Chapter 8 Statistical Mechanics of Non-Equilibrium Systems

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August 27, 2018

8.1

The orientational correlation function $\langle u_z(0)u_z(t)\rangle$ indicates the rotational correlation of the molecules. In a gas phase, the molecules are allowed to rotate freely. In the figure 8.5 in the text, the peak at ~ 1 psec indicates the molecule rotates back to its original direction, or has gone through a 2π rotation in ~ 1 psec.

However, in a liquid phase the rotation of a molecule can be limited, for it may frequently collide with its neighbors to keep its original direction.

8.2

In a perfect $T = 0$ crystal, the orientation of the molecules are frozen. Thus the orientational correlation function should be $\frac{1}{3}$ forever. However, if the temperature is above zero, molecules still have a chance to rotate and flip with certain frequency. In such a situation, the orientational correlation function can slightly decreases with time, and the speed of decreasing is related to the temperature. A sketch is shown in figure 1.

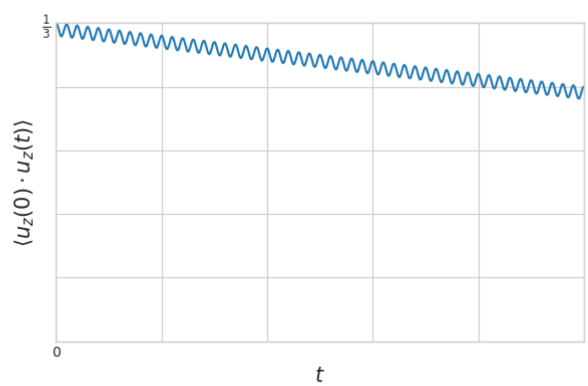

Figure 1: Orientational correlation function for a liquid.

8.3

$$\Delta \bar{A}(t) = \bar{A}(t) - \langle A\rangle \tag{1}$$

$$\begin{aligned}\bar{A}(t) &= \int d\mathbf{r}^N d\mathbf{p}^N A(t;\mathbf{r}^N,\mathbf{p}^N)F(\mathbf{r}^N,\mathbf{p}^N)\\ &= \int d\mathbf{r}^N d\mathbf{p}^N A(t;\mathbf{r}^N,\mathbf{p}^N)\langle A\rangle^{-1} f(\mathbf{r}^N,\mathbf{p}^N)A(\mathbf{r}^N,\mathbf{p}^N)\end{aligned} \tag{2}$$

where indeed $A(0;\mathbf{r}^N,\mathbf{p}^N) = A(\mathbf{r}^N,\mathbf{p}^N)$.

$$\begin{aligned}\langle A\rangle\Delta\bar{A}(t) =& \langle A\rangle \int d\mathbf{r}^N d\mathbf{p}^N A(t;\mathbf{r}^N,\mathbf{p}^N)\langle A\rangle^{-1} f(\mathbf{r}^N,\mathbf{p}^N)A(\mathbf{r}^N,\mathbf{p}^N) - \langle A\rangle^2\\ =& \int d\mathbf{r}^N d\mathbf{p}^N [A(t;\mathbf{r}^N,\mathbf{p}^N)A(\mathbf{r}^N,\mathbf{p}^N) - \langle A\rangle^2] f(\mathbf{r}^N,\mathbf{p}^N)\\ =& \langle A(t)A(0)\rangle - \langle A\rangle^2\\ =& C(t).\end{aligned} \tag{3}$$

8.4

The rate equations are

$$\begin{cases}\dfrac{dc_A}{dt} = -k_{BA}c_A(t) + k_{AB}c_B(t)\\ \dfrac{dc_B}{dt} = k_{BA}c_A(t) - k_{AB}c_B(t)\end{cases} \tag{4}$$

and the initial condition is $c_A(0) + c_B(0) = c$. Thus $c_A(t) + c_B(t) = c$. The rate equation reduces to

$$\frac{dc_A}{dt} = -(k_{BA} + k_{AB})c_A(t) + k_{AB}c. \tag{5}$$

The solution to this non-homogeneous linear differential equation is

$$c_A(t) = \frac{k_{AB}}{k_{BA} + k_{AB}}c + \left[c_A(0) - \frac{k_{AB}}{k_{BA} + k_{AB}}c\right] e^{-(k_{BA}+k_{AB})t}. \tag{6}$$

Because

$$\frac{\langle c_B\rangle}{\langle c_A\rangle} = \frac{k_{BA}}{k_{AB}} \tag{7}$$

$$\langle c_A\rangle = \frac{k_{AB}}{k_{BA} + k_{AB}}c \tag{8}$$

Therefore the solution (6) is

$$c_A(t) = \langle c_A\rangle + [c_A(0) - \langle c_A\rangle]e^{-(k_{BA}+k_{AB})t} \tag{9}$$

Therefore

$$\Delta c_A(t) \equiv c_A(t) - \langle c_A\rangle = [c_A(0) - \langle c_A\rangle]e^{-(k_{BA}+k_{AB})t} = \Delta c_A(0)e^{-(k_{BA}+k_{AB})t}. \tag{10}$$

Let $\tau_{rxn}^{-1} = k_{BA} + k_{AB}$, and the equation above becomes

$$\Delta c_A(t) = \Delta c_A(0)e^{-t/\tau_{rxn}}. \tag{11}$$

8.5

Since

$$H_A(z) = \begin{cases}1, & z < q^*,\\ 0, & z > q^*.\end{cases} \tag{12}$$

$$\langle H_A\rangle = \int_{-\infty}^{\infty} H_A(z)p(z)dz = \int_{-\infty}^{q^*} p(z)dz = \frac{\langle c_A\rangle}{\langle c_A\rangle + \langle c_B\rangle} = x_A. \tag{13}$$

Obviously $H_A^2(z) = H_A(z)$. Thus $\langle H_A^2\rangle = \langle H_A\rangle = x_A$.

$$\langle(\delta H_A)^2\rangle = \langle H_A^2\rangle - \langle H_A\rangle^2 = x_A - x_A^2 = x_A(1 - x_A) = x_A x_B. \tag{14}$$

