(0)\right) + V_{12} \Lambda'_{22}(0) V_2(t) - V_{12} \Lambda'_{22}(t) V_2(0) - \int_0^t V_{12} \Lambda'_{22}(t-\tau) \dot{V}_2(\tau)\, d\tau$$

- With the same definition of the random force:

$$R_1(t) = -V_{12}\left(\dot{\Omega}_{22}(t) X_2(0) + \Omega_{22}(t) \dot{X}_2(0) + \Pi_{22}(t) V_2(0)\right),$$

we obtain:

$$m_1 \ddot{r}_1 = f_1 + R_1(t) + V_{12} \Lambda'_{22}(0) V_2(t) - V_{12}\left(\Lambda'_{22}(t) - \Pi_{22}(t)\right) V_2(0) - \int_0^t V_{12} \Lambda'_{22}(t-\tau) \dot{V}_2(\tau)\, d\tau$$

- Then,

$$\Lambda'_{22}(0) = \int_0^\infty \Omega_{22}(\tau)\, d\tau = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \int_0^\infty \sin\omega_\lambda \tau\, d\tau$$

$$= \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda} \frac{\cos\omega_\lambda \tau}{\omega_\lambda}\Big|_\infty^0 = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} - \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \cos\omega_\lambda \tau \Big|_{\tau\to\infty}$$

$$= D_{22}^{-1} - \Pi_{22}(\infty).$$

Also, $\frac{d}{dt}\left(\Lambda'_{22}(t) - \Pi_{22}(t)\right) = -\Omega_{22}(t) - \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}(-\omega_\lambda \sin\omega_\lambda t) =$

$$= -\Omega_{22}(t) + \Omega_{22}(t) = 0,$$

i.e. $\Lambda'_{22}(t) - \Pi_{22}(t)$ is a constant, C_{22}:

$$C_{22} = \Lambda'_{22}(t) - \Pi_{22}(t) \equiv \Lambda'_{22}(0) - \Pi_{22}(0) =$$

$$= D_{22}^{-1\prime} - \Pi_{22}(\infty) - D_{22}^{-1\prime} \equiv -\Pi_{22}(\infty).$$

This gives for the two terms in the EOM:

$$V_{12}\Lambda'_{22}(0)\, V_2(t) - V_{12}\left(\Lambda'_{22}(t) - \Pi_{22}(t)\right) V_2(0)$$

$$= V_{12}\left(D_{22}^{-1\prime} - \Pi_{22}(\infty)\right) V_2(t) + V_{12}\Pi_{22}(\infty)\, V_2(0)$$

$$= \underbrace{V_{12} D_{22}^{-1\prime} V_2(t)}_{\substack{\text{additional} \\ \text{force for } f_1}} - \underbrace{V_{12}\Pi_{22}(\infty)\left(V_2(t) - V_2(0)\right)}_{\substack{\text{this term should tend to} \\ \underline{\text{zero}} \text{ at large times based on the} \\ \text{same assumption as in the previous method.}}}$$

We thus obtain:

$$\boxed{m_1 \ddot{r}_1 = \tilde{f}_1 + R_1(t) - \int_0^t V_{12}\Lambda'_{22}(t-\tau)\, \dot{V}_2(\tau)\, d\tau}$$