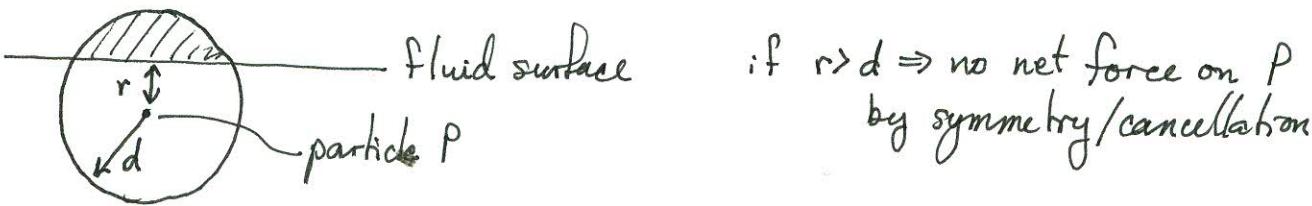


Internal energy of a liquid Dupré (1869), Massieu (1) (1)

- suppose there is a simple pairwise interaction $u(r)$ with some range d



for $r < d$ net force is negative of outwards force due to shaded region:

- suppose $f(s) =$ Force between two molecules at separation s

$$\begin{aligned} F(r) &= -2\pi \rho \int_r^d s^2 f(s) \int_0^{\cos^{-1}(r/s)} d\theta \sin\theta \cos\theta \quad - \frac{du}{ds} = f(s) \\ &= \left[-\pi \rho \int_r^d (s^2 - r^2) f(s) ds \right] \frac{1}{2} \sin^2(\cos^{-1}(r/s)) \\ &\quad f < 0 \quad (0 < s < d) \\ &\therefore F > 0 \end{aligned}$$

$\sqrt{s^2 - r^2}$

work to remove particle is

$$\begin{aligned} \int_{-d}^d F(r) dr &= \pi \rho \int_{-d}^d dr \int_r^d du(s) (s^2 - r^2) \\ &\quad (d^2 - r^2) u(s) \Big|_r^d - 2s u(s) ds \\ &= -2\pi \rho \int_{-d}^d dr \int_r^d s ds u(s) = -2\pi \rho \left[r \int_r^d s ds u(s) \right]_{r=-d}^d - \int_{-d}^d dr (-r) r u(r) \\ &\quad dv = dr \quad u = \int_s^d s ds u(s) \\ &\quad v = r \quad r \\ &\quad du = -r dr u(r) \\ &= -2\pi \rho \int_{-d}^d r^2 u(r) dr = \boxed{-\rho \int_0^d u(r) d^3 r} \end{aligned}$$

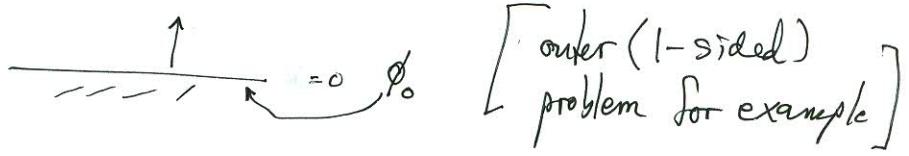
work is $-2x$ energy
to disintegrate
liquid

internal energy $\rightarrow -\frac{1}{2}$

$$\boxed{\frac{U}{N} = \frac{1}{2} \rho \int_0^d d^3 r u(r)}$$

Electrostatic contribution to elastic energy of surfaces

Take $\phi = \phi_0$ for simplicity

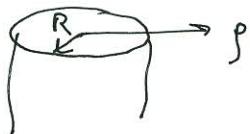


a) flat surface

$$\left(\frac{d^2}{dz^2} - \frac{1}{\lambda_{DH}^2} \right) \phi = 0 \quad \phi = \phi_0 e^{-z/\lambda_{DH}} \quad E\text{-field} = \frac{4\pi \sigma_0}{\epsilon} = -\frac{d\phi}{dz} \Rightarrow \phi_0 = \frac{4\pi \sigma_0}{\epsilon} \lambda_{DH}$$

energy density $\int_0^\infty \phi(\sigma) d\sigma = \frac{2\pi \sigma_0^2}{\epsilon} \lambda_{DH} = \boxed{\frac{\epsilon}{8\pi \lambda_{DH}} \phi_0^2}$

cylindrical surface



$$\frac{1}{S} \frac{d}{dg} \left(S \frac{d\phi}{dg} \right) - \frac{\phi}{\lambda_{DH}^2} = 0$$