8.6

The notations are a little confusing in the text. By definition

$$n_A(t) = H_A[q(t)]. \tag{15}$$

$$\langle n_A \rangle = \langle H_A \rangle, \quad \langle n_A^2 \rangle = \langle H_A \rangle, \quad \langle (\delta n_A)^2 \rangle = \langle (\delta H_A)^2 \rangle. \tag{16}$$

$$\begin{aligned} \exp(-t/\tau_{rxn}) =& \langle \delta n_A(0) \delta n_A(t) \rangle / \langle (\delta n_A)^2 \rangle \\ =& (x_A x_B)^{-1} (\langle n_A(0) n_A(t) \rangle - \langle n_A \rangle^2) \\ =& (x_A x_B)^{-1} (\langle n_A(0) n_A(t) \rangle - x_A^2). \end{aligned} \tag{17}$$

The time derivative gives

$$\tau_{rxn}^{-1} \exp(-t/\tau_{rxn}) = -(x_A x_B)^{-1} \langle n_A(0) \dot{n}_A(t) \rangle \tag{18}$$

Because

$$\langle n_A(0) n_A(t) \rangle = \langle n_A(-t) n_A(0) \rangle \tag{19}$$

$$\langle n_A(0) \dot{n}_A(t) \rangle = \frac{d}{dt} \langle n_A(0) n_A(t) \rangle = \frac{d}{dt} \langle n_A(-t) n_A(0) \rangle = -\langle \dot{n}_A(-t) n_A(0) \rangle = -\langle \dot{n}_A(0) n_A(t) \rangle. \tag{20}$$

Thus

$$\tau_{rxn}^{-1} \exp(-t/\tau_{rxn}) = (x_A x_B)^{-1} \langle \dot{n}_A(0) n_A(t) \rangle \tag{21}$$

8.7

We need to understand the initial rate in a way of limit,

$$k_{BA}(0) = \lim_{t \to 0^+} k_{BA}(t) = \lim_{t \to 0^+} x_A^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(t)] \rangle. \tag{22}$$

In the limit $t \to 0^+$, $q(t) = q(0) + v(0)t$. Notice that $H_B[q(t)] = H[q(t) - q^*]$, where $H(x)$ is the Heaviside function.

$$\begin{aligned} k_{BA}(0) =& \lim_{t \to 0^+} x_A^{-1} \langle v(0) \delta[q(0) - q^*] H[v(0)t + q(0) - q^*] \rangle \\ =& \lim_{t \to 0^+} x_A^{-1} \langle v(0) \delta[q(0) - q^*] H[v(0)t] \rangle \\ =& x_A^{-1} \langle v(0) \delta[q(0) - q^*] H[v(0)] \rangle \end{aligned} \tag{23}$$

Notice that the initial velocity and the initial coordinates are not correlated.

$$k_{BA}(0) = x_A^{-1} \langle v(0) H[v(0)] \rangle \langle \delta(q_0 - q^*) \rangle. \tag{24}$$

Since the distribution of $v(0)$ is even, $\langle v(0) H[v(0)] \rangle = \frac{1}{2} \langle |v(0)| \rangle = \frac{1}{2} \langle |v| \rangle$. Thus

$$k_{BA}(0) = \frac{1}{2x_A} \langle |v| \rangle \langle \delta(q - q^*) \rangle. \tag{25}$$

For the initial rate obtained from the transition state theory approximation, because

$$H_B^{(\mathrm{TST})}[q(t)] = H[v(0)] \tag{26}$$

$$k_{BA}^{(\mathrm{TST})} = x_A^{-1} \langle v(0) \delta[q(0) - q^*] H[v(0)] \rangle \tag{27}$$

which is identical to equation (23), the expression for k_{BA} is exactly the same.

8.8

From the Exercise 8.7 we know $k_{BA}^{(\mathrm{TST})}$ is calculated assuming no trajectories recrossed the transition states after a short time. However, in fact there might be trajectories that recross the transition state from B side back to A side. Therefore in reality the reaction rate k_{BA} should be lower than the approximation $k_{BA}^{(\mathrm{TST})}$. The shorter the time is, the closer these two are.

8.9

Obviously,

$$\int d\mathbf{r}^N \rho(\mathbf{r}, t) = N, \qquad \int_{U[\mathbf{r}_j(t)]} d\mathbf{r}^N \rho(\mathbf{r}, t) = 1 \tag{28}$$

where $U[\mathbf{r}_j(t)]$ indicates an infinitesimal neighborhood of $\mathbf{r}_j(t)$. These properties validate that $\rho(\mathbf{r}, t)$ has the form

$$\rho(\mathbf{r}, t) = \sum_{j=1}^{N} \delta[\mathbf{r} - \mathbf{r}_j(t)]. \tag{29}$$

8.10

We can define a quantity $\mathbf{k}$

$$\mathbf{k}(\mathbf{r}, t) = \sum_{j=1}^{N} \mathbf{v}_j(t)\delta[\mathbf{r} - \mathbf{r}_j(t)] = \sum_{j=1}^{N} \dot{\mathbf{r}}_j(t)\delta[\mathbf{r} - \mathbf{r}_j(t)] \tag{30}$$

Therefore

$$\begin{aligned}
\frac{\partial \rho(\mathbf{r}, t)}{\partial t} &= \sum_{j=1}^{N} \frac{\partial}{\partial t}\delta[\mathbf{r} - \mathbf{r}_j(t)] \\
&= -\sum_{j=1}^{N} \nabla\delta[\mathbf{r} - \mathbf{r}_j(t)] \cdot \frac{d}{dt}\mathbf{r}_j(t) \\
&= -\sum_{j=1}^{N} \dot{\mathbf{r}}_j(t) \cdot \nabla\delta[\mathbf{r} - \mathbf{r}_j(t)] \\
&= -\nabla \cdot \sum_{j=1}^{N} \dot{\mathbf{r}}_j\delta[\mathbf{r} - \mathbf{r}_j(t)] \\
&= -\nabla \cdot \mathbf{k}(\mathbf{r}, t).
\end{aligned} \tag{31}$$

Comparing with the example of an activated process, $H_A[q]$ can be the density in the area $q < q^*$, and q is a generalized coordinate. In one dimension, $\dot{q}\delta(q - q^*)$ is the divergence of the flux at the boundary $q = q^*$. Therefore the equation $\dot{H}_A[q] = -\dot{q}\delta(q - q^*)$ resembles the equation of continuity.

