24.04.08

Distribution for a subsystem which is in contact with harmonic thermostat.	this was apparently done in Teleshun's book, pp. 103-104

1. The Hamiltonian:

$$\mathcal{H} = \mathcal{H}_1(u_1, \dot{u}_1) + \frac{1}{2} u_2^+ \Phi_{22} u_2 + \frac{1}{2} \dot{u}_2^+ M_2 u_2 + h_2^+ u_2$$

$$u_2 = \frac{1}{\sqrt{m_2}} X_2, \quad \dot{u}_2 = m_2^{-1/2} \dot{X}_2 \quad \left(p_2 = m_2 \dot{u}_2 = m_2 m_2^{-1/2} \dot{X}_2 = m_2^{1/2} \dot{X}_2 \right)$$

$$\hookrightarrow \mathcal{H} = \mathcal{H}_1 + \overbrace{\frac{1}{2} X_2^+ D_{22} X_2 + \frac{1}{2} \dot{X}_2^+ \dot{X}_2}^{\mathcal{H}_2} + \overbrace{V_2^+ X_2}^{\mathcal{H}_{12}}$$

2. The canonical distribution

$$\rho(u_1, u_2; p_1, p_2) = \frac{1}{Z} e^{-\beta(\mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12})},$$

$$Z = \int du_1 \int du_2 \int dp_1 \int dp_2 \; e^{-\beta(\mathcal{H}_1 + \mathcal{H}_{12} + \mathcal{H}_2)}$$

$$= \int du_1 \int dp_1 \, e^{-\beta \mathcal{H}_1} \Big[\underbrace{\int du_2 \int dp_2 \, e^{-\beta(\mathcal{H}_2 + \mathcal{H}_{12})}}_{Z_2(u_1)} \Big]$$

$$\hookrightarrow \rho = \frac{Z_2(u_1)}{Z} \underbrace{\left[\frac{1}{Z_2(u_1)} e^{-\beta(\mathcal{H}_2 + \mathcal{H}_{12})} \right]}_{\rho_2(u_2, p_2; u_1)} e^{-\beta \mathcal{H}_1}$$

$\rho_2(u_2, p_2; u_1) \to$ "conditional" distribution when u_1 is fixed.

$$\boxed{\rho = \frac{Z_2(u_1)}{Z} e^{-\beta \mathcal{H}_1} \cdot \rho_2(u_2, p_2; u_1)}$$

$$\boxed{Z = \int du_1 \int dp_1 \, e^{-\beta \mathcal{H}_1} Z_2(u_1)}$$

3. The distribution for region 1 is obtained by integrating over region 2:

$$\rho_1(u_1, p_1) = \int du_2 \int dp_2\, \rho =$$

$$= \frac{Z_2(u_1)}{Z} e^{-\beta \mathcal{H}_1} \left[\int du_2 dp_2\, \rho_2'(u_2, p_2; u_1) \right]$$

Let us do the integration:

$$\int du_2\, dp_2\, \rho_2 = \int dx_2\, d\dot{x}_2 \left| \frac{\partial(u_2, p_2)}{\partial(x_2, \dot{x}_2)} \right| \rho_2(x_2, \dot{x}_2)$$

The Jacobian:

$$\frac{\partial(u_2, p_2)}{\partial(x_2, \dot{x}_2)} = \begin{vmatrix} \partial u_2/\partial x_2 & \partial p_2/\partial x_2 \\ \partial u_2/\partial \dot{x}_2 & \partial p_2/\partial \dot{x}_2 \end{vmatrix} = \begin{vmatrix} m_2^{-1/2} & 0 \\ 0 & m_2^{1/2} \end{vmatrix} = 1$$

