

STAT MECH SOLUTIONS: Problems II

①

1a Langevin equation of form

$$m \frac{dv}{dt} = -\alpha v + F$$

↑ mass
↑ friction
↑ random force

Expect α to be function of viscosity η and particle radius r . Dimensional analysis gives

$$[\alpha]_{\text{units}} = \text{kg/s}$$

$$\Rightarrow \alpha \propto \eta r$$

since $[\eta]_{\text{units}} = \text{kg/(m.s)}$.

Set $\alpha = a \eta r$ where a is a constant we don't know.

From notes on Langevin equation, $\frac{\alpha}{m} = \frac{1}{\tau}$

and

$$D = \frac{k_B T}{m} \tau = \frac{k_B T}{\alpha}$$

But $\langle x^2 \rangle = 6 D t = \frac{6 k_B T}{\alpha} t$

With $k_B = R/N_A$,

(2)

$$\langle x^2 \rangle = \frac{6RT}{N_A} t$$

$$\Rightarrow N_A = \frac{6RT}{\langle x^2 \rangle} t = \frac{6RTt}{\langle x^2 \rangle a \eta r}$$

$$= \frac{6 \left(8.314 \frac{\text{cm}^3 \text{MPa}}{\text{K mol}} \right) (273.15 + 19.8) 10^9}{(3.3 \times 10^{-8} \text{ cm}^2) a (0.0278 \text{ g}^{\text{cm}}/\text{cm}^3 \text{ s})}$$

(0.4 x 10⁻⁴ cm)

$$= \frac{1}{a} \cdot 6.6 \times 10^{17} \times 10^7 \text{ mol}^{-1}$$

$$= \frac{1}{a} 6.6 \times 10^{24} \text{ mol}^{-1}$$

Comparison to known value for N_A ($6 \times 10^{23} \text{ mol}^{-1}$) gives

$$a = 11$$

In fact, a is given by Stokes law for motion of a sphere in a viscous liquid as $a = 6\pi$.

1 b i) Let $F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} F_{\omega}$

$$V(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} V_{\omega}$$

Then $\frac{dV}{dt} = -\gamma V + \frac{1}{m} F$

because

$$i\omega V_{\omega} = -\gamma V_{\omega} + \frac{1}{m} F_{\omega}$$

$$\Rightarrow \boxed{V_{\omega} = \frac{F_{\omega}/m}{\gamma + i\omega}}$$

ii) The Wiener-Khinchine relation in complex Fourier transform is

$$\Omega(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{-i\omega s} \langle V(0)V(s) \rangle$$

$$= \frac{\langle V^2(0) \rangle}{2\pi} \int_{-\infty}^{\infty} ds e^{-i\omega s} e^{-\gamma|s|}$$

$$= \frac{\langle V^2(0) \rangle}{2\pi} \left\{ \int_0^{\infty} ds e^{-i\omega s} e^{-\gamma s} + \int_{-\infty}^0 ds e^{-i\omega s} e^{\gamma s} \right\}$$

$$= \frac{\langle V^2(0) \rangle}{2\pi} \left\{ -\frac{1}{\gamma + i\omega} (-1) + \frac{1}{\gamma - i\omega} (1) \right\}$$

$$= \frac{\langle v^2(\omega) \rangle}{2\pi} \left[\frac{1}{\gamma + i\omega} + \frac{1}{\gamma - i\omega} \right]$$

$$= \frac{\langle v^2(\omega) \rangle}{2\pi} \left(\frac{2\gamma}{\gamma^2 + \omega^2} \right)$$

$$\boxed{= \frac{k_B T}{2\pi m} \left(\frac{2\gamma}{\gamma^2 + \omega^2} \right)}$$

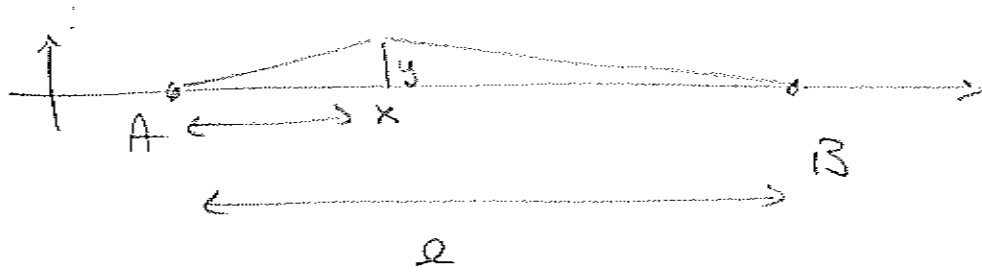
iii) Form $\langle v_w^* v_w \rangle = \frac{\frac{1}{m^2} \langle F_w^* F_w \rangle}{\gamma^2 + \omega^2}$