8.11

Suppose $P(\mathbf{r}^N(t), \mathbf{r}^N(0))$ is the joint configurational distribution at time t and time 0. By definition,

$$P_1(\mathbf{r}_1(t), \mathbf{r}_1(0)) = \int d\mathbf{r}_2(t) \cdots d\mathbf{r}_N(t) \int d\mathbf{r}_2(0) \cdots d\mathbf{r}_N(0) P(\mathbf{r}^N(t), \mathbf{r}^N(0)) \tag{32}$$

$$P_1^{(t)}(\mathbf{r}_1(t)) = \int d\mathbf{r}_1(0) P_1(\mathbf{r}^N(t), \mathbf{r}^N(0)) \tag{33}$$

$$P_1^{(0)}(\mathbf{r}_1(0)) = \int d\mathbf{r}_1(t) P_1(\mathbf{r}^N(t), \mathbf{r}^N(0)) \tag{34}$$

$$\bar{\rho}(\mathbf{r}(t), t, \mathbf{r}(0), 0) = N P_1(\mathbf{r}_1(t), \mathbf{r}_1(0)) \tag{35}$$

$$\bar{\rho}(\mathbf{r}, t) = N P_1^{(t)}(\mathbf{r}) \tag{36}$$

$$\bar{\rho}(\mathbf{r}, 0) = N P_1^{(0)}(\mathbf{r}) \tag{37}$$

By definition,

$$P(\mathbf{r}, t) = N \frac{P_1(\mathbf{r}(t), \mathbf{r}(0))}{P_1^{(0)}(\mathbf{0})} = N \frac{\bar{\rho}(\mathbf{r}, t, \mathbf{0}, 0)}{\bar{\rho}(\mathbf{0}, 0)} = N \frac{\langle \rho(\mathbf{r}, t) \rho(\mathbf{0}, 0) \rangle}{\bar{\rho}(\mathbf{0}, 0)}. \tag{38}$$

8.12

$$\begin{aligned}
\frac{d}{dt} \Delta R^2(t) = & \int d\mathbf{r}\ r^2 \frac{\partial}{\partial t} P(\mathbf{r}, t) = \int d\mathbf{r}\ r^2 D \nabla^2 P(\mathbf{r}, t) \\
= & r^2 D \nabla P(\mathbf{r}, t)|_\infty - \int d\mathbf{r} D \nabla \mathbf{r}^2 \nabla P(\mathbf{r}, t) \\
= & r^2 D \nabla P(\mathbf{r}, t)|_\infty - D \nabla r^2 P(\mathbf{r}, t)|_\infty + \int d\mathbf{r} D \nabla^2 r^2 P(\mathbf{r}, t)
\end{aligned} \tag{39}$$

Because the distribution should be bounded in finite space, itself as well as its gradient should vanish at infinity. Thus

$$\frac{d}{dt} \Delta R^2(t) = \int d\mathbf{r} D \nabla^2 r^2 P(\mathbf{r}, t) = 6 \int d\mathbf{r} D P(\mathbf{r}, t). \tag{40}$$

Since $P(\mathbf{r}, t)$ is normalized for any t, we have

$$\frac{d}{dt} \Delta R^2(t) = 6D. \tag{41}$$

8.13

Since

$$\frac{d}{dt} \Delta R^2(t) = 2 \int_0^t dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \tag{42}$$

and

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \approx \langle v^2 \rangle e^{-t/\tau}, \tag{43}$$

$$\frac{d}{dt} \Delta R^2(t) \approx 2 \int_0^t \langle v^2 \rangle e^{-t/\tau} = -2 \langle v^2 \rangle \tau \left(e^{-t/\tau} - 1 \right). \tag{44}$$

$$\Delta R^2(t) \approx 2 \langle v^2 \rangle \tau^2 (e^{-t/\tau} - 1) + 2 \langle v^2 \rangle \tau t. \tag{45}$$

Given $D \sim 1 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$, $\Delta R^2(t) = 6Dt$,

$$3D = \langle v^2 \rangle \tau. \tag{46}$$

Because

$$\langle v^2 \rangle = 3 k_B T / m, \tag{47}$$

$$\tau = \frac{mD}{k_B T} \tag{48}$$

For a small molecule, $m \sim N_A^{-1} \times 1\,\mathrm{kg}$. At room temperature $T \sim 300\,\mathrm{K}$. Then $\tau \sim 4 \times 10^{-13}\,\mathrm{s}$.

Figsure 2 shows the mean square displacement versus time with reduced units.

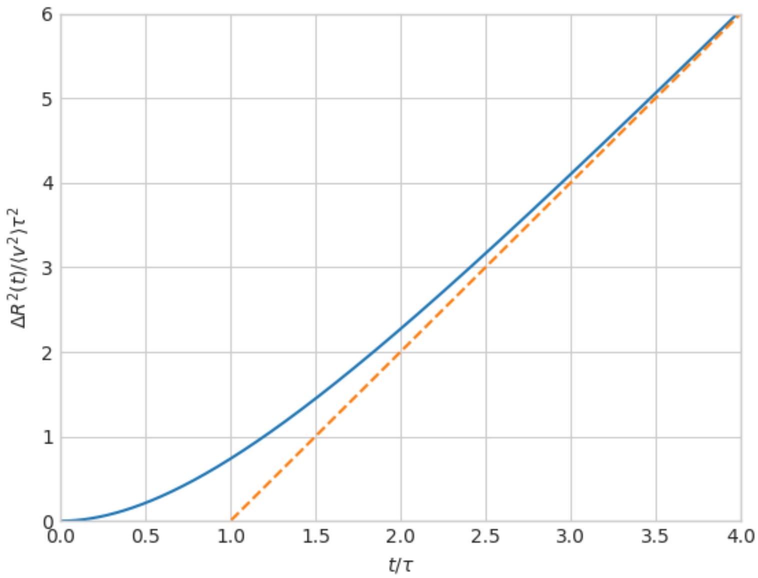

Figure 2: Diffusion curve of particles in Exercise 8.13.

