

(1.)

$$S = kN \ln \left[\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{3/2} \right] + \frac{3}{2} kN \left(\frac{5}{3} + \ln \frac{4\pi m}{3h^2} \right)$$

$$U = -T \left(\frac{dS}{dN} \right)_{U,V}$$

$$\frac{dS}{dN} = k \ln \left[\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{3/2} \right] + \frac{kN}{\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{3/2}} + \frac{3kN}{2} \frac{kN}{\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{3/2}}$$

$$+ \frac{3}{2} k \left(\frac{5}{3} + \ln \frac{4\pi m}{3h^2} \right)$$

$$= k \ln \left[\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{3/2} \right] - k - \frac{3}{2} k + \frac{15}{6} k + k \ln \frac{4\pi m}{3h^2}$$

$$= k \ln \left[\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{3/2} \right] + A$$

$$A = \frac{5}{6} k + k \ln \frac{4\pi m}{3h^2}$$

$$\frac{U}{N} = \frac{3}{2} kT$$

for ideal gas.

$$c = \frac{N}{V}$$

$$U = -kT \ln \left(\frac{1}{c} \right) - \frac{3}{2} kT \ln \left(\frac{3}{2} kT \right) - AT$$

$$U = kT \ln \left(\frac{c}{c_0} \right) + U_0(T)$$

$$U_0(T) = -kT \ln c_0 - \frac{3}{2} kT \ln \left(\frac{3}{2} kT \right) - AT$$

using moles
instead of particles
gives us RT

reference concentration affects $U_0(T)$

2.

$$D = \frac{k_B T}{4\pi\eta_m h} \left[\ln \left(\frac{h\eta_m}{a\eta_w} \right) - \gamma \right] \quad \gamma \sim 0.577$$

assume η_w is viscosity of water

$$\eta_w = 10^{-3} \text{ Pa}\cdot\text{s}$$

when $a = 1.0 \text{ nm}$, $D = 1 \mu\text{m}^2/\text{s}$.

solve for η_m

$$\eta_m = \frac{k_B T}{4\pi D h} \left[\ln \left(\frac{h\eta_m}{a\eta_w} \right) - \gamma \right]$$

← this is
transcendental
equation.

see HW 3.2, m

For N proteins in a cluster, from conservation of area,

$$r_N^2 \approx N r_1^2$$

$$r_N = \sqrt{N} r_1$$

3.

$$\frac{\partial P(x,t)}{\partial t} = D \nabla^2 P(x,t)$$

for a closed 1D box of length L ,

$$\left. \frac{\partial P}{\partial x} \right|_{x=0} = \left. \frac{\partial P}{\partial x} \right|_{x=L} = 0 \quad \leftarrow \text{no flux through boundary}$$

write

$$P(x,t) = X(x) T(t)$$

$$X(x) \frac{dT(t)}{dt} = DT(t) \frac{d^2 X(x)}{dx^2}$$

can show that α must be positive

$$\frac{1}{D} \frac{T'}{T} = \frac{X''}{X} = -\alpha \quad \leftarrow \text{zero from B.C.}$$

$$X(x) = A \sin(\sqrt{\alpha} x) + B \cos(\sqrt{\alpha} x) \quad \text{and } \sqrt{\alpha} = \frac{n\pi}{L}$$

$$T(t) = C e^{-\alpha D t} = C e^{-\left(\frac{n\pi}{L}\right)^2 D t}$$

$$P(x,t) = \frac{P_0}{2} + \sum_{n=1}^{\infty} D_n \cos\left(\frac{n\pi x}{L}\right) e^{-\left(\frac{n\pi}{L}\right)^2 D t}$$

$$D_n = \frac{2}{L} \int_0^L f(x,0) \cos\left(\frac{n\pi x}{L}\right) dx$$

for a particle initially at x ,

$$f(x,0) = \delta(x)$$

$$D_n = \frac{2}{L} \int_0^L \delta(x) \cos\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L} \cos\left(\frac{n\pi x}{L}\right)$$

to find $\langle x^2 \rangle$, average over all

possible start and end positions.

$$P(y, t | x, 0) = \frac{1}{L} + \frac{2}{L} \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi y}{L}\right) e^{-\left(\frac{n\pi}{L}\right)^2 Dt}$$

$$P(x, 0) = \frac{1}{L}$$

$$\langle x^2 \rangle = \int_0^L \int_0^L (y-x)^2 P(y, t | x, 0) P(x, 0) dx dy$$

$$= \frac{1}{L} \int_0^L \int_0^L (y-x)^2 \left[\frac{1}{L} + \frac{2}{L} \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi y}{L}\right) e^{-\left(\frac{n\pi}{L}\right)^2 Dt} \right] dx dy$$

$$\int_0^L \int_0^L (y^2 - 2xy + x^2) dx dy = \frac{L^4}{6}$$

$$\int_0^L \int_0^L \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi y}{L}\right) x^2 dx dy = 0$$

$$\int_0^L \cos\left(\frac{n\pi x}{L}\right) x dx = L^2 \frac{\cos(\pi n) - 1}{\pi^2 n^2} = -\frac{2L^2}{\pi^2 n^2} \quad n \text{ odd}$$

$$0 \quad n \text{ even}$$

$$\langle x^2 \rangle = \frac{L^2}{6} - \frac{16L^2}{\pi^4} \sum \frac{1}{n^4} e^{-\left(\frac{n\pi}{L}\right)^2 Dt}$$

for a rectangular volume of size
 L_1, L_2, L_3

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$$

$$= \sum_{i=1}^3 \left[\frac{L_i^2}{6} - \frac{16L_i^2}{\pi^4} \sum \frac{1}{n^4} e^{-\left(\frac{n\pi}{L_i}\right)^2 Dt} \right]$$