But $\langle R(\omega) \rangle = \langle v_w^* v_w \rangle$, so

$$\frac{\frac{1}{m^2} \langle F_w^* F_w \rangle}{\gamma^2 + \omega^2} = \frac{k_B T}{2\pi m} \cdot \frac{2\gamma}{\gamma^2 + \omega^2}$$

$$\Rightarrow \boxed{\langle F_w^* F_w \rangle = \frac{2m\gamma}{\pi} k_B T}$$

2a



From analysis of forces at x , we know that force on element dx of string at x is

$$d\mathcal{F} = \left(F \frac{d^2 y}{dx^2} \right) dx$$

Summed over string,

$$\mathcal{F} = F \int_0^l dx \frac{d^2 y}{dx^2} = F \left[\frac{dy}{dx} \Big|_l - \frac{dy}{dx} \Big|_0 \right]$$

From geometry, have slopes:

$$\frac{dy}{dx} \Big|_0 = \frac{y}{x} \quad \neq \quad \frac{dy}{dx} \Big|_l = \frac{y}{x-l}$$

so

$$\mathcal{F} = F y \left(\frac{1}{x} - \frac{1}{x-l} \right) = - \frac{F y l}{x(x-l)}$$

The energy is equal to work done in changing y :

$$\mathcal{E} = \int_0^y dy \frac{F l}{x(l-x)} y = \frac{1}{2} F l \frac{y^2}{x(l-x)}$$

Define the thermal average in terms of probability $P(\epsilon)$. Then we can write

$$\langle \epsilon \rangle = \frac{1}{2} k_B T = \frac{1}{2} F l \frac{\langle y^2 \rangle}{x(l-x)}$$

or

$$\langle y^2 \rangle = \frac{k_B T}{F l} x(l-x)$$

2b Evaluate

$$\begin{aligned}
 \Omega(f) &= \int_{-\infty}^{\infty} ds \, k(\omega) e^{-\alpha^2 s^2} \cos(\omega s) e^{-if s} \\
 &= \int_{-\infty}^{\infty} ds \, k(\omega) e^{-\alpha^2 s^2} \cos(\omega s) (\cos fs + i \sin fs) \\
 &= \int_{-\infty}^{\infty} ds \, k(\omega) e^{-\alpha^2 s^2} \cos \omega s \cos fs \\
 &= 2 \int_0^{\infty} ds \, k(\omega) e^{-\alpha^2 s^2} \frac{1}{2} (\cos(s(\omega+f)) + \cos(s(\omega-f))) \\
 &= \frac{1}{2} \sqrt{\frac{\pi}{\alpha^2}} k(\omega) \left(e^{-\frac{(\omega+f)^2}{4\alpha^2}} + e^{-\frac{(\omega-f)^2}{4\alpha^2}} \right)
 \end{aligned}$$

(using $\int_0^{\infty} \cos(kx) e^{-\gamma k^2} dk = \sqrt{\frac{\pi}{\gamma}} e^{-x^2/4\gamma}$)

$$\text{i) } \lim_{\alpha \rightarrow 0} \Omega = \lim_{\alpha \rightarrow \infty} \frac{1}{2} \sqrt{\pi \alpha^2} k(\omega) \left[e^{-\frac{\alpha^2}{4}(\omega+f)^2} + e^{-\frac{\alpha^2}{4}(\omega-f)^2} \right]$$

$\rightarrow 0$ if $\omega \neq f$. Otherwise a sharp peak at $\omega = f$ & $\omega = -f$

$$\text{ii) } \lim_{\omega \rightarrow 0} \Omega = \sqrt{\frac{\pi}{\alpha^2}} k(\omega) e^{-\frac{f^2}{4\alpha^2}}$$

$$\text{iii) } \lim_{\substack{\alpha \rightarrow 0 \\ \omega \rightarrow 0}} \Omega \rightarrow 0 \text{ unless } f = 0$$

The spectral density is largest for $f = \pm \omega$, and the breadth of frequencies around ω are determined by α .