8.14

The perturbation is

$$\Delta\mathscr{H} = -\sum_i f_i A_i(0). \tag{49}$$

$$\begin{aligned}\bar{A}_j(t) =& \frac{\mathrm{Tr}\left[e^{-\beta(\mathscr{H}+\Delta\mathscr{H})}A_j(t)\right]}{\mathrm{Tr}e^{-\beta(\mathscr{H}+\Delta\mathscr{H})}}\\ =& \frac{1}{\mathrm{Tr}e^{-\beta\mathscr{H}}}\mathrm{Tr}\left\{e^{-\beta\mathscr{H}}\left[A_j(t) - (\beta\Delta\mathscr{H})A_j(t) + A_j(t)\frac{\mathrm{Tr}[e^{-\beta\mathscr{H}}(\beta\Delta\mathscr{H})]}{\mathrm{Tr}e^{-\beta\mathscr{H}}}\right]\right\} + O[(\beta\Delta\mathscr{H})^2]\\ =& \langle A_j\rangle - \beta[\langle\Delta\mathscr{H}A_j(t)\rangle - \langle A_j\rangle\langle\Delta\mathscr{H}\rangle] + O[(\beta\Delta\mathscr{H})^2]\end{aligned} \tag{50}$$

$$\begin{aligned}\Delta\bar{A}_j(t) =& \bar{A}_j(t) - \langle A_j\rangle = \beta\left[\sum_i f_i\langle A_i(0)A_j(t)\rangle - \sum_i f_i\langle A_j\rangle\langle A_i\rangle\right] + O(f^2)\\ =& \beta\sum_i f_i\langle\delta A_i(0)\delta A_j(t)\rangle + O(f^2).\end{aligned} \tag{51}$$

8.15

Since it is proved that

$$\Delta n(\mathbf{r},t) = \beta\int d\mathbf{r}'\Phi(\mathbf{r}')\langle\delta\rho(\mathbf{r}',0)\delta\rho(\mathbf{r},t)\rangle \tag{52}$$

According to Fick's law

$$\frac{\partial}{\partial t}n(\mathbf{r},t) = D\nabla^2 n(\mathbf{r},t), \tag{53}$$

$$\frac{\partial}{\partial t}n(\mathbf{r},t) = \frac{\partial}{\partial t}\Delta n(\mathbf{r},t) = \beta \int d\mathbf{r}'\Phi(\mathbf{r}')\frac{\partial}{\partial t}\langle \delta\rho(\mathbf{r}',0)\delta\rho(\mathbf{r},t)\rangle \tag{54}$$

$$D\nabla^2 n(\mathbf{r},t) = D\beta \int d\mathbf{r}'\Phi(\mathbf{r}')\nabla^2\langle \delta\rho(\mathbf{r}',0)\delta\rho(\mathbf{r},t)\rangle \tag{55}$$

Since $\Phi(\mathbf{r})$ is arbitraty external field, for any $\mathbf{r}'$

$$\frac{\partial}{\partial t}\langle \delta\rho(\mathbf{r}',0)\delta\rho(\mathbf{r},t)\rangle = D\nabla^2\langle \delta\rho(\mathbf{r}',0)\delta\rho(\mathbf{r},t)\rangle \tag{56}$$

Thus

$$\frac{\partial C(\mathbf{r},t)}{\partial t} = D\nabla^2 C(\mathbf{r},t). \tag{57}$$

8.16

First we calculate the response function at $t > 0$,

$$\chi(t) = -\beta\frac{d}{dt}\langle \delta A(0)\delta A(t)\rangle = \beta\tau^{-1}\langle(\delta A)^2\rangle e^{-t/\tau}. \tag{58}$$

Then we start with

$$\Delta\bar{A}(t) = f\int_{t_1}^{t_2} dt'\chi(t-t'). \tag{59}$$

For the case $t < t_1$, because $\chi(t) = 0$ when $t < 0$, $\Delta\bar{A}(t) = 0$.

For the case $t_1 < t < t_2$,

$$\Delta\bar{A}(t) = f\int_{t_1}^{t} dt'\chi(t-t') = f\beta\tau^{-1}\langle(\delta A)^2\rangle\int_{t_1}^{t} dt' e^{-(t-t')/\tau} = f\beta\langle(\delta A)^2\rangle\left(1 - e^{-(t-t_1)/\tau}\right) \tag{60}$$

For the case $t > t_2$,

$$\Delta\bar{A}(t) = f\int_{t_1}^{t_2} dt'\chi(t-t') = f\beta\langle(\delta A)^2\rangle\left(e^{-(t-t_2)/\tau} - e^{-(t-t_1)/\tau}\right) \tag{61}$$

gradually fades to zero.

A demonstration of the deviation of A under different τ is shown in figure 3. From the figure it can be seen that if $\tau \ll t_2 - t_1$, the system will be driven immediately following the square perturbation; if $\tau \gg t_2 - t_1$, the system will be perturbed and will restore slowly. $\tau = t_2 - t_1$ should resemble a critical damping.

The energy absorbed is

$$\begin{aligned} \text{Abs} = -\int_{-\infty}^{\infty} dt\dot{f}(t)\bar{A}(t) = \int_{-\infty}^{\infty} dt\dot{\bar{A}}(t)f(t) = f\int_{t_1}^{t_2} dt\dot{\bar{A}}(t) \\ = f[\bar{A}(t_2) - \bar{A}(t_1)] = f[\Delta\bar{A}(t_2) - \Delta\bar{A}(t_1)] \\ = f^2\beta\langle(\delta A)^2\rangle\left(1 - e^{-(t_2-t_1)/\tau}\right). \end{aligned} \tag{62}$$

8.17

If $n = 0$,

$$\frac{1}{T}\int_0^T dt\ e^{in\omega t} = \frac{1}{T}\int_0^T dt = \frac{T}{T} = 1. \tag{63}$$

If $n \neq 0$,

$$\frac{1}{T}\int_0^T dt\ e^{in\omega t} = \frac{1}{in\omega T}\left(e^{in\omega T} - 1\right) = \frac{2e^{in\omega T/2}}{n\omega T}\sin(n\omega T/2). \tag{64}$$