Next,

$$\int d\dot{x}_2\, e^{-\beta \frac{1}{2} \dot{x}_2^\dagger \dot{x}_2} = \prod_j \int d\dot{x}_j\, e^{-\beta \frac{1}{2} \dot{x}_j^2} = \prod_j \sqrt{\frac{\pi}{\frac{1}{2}\beta}} = \prod_j \sqrt{\frac{2\pi}{\beta}} ;$$

also, if $D_{22} e_\lambda = \omega_\lambda^2 e_\lambda$, then

$$x_2^\dagger D_{22} x_2 = x_2^\dagger \left(\sum_\lambda \omega_\lambda^2 e_\lambda e_\lambda^\dagger \right) x_2 = \sum_\lambda \omega_\lambda^2 (e_\lambda^\dagger x_2)^\dagger (e_\lambda^\dagger x_2) \cancel{(x_2^\dagger e_\lambda)(x_2^\dagger e_\lambda)^\dagger}$$

$$\cancel{\xi_\lambda = x_2^\dagger e_\lambda}$$

$$= \sum_\lambda \omega_\lambda^2 \xi_\lambda \xi_\lambda^\dagger \to \sum_\lambda \omega_\lambda^2 \xi_\lambda^2 , \quad \xi_\lambda \text{ - real number}$$

$$\xi_\lambda = e_\lambda^\dagger x_2 , \quad x_2 = e_\lambda \xi_\lambda$$

and

$$\cancel{\int dx_2\, e^{-\beta \frac{1}{2} x_2^\dagger D_{22} x_2} = \int \left| \frac{\partial(x_2)}{\partial(\xi_\lambda)} \right| (d\xi_\lambda)\, e^{-\sum_\lambda \omega_\lambda^2 \frac{\beta}{2} \xi_\lambda^2}}$$

Since

$$\left| \frac{\partial(x_2)}{\partial(\xi_\lambda)} \right| = \left| \partial x_2 / \partial \xi_\lambda \right| = \left| e_{\lambda j} \right| = 1 \quad \left(\text{the transformation is unitary} \right)$$

we ~~get~~:

$$\cancel{\int dx_2\, e^{-\beta \frac{1}{2} x_2^\dagger D_{22} x_2} = \prod_\lambda \int d\xi_\lambda\, e^{-\frac{\beta}{2} \omega_\lambda^2 \xi_\lambda^2} = \prod_\lambda \sqrt{\frac{\pi}{\frac{\beta}{2}\omega_\lambda^2}} = \prod_\lambda \sqrt{\frac{2\pi}{\beta \omega_\lambda^2}}}$$

~~Therefore,~~

$$\cancel{\int dX_2\, d\dot{X}_2\, e^{-\beta(\mathcal{H}_2+\mathcal{H}_{12})}}$$

Therefore, $V_2^\dagger X_2 = V_2^\dagger e_\lambda \xi_\lambda = (e_\lambda^\dagger V_2)^\dagger \xi_\lambda \equiv V_\lambda \xi_\lambda$, and

$$\frac{1}{2} X_2^\dagger D_{21} X_2 + V_2^\dagger X_2 = \frac{1}{2}\sum_\lambda \omega_\lambda^2 \xi_\lambda^2 + \sum_\lambda V_\lambda \xi_\lambda ,$$

where $V_\lambda = e_\lambda^\dagger V_2$.

Integration:

$$\int dX_2\, e^{-\beta(\frac{1}{2} X_2^\dagger D_{21} X_2 + V_2 X_2)} \equiv \prod_\lambda \int d\xi_\lambda\, e^{-\beta\left(\frac{1}{2}\omega_\lambda^2 \xi_\lambda^2 + V_\lambda \xi_\lambda\right)}$$

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

$$= \prod_\lambda e^{+\frac{\beta}{2}\frac{V_\lambda^2}{\omega_\lambda^2}} \cdot \sqrt{\frac{\pi}{\frac{\beta\omega_\lambda^2}{2}}} = \prod_\lambda \sqrt{\frac{2\pi}{\beta\omega_\lambda^2}}\, e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}} .$$

~~The same~~ Thus,

$$\cancel{Z_2(u_1) \approx} \int du_2 \int dp_2\, e^{-\beta(\mathcal{H}_2+\mathcal{H}_{12})} = \left(\sqrt{\frac{2\pi}{\beta}}\right)^{3n} \prod_\lambda \sqrt{\frac{2\pi}{\beta\omega_\lambda^2}}\, e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}}$$

$$= \left(\frac{2\pi}{\beta}\right)^{3n} \prod_\lambda \frac{1}{\omega_\lambda} e^{\beta V_\lambda^2/2\omega_\lambda^2} ,$$

n – # of atoms in region 2; V_λ depends on u_1.