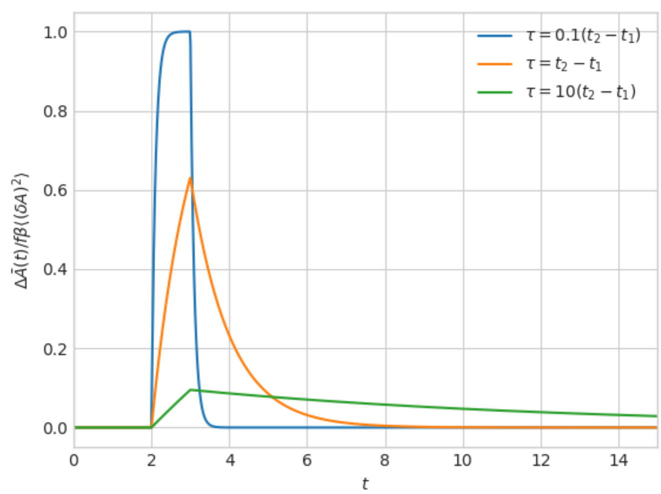

Figure 3: Response to a square pulse in Exercise 8.16.

$$\lim_{\omega T\to\infty}\left|\frac{1}{T}\int_0^T dt\ e^{-n\omega t}\right| = \lim_{\omega T\to\infty}\left|\frac{2e^{in\omega T/2}}{n\omega T}\sin(n\omega T/2)\right| \leqslant \lim_{\omega T\to\infty}\left|\frac{2}{n\omega T}\right| = 0. \tag{65}$$

Thus when $n \neq 0$, $\omega T \to \infty$,

$$\frac{1}{T}\int_0^T dt\ e^{in\omega t} \to 0. \tag{66}$$

8.18

First expand $f(t) = \frac{1}{2}\left(f_\omega e^{-i\omega t} + f_\omega^* e^{i\omega t}\right)$,

$$\begin{aligned}\mathrm{abs}(\omega) =& \frac{1}{T}\int_0^T dt \left\{\frac{i\omega}{2}\left(f_\omega e^{-i\omega t} - f_\omega^* e^{i\omega t}\right)\left[\langle A\rangle + \int_{-\infty}^{\infty} dt'\chi(t')f(t-t') + O(f^2)\right]\right\} \\ =& \frac{1}{T}\int_0^T dt \left\{\frac{i\omega}{2}\left(f_\omega e^{-i\omega t} - f_\omega^* e^{i\omega t}\right)\left[\langle A\rangle + \int_{-\infty}^{\infty} dt'\chi(t')\frac{1}{2}\left(f_\omega e^{-i\omega(t-t')} + f_\omega^* e^{i\omega(t-t')}\right) + O(f^2)\right]\right\}\end{aligned} \tag{67}$$

Notice Chandler's book has a typo in abs equation: a redundant minus sign. Use the result in Exercise 8.17, and suppose $\omega T \to \infty$.

$$\begin{aligned}\mathrm{abs}(\omega) =& \frac{1}{T}\int_0^T dt \left\{\frac{i\omega}{2}\left(f_\omega e^{-i\omega t} - f_\omega^* e^{i\omega t}\right)\left[\int_{-\infty}^{\infty} dt'\chi(t')\frac{1}{2}\left(f_\omega e^{-i\omega(t-t')} + f_\omega^* e^{i\omega(t-t')}\right) + O(f^2)\right]\right\} \\ =& \frac{i\omega}{4}\left[\int_{-\infty}^{\infty} dt'\chi(t')\left(f_\omega f_\omega^* e^{-i\omega t'} - f_\omega^* f_\omega e^{i\omega t'}\right) + O(f^3)\right] \\ =& \frac{i\omega}{4}|f_\omega|^2\left[\int_{-\infty}^{\infty} dt'\chi(t')\left(e^{-i\omega t'} - e^{i\omega t'}\right)\right] + O(f^3) \\ =& \frac{\omega}{2}|f_\omega|^2\int_{-\infty}^{\infty} dt\chi(t)\sin(\omega t) + O(f^3).\end{aligned} \tag{68}$$

8.19

Suppose $A(t)$ obeyed simple harmonic oscillator dynamics,

$$\frac{d^2A(t)}{dt^2} = -\omega_0^2 A(t) \tag{69}$$

The real solution to this differential equation is

$$A(t) = C\sin(\omega_0 t) + D\cos(\omega_0 t) \tag{70}$$

$$\dot{A}(t) = C\omega_0\cos(\omega_0 t) - D\omega_0\sin(\omega_0 t) \tag{71}$$

$$A(0) = D, \quad \dot{A}(0) = C\omega_0 \tag{72}$$

Once the initial condition C and D given, the evolution of the system is determined. However, required by statistical mechanics,

$$\langle A\dot{A}\rangle = \langle DC\omega_0\rangle = 0 \tag{73}$$

Thus

$$\langle CD\rangle = 0. \tag{74}$$

The distribution of C and D should be even for equilibrium, thus $\langle C\rangle = \langle D\rangle = 0$. Thus $\langle \delta C\delta D\rangle = 0$.

$$\delta A(t) = \delta C\sin(\omega_0 t) + \delta D\cos(\omega_0 t), \qquad \delta A(0) = \delta D \tag{75}$$

$$\begin{aligned}
\langle \delta A(0)\delta A(t)\rangle =& \langle \delta D[\delta C\sin(\omega_0 t) + \delta D\cos(\omega_0 t)]\rangle \\
=& \langle (\delta D)^2\cos(\omega_0 t) + \delta C\delta D\sin(\omega_0 t)\rangle \\
=& \langle (\delta D)^2\rangle\cos(\omega_0 t) + \langle \delta C\delta D\rangle\sin(\omega_0 t) \\
=& \langle (\delta D)^2\rangle\cos(\omega_0 t) = \langle (\delta A(0))^2\rangle\cos(\omega_0 t).
\end{aligned} \tag{76}$$

8.20

The model described in section 8.8 in the text is an oscillator coupled to a random harmonic bath. The target is to describe the dynamics of the oscillator. The Hamitonian of the system is

$$\mathscr{H} = \mathscr{H}_0(x) - xf + \mathscr{H}_b(y_1, \cdots, y_N) \tag{77}$$

where

$$\mathscr{H}_0 = \frac{1}{2}m\dot{x}^2 + V(x), \quad f = \sum_i c_i y_i \tag{78}$$

Here y_i are the normal modes of the harmonic bath. Because the bath is purely harmonic, the evolution and response to evolving x is exactly linear. Thus the evolution of f can be written as

$$f(t) = f_b(t) + \int_{-\infty}^{\infty} dt'\chi_b(t-t')x(t') \tag{79}$$

where

$$\chi_b(t-t') = \begin{cases} -\beta\dfrac{dC_b(t-t')}{d(t-t')}, & t > t' \\ 0, & t < t'. \end{cases} \tag{80}$$

From the Hamiltonian the equation of state is

$$m\ddot{x}(t) = f_0[x(t)] + f_b(t) + \int_{-\infty}^{\infty} dt'\chi_b(t-t')x(t') \tag{81}$$

where f_0 comes from $\mathscr{H}_0$

$$f_0[x] = -\frac{dV}{dx}. \tag{82}$$

Plug in the equation (80), and notice that the time origin is 0,

$$m\ddot{x}(t) = f_0[x(t)] + f_b(t) - \beta \int_0^t dt' C_b'(t-t')x(t') \tag{83}$$

Integrated by part,

$$\begin{aligned}\int_{-\infty}^t dt' C_b'(t-t')x(t') =& - C_b(t-t')x(t')\Big|_0^t + \int_0^t C_b(t-t')\dot{x}(t')dt' \\ =& - C_b(0)x(t) + C_b(t)x(0) + \int_0^t C_b(t-t')\dot{x}(t')dt'\end{aligned} \tag{84}$$

Thus

$$\begin{aligned}m\ddot{x}(t) =& f_0[x(t)] + f_b(t) + \beta C_b(0)x(t) - \beta C_b(t)x(0) - \beta \int_0^t C_b(t-t')\dot{x}(t')dt' \\ =& \{f_0[x(t)] + \beta C_b(0)x(t)\} + [f_b(t) - \beta C_b(t)x(0)] - \beta \int_0^t C_b(t-t')\dot{x}(t')dt'\end{aligned} \tag{85}$$

Define

$$\bar{V}(x) = V(x) - \frac{1}{2}\beta C_b(0)x^2(t) \tag{86}$$

$$\delta f(t) = f_b(t) - \beta C_b(t)x(0) \tag{87}$$

and

$$\bar{f}[x(t)] = -\frac{d\bar{V}}{dx} = -\frac{dV}{dx} + \beta C_b(0)x(t). \tag{88}$$

Thus

$$m\ddot{x}(t) = \bar{f}[x(t)] + \delta f(t) - \beta \int_0^t dt' C_b(t-t')\dot{x}(t'). \tag{89}$$

Notice that the distribution of $f_b(t)$ is Gaussian with mean value $\beta C_b(t)x(0)$ and variance $C_b(t-t')$.

8.21

(i) Since

$$\begin{aligned}m\frac{d^2}{dt^2}x(t) =& \bar{f}[x(t)] + \delta f(t) - \beta \int_0^t dt' C_b(t-t')\frac{d}{dt'}x(t') \\ =& - m\bar{\omega}^2 x(t) + \delta f(t) - \beta \int_0^t dt' C_b(t-t')\frac{d}{dt'}x(t')\end{aligned} \tag{90}$$

multiply by $x(0)$ and take the average on both side

$$\frac{d^2}{dt^2}\langle x(0)x(t)\rangle = -\bar{\omega}^2\langle x(0)x(t)\rangle - \frac{\beta}{m}\int_0^t dt' C_b(t-t')\frac{d}{dt'}\langle x(0)x(t)\rangle. \tag{91}$$

(ii) The Laplace transform gives

$$s^2\tilde{C}(s) - s\langle x^2(0)\rangle - \langle x(0)\dot{x}(0)\rangle = -\bar{\omega}^2\tilde{C}(s) - \frac{\beta}{m}\tilde{C}_b(s)\left[s\tilde{C}(s) - \langle x^2(0)\rangle\right] \tag{92}$$

Required by statistical mechanics, $\langle x(0)\dot{x}(0)\rangle = 0$. Then

$$\tilde{C}(s) = \frac{s\langle x^2\rangle + \frac{\beta}{m}\tilde{C}_b(s)\langle x^2\rangle}{s^2 + \bar{\omega}^2 + s\frac{\beta}{m}\tilde{C}_b(s)} = \frac{s + \frac{\beta}{m}\tilde{C}_b(s)}{s^2 + \bar{\omega}^2 + s\frac{\beta}{m}\tilde{C}_b(s)}\langle x^2\rangle. \tag{93}$$

(iii) Assume

$$C_b(t) = C_b(0)e^{-t/\tau}. \tag{94}$$

Consequently,

$$\tilde{C}_b(s) = \frac{C_b(0)}{s + \tau^{-1}}. \tag{95}$$

The cosine Fourier transform of $\langle x(0)x(t)\rangle$ is

$$\begin{aligned}
\hat{C}(\omega) = \int_0^\infty \cos(\omega t)\langle x(0)x(t)\rangle = \frac{1}{2}[\tilde{C}(i\omega) + \tilde{C}(-i\omega)]& \\
=\frac{1}{2}\left[\frac{i\omega + \frac{\beta}{m}\tilde{C}_b(i\omega)}{-\omega^2 + \bar{\omega}^2 + i\omega\frac{\beta}{m}\tilde{C}_b(i\omega)} + \frac{-i\omega + \frac{\beta}{m}\tilde{C}_b(-i\omega)}{-\omega^2 + \bar{\omega}^2 - i\omega\frac{\beta}{m}\tilde{C}_b(-i\omega)}\right]\langle x^2\rangle& \\
=\frac{1}{2}\left[\frac{i\omega + \frac{\beta C_b(0)}{m(i\omega + \tau^{-1})}}{-\omega^2 + \bar{\omega}^2 + i\omega\frac{\beta C_b(0)}{m(i\omega + \tau^{-1})}} + \frac{-i\omega + \frac{\beta C_b(0)}{m(-i\omega + \tau^{-1})}}{-\omega^2 + \bar{\omega}^2 - i\omega\frac{\beta C_b(0)}{m(-i\omega + \tau^{-1})}}\right]\langle x^2\rangle.&
\end{aligned} \tag{96}$$