Therefore,

$$\rho_1 = \frac{\cancel{Z_2(u_1)}\, 1}{Z} e^{-\beta\mathcal{H}_1} \cdot \int du_2\, dp_2\, e^{-\beta(\mathcal{H}_2+\mathcal{H}_{12})}$$

$$Z = \int du_1\, dp_1\, e^{-\beta\mathcal{H}_1}\left[\int du_2\, dp_2\, e^{-\beta(\mathcal{H}_2+\mathcal{H}_{12})}\right]$$

so that

$$\rho_{\underline{1}} = \frac{e^{-\beta \mathcal{H}_1} \left(\frac{2\pi}{\beta}\right)^{3n} \prod_\lambda \frac{1}{\omega_\lambda} e^{\frac{\beta V_\lambda^2}{2\omega_\lambda^2}(u_1)}}{\int du_1' dp_1' e^{-\beta \mathcal{H}_1'} \left(\frac{2\pi}{\beta}\right)^{3n} \prod_\lambda \frac{1}{\omega_\lambda} e^{\frac{\beta V_\lambda^2(u_1')}{2\omega_\lambda^2}}}$$

$$= \frac{e^{-\beta \mathcal{H}_1} \prod_\lambda e^{\beta V_\lambda^2 / 2\omega_\lambda^2}}{\int du_1' dp_1' \, e^{-\beta \mathcal{H}_1(u_1', p_1')} \prod_\lambda e^{\beta V_\lambda^2(u_1')/2\omega_\lambda^2}}$$

$$\equiv \frac{e^{-\beta \mathcal{H}_1^{eff}}}{\int du_1 dp_1 \, e^{-\beta \mathcal{H}_1^{eff}}} = \frac{1}{Z} e^{-\beta \mathcal{H}_1^{eff}},$$

where

$$\mathcal{H}_1^{eff} = \mathcal{H}_1 \cancel{+} \sum_\lambda \frac{V_\lambda^2}{2\omega_\lambda^2} = \mathcal{H}_1 - \sum_\lambda \frac{(e_\lambda^\dagger V_2)^\dagger (e_\lambda^\dagger V_2)}{2\omega_\lambda^2}$$

$$= \mathcal{H}_1 - \frac{1}{2} \sum_\lambda \frac{V_2^\dagger e_\lambda e_\lambda^\dagger V_2}{\omega_\lambda^2} = \mathcal{H}_1 - \frac{1}{2} V_2^\dagger \underbrace{\left(\sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2} \right)}_{D_{22}^{-1}} V_2$$

$$= \mathcal{H}_1 - \frac{1}{2} V_2^\dagger D_{22}^{-1} V_2$$

If $\mathcal{H}_1 = T_1 + \frac{1}{2} u_{\underline{1}}^\dagger \Phi_{11} u_1 + V_{anharm}$,

and $h_2^\dagger = u_{\underline{1}}^\dagger \Phi_{12}, \; h_2 = \Phi_{21} u_1$

then $V_2 = m_2^{-1/2} h_2 = m_{\underline{1}}^{-1/2} \Phi_{21} u_1$

$\hookrightarrow V_2^\dagger D_{22}^{-1} V_2 = u_{\underline{1}}^\dagger \Phi_{12} m_1^{-1/2} D_{22}^{-1} m_1^{-1/2} \Phi_{21} u_1 =$

$$= u_1^{+}\left(\Phi_{12}\Phi_{22}^{-1}\Phi_{21}\right)u_1 ,$$

$$\boxed{\mathcal{H}_1^{eff} = T_1 + \frac{1}{2} u_1^{+}\left(\Phi_{11} - \Phi_{12}\Phi_{22}^{-1}\Phi_{22}\right)u_1 + V_{anharm}}$$