The function at $\omega = \bar{\omega}$ should be a peak

$$\begin{aligned}
\hat{C}(\bar{\omega}) =&\frac{1}{2}\left[\frac{i\bar{\omega} + \frac{\beta C_b(0)}{m(i\bar{\omega} + \tau^{-1})}}{i\bar{\omega}\frac{\beta C_b(0)}{m(i\bar{\omega} + \tau^{-1})}} + \frac{-i\bar{\omega} + \frac{\beta C_b(0)}{m(-i\bar{\omega} + \tau^{-1})}}{-i\bar{\omega}\frac{\beta C_b(0)}{m(-i\bar{\omega} + \tau^{-1})}}\right]\langle x^2\rangle \\
=&\frac{1}{2}\left[\frac{i\bar{\omega}m(i\bar{\omega} + \tau^{-1}) + \beta C_b(0)}{i\bar{\omega}\beta C_b(0)} + \frac{-i\bar{\omega}m(-i\bar{\omega} + \tau^{-1}) + \beta C_b(0)}{-i\bar{\omega}\beta C_b(0)}\right]\langle x^2\rangle \\
=&\frac{1}{2}\left[\frac{2i\bar{\omega}m\tau^{-1}}{i\bar{\omega}\beta C_b(0)}\right]\langle x^2\rangle \\
=&\frac{m\langle x^2\rangle}{\beta\tau C_b(0)},
\end{aligned} \tag{97}$$

which indicates a strong absorption.

8.22

The corresponding sketches are shown in figure 4. Plot (a) shows a smooth decay, while plot (b) shows a pattern of periodicity. This is because in the solid state, the particles may oscillate with a certain period T. Plot (c) shows the decay in $\langle v^(0)v^2(t)\rangle$. Because $\langle v^2(t)\rangle \neq 0$, when T goes to infinity, $\langle v^2(0)v^2(t)\rangle \to \langle v^2(0)\rangle\langle v^2(t)\rangle = \langle v^2\rangle^2$ nonzero. Plot (d) shows the direction of velocity coupling, exactly the three times as that is shown in figure 1.

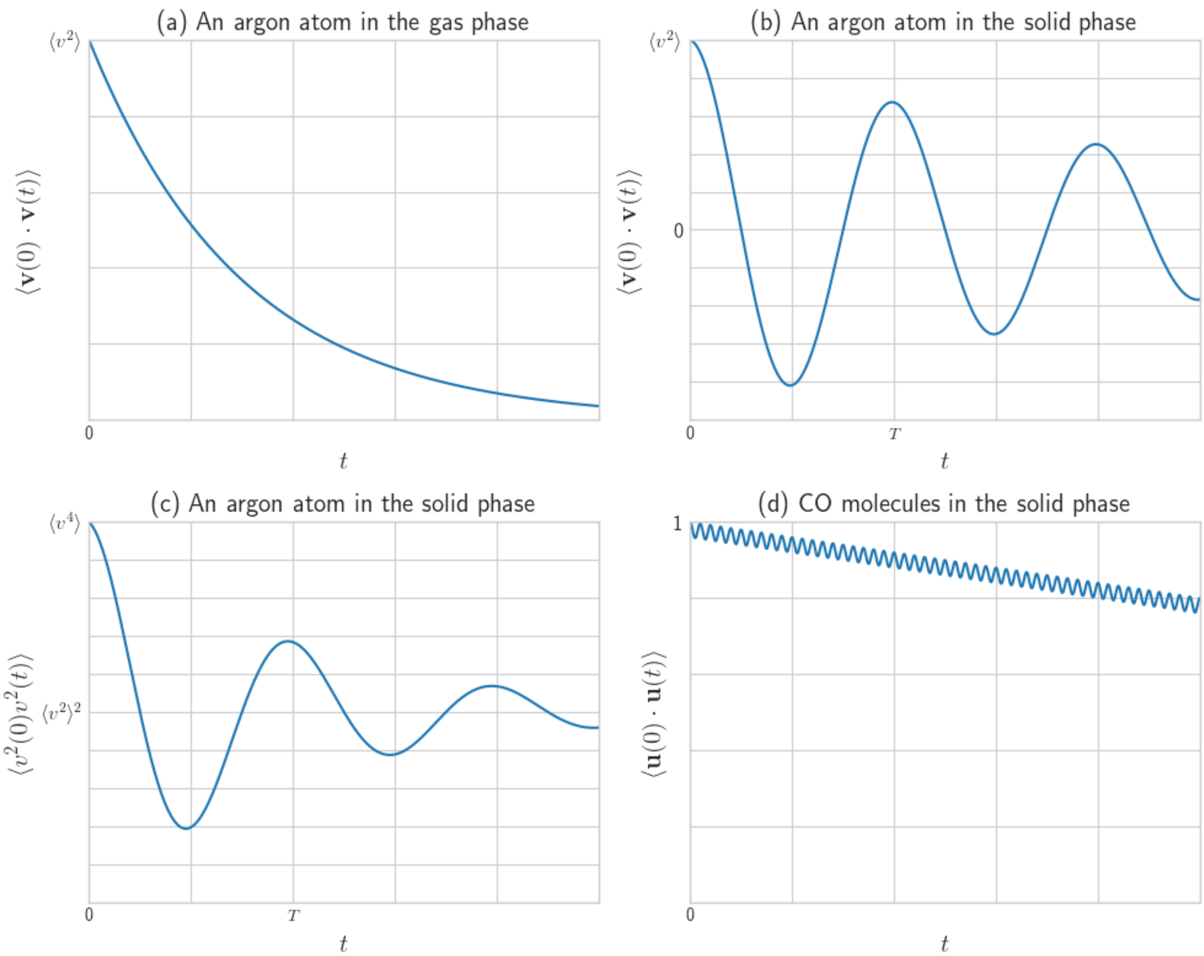

Figure 4: The sketches in Exercise 8.22.

8.23

Since

$$D = \frac{1}{3}\int_0^\infty dt\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle \approx \frac{1}{3}\int_0^\infty dt\langle v^2\rangle e^{-t/\tau} = \frac{1}{3}\langle v^2\rangle\tau. \tag{98}$$

$$\tau \approx \frac{3D}{\langle v^2\rangle} \tag{99}$$

At the time right after turning down the external electric field, the ensemble average of v^2 can be describes by the temperature

$$\langle v^2\rangle = \frac{3k_BT}{m}. \tag{100}$$

Thus

$$\tau \approx \frac{mD}{k_BT}. \tag{101}$$

8.24

At room temperature $T \approx 300\,\mathrm{K}$, $\beta \approx 2.4\times 10^{20}\ \mathrm{J}^{-1}$,

$$D \approx \frac{1}{2\pi\beta\sigma\eta} \sim 1\times 10^{-10}\,\mathrm{m}^2/\mathrm{s}. \tag{102}$$

8.25

Because

$$\Delta R^2(t) = 6Dt \tag{103}$$

Consider the particles doing a Brownian motion. For $t = 5\,\mathrm{psec}$, $\Delta R^2 = 3\,\text{Å}$. Since $r_i(t) = \sqrt{|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2}$, $r_i(t)/\text{Å}$ satisfies $\chi^2(3)$ distribution. $F_{\chi^2(3)}(5) = 0.828$. Thus 17.2% particles have moved more than $5\,\text{Å}$.

8.26

Adopted from the official solution manual. (a) Solving the differential equations we get

$$\Delta c_1(t) = A_1e^{-\lambda_1 t} + B_1e^{-\lambda_2 t} \tag{104}$$

$$\Delta c_2(t) = A_2e^{-\lambda_1 t} + B_2e^{-\lambda_2 t} \tag{105}$$

where

$$\lambda_{1,2} = \frac{1}{2}[(k_{31}+k_{13})+(k_{32}+k_{23})] \pm \sqrt{\left\{\frac{1}{2}[(k_{31}+k_{13})-(k_{32}+k_{23})]\right\}^2 + k_{13}k_{23}}. \tag{106}$$

(b)

$$\lambda_1 \approx k_{13}+k_{23} = \tau_{\mathrm{transient}}^{-1} \tag{107}$$

$$\lambda_2 \approx \frac{k_{31}k_{23}+k_{13}k_{32}}{k_{13}+k_{23}} = \tau_{\mathrm{rxn}}^{-1}. \tag{108}$$

$$\tau_{\mathrm{rxn}}^{-1} \approx k_{31}\frac{k_{32}}{k_{13}+k_{23}} + k_{32}\frac{k_{13}}{k_{13}+k_{23}} \approx k_{31}+k_{32} \ll k_{13}+k_{23} \approx \tau_{\mathrm{transient}}^{-1}. \tag{109}$$

Therefore the relaxation is dominated by τ_{rxn}.
(c) As shown above, the faster transient decay occurs on a time scale of $(k_{13}+k_{23})^{-1} \approx k_{13}^{-1}$ or k_{23}^{-1}.

(d) The two decay rates are analogous to the two rates in the reactive flux description:

$$\tau_{\text{mol}} \approx \tau_{\text{transient}} \ll \tau_{\text{rxn}}. \tag{110}$$

The connection can be made by imagining preparing the system at the transition state, i.e., in state 3. Then the decay into states 1 and 2, $c_1(t)$ and $c_2(t)$, follow the two decay rates, one much faster than the other. But $c_1(t) \propto \langle \delta n_A(0)\delta n_A(t)\rangle$ by the regression hypothesis, and the time derivative of $\rangle \delta n_A(0)\delta n_A(t)\rangle$ is just the flux in the reactive flux picture. In particular, τ_{rxn}^{-1} is on the order of k_{31} or k_{32}, and is the plateau value for the reaction rate.
(e) This is similar to the transition state theory idea where $e^{-\beta Q}$ is the probability o getting to the transition states 3, and $D \propto 1/\eta$ is the rate to cross the barrier 3 once there. As we showed previously,

$$k^{(\text{TST})} \propto \langle |v|\rangle \langle \delta(q - q^*)\rangle. \tag{111}$$

8.27

From transition state theory, we still have

$$k_{12} = \frac{1}{2x_2} \langle |v|\rangle \langle \delta[q(0) - q^*]\rangle \tag{112}$$

because when $t \to 0$, the trajectories starting from region 3 do not have a chance to cross the barrier at q^*.

8.28

(a) The RMS velocity of an argon atom in the vapor is

$$v_g = \sqrt{\frac{3k_BT}{m}} = 4.3 \times 10^2 \,\text{m/s}. \tag{113}$$

(b) The RMS velocity of an argon atom in the solution is the same as that in (a)

$$v_l = v_g = \sqrt{\frac{3k_BT}{m}} = 4.3 \times 10^2 \,\text{m/s}. \tag{114}$$

(c) Because in the gas phase, the spaces of the particles are larger than $l = 10\,\text{Å}$, the motion is in the inertial regime

$$t = \frac{l}{v_g} = 2.3 \times 10^{-12}\,\text{s} = 2.3\,\text{psec}. \tag{115}$$

(d) Because in the solution, the particles are effected by the solvent molecules, the motion is in the diffusion regime

$$t = \frac{l^2}{6D} = 1.67 \times 10^{-9}\,\text{s} = 167\,\text{psec}. \tag{116}$$

(e) In the solution,

$$\tau_{\text{relax}} = \frac{mD}{k_BT} = 1.6 \times 10^{-14}\,\text{s} = 1.6 \times 10^{-2}\,\text{psec}. \tag{117}$$

(f) When $\eta_2 = 2\eta_1$, according to Stokes' law $D \propto \eta^{-1}$,

$$t_2 = 2t_1 = 333\,\text{psec}. \tag{118}$$

The velocity is not influenced since the temperature does not change.