outside

$$\phi(g) = \phi_0 \frac{K_0(S/\lambda_{DH})}{K_0(R/\lambda_{DH})} \quad \text{fixed potential}$$

$$\sigma_0 = -\frac{\epsilon}{4\pi} \frac{\partial \phi}{\partial g} \Big|_R = \frac{\epsilon}{4\pi} \frac{\phi_0}{\lambda_{DH}} \frac{K_1(R/\lambda_{DH})}{K_0(R/\lambda_{DH})} \Rightarrow \phi(g) = \frac{4\pi}{\epsilon} \lambda_{DH} \sigma_0 \frac{K_0(S/\lambda_{DH})}{K_1(R/\lambda_{DH})}$$

fixed σ

$$\text{energy density} = \frac{\epsilon}{8\pi} \frac{\phi_0^2}{\lambda_{DH}} \frac{K_1(R/\lambda)}{K_0(R/\lambda)} = \frac{2\pi}{\epsilon} \lambda \sigma^2 \frac{K_0(R/\lambda)}{K_1(R/\lambda)}$$

spherical surface

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) - \frac{1}{\lambda^2} \phi = 0 \quad \frac{d^2}{dr^2} (r\phi) - \frac{1}{\lambda^2} (r\phi) = 0 \quad \phi(r) = \phi_0 \frac{R}{r} e^{-(r-R)/\lambda_{DH}}$$

$$\phi(r) = \frac{4\pi}{\epsilon} \frac{\lambda R}{\lambda + R} \sigma_0 \frac{R}{r} e^{-(r-R)/\lambda} \quad \text{fixed } \sigma$$

$$\Sigma = \frac{\epsilon}{8\pi} \left(\frac{1}{R} + \frac{1}{\lambda} \right) \phi_0^2 = \frac{2\pi}{\epsilon} \frac{\lambda R}{\lambda + R} \sigma_0^2$$

expand in $1/R$ and match coefficients

$$\text{cylindrical surface} \quad H = \frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{R} + \frac{1}{\infty} = \frac{1}{R} \quad K = \frac{1}{R_1 R_2} = 0$$

$$\Sigma = \frac{2\pi}{\epsilon} \lambda \sigma^2 \frac{K_0}{K_1} \rightarrow \frac{2\pi}{\epsilon} \lambda \sigma^2 \frac{1 - \frac{1}{8} \frac{1}{R}}{1 + \frac{3}{8} \frac{1}{R}} \approx \frac{2\pi}{\epsilon} \lambda \sigma^2 \left[1 - \frac{1}{2} \frac{1}{R} + \dots \right]$$

$$\frac{1}{2} \chi H_0^2 = \frac{2\pi}{\epsilon} \lambda \sigma^2$$

$$\frac{2}{2} \chi H_0 = \frac{1}{2} \lambda^2 \cdot \frac{2\pi}{\epsilon} \sigma^2$$

$$\Rightarrow \left\{ \begin{array}{l} H_0 = \frac{4}{\lambda_{DH}} \\ \chi = \frac{\pi \lambda_{DH}^3 \sigma^2}{4\epsilon} \end{array} \right.$$

spherical surface $H = \frac{2}{R}$ $K = \frac{1}{R^2}$ expand to 2nd order

$$\epsilon = \frac{2\pi \lambda R}{2+R} \sigma_0^2 \approx 2\pi \frac{\lambda \sigma_0^2}{\epsilon} \left[1 - \frac{1}{R} + \frac{1}{2} \left(\frac{1}{R} \right)^2 \right]$$

$$\frac{1}{2} \chi H_0^2 = \frac{2\pi \lambda \sigma^2}{\epsilon}$$

$$2\chi H_0 = \frac{2\pi \lambda^2 \sigma^2}{\epsilon}$$

$$\frac{4}{2} \chi + \frac{1}{2} \chi_K = \pi \frac{\lambda \sigma^2}{\epsilon} \lambda^2$$

$$\Rightarrow \left\{ \begin{array}{l} H_0 = \frac{4}{\lambda_{DH}} \\ \chi = \frac{\pi \lambda_{DH}^3 \sigma^2}{4\epsilon} \\ \chi_K = \frac{\pi \lambda^3 \sigma^2}{\epsilon} \end{array} \right.$$

there are many other variants that can be calculated
 (inner problem, different boundary conditions...)

typical values: $\sigma_0 \sim 4 \times 10^4$ $\lambda_{DH} \sim 4 \times 10^{-7} \text{ cm}$ $\epsilon \approx 80$

$$R_0 \sim \frac{1}{H_0} \approx \frac{\lambda_{DH}}{4} \approx 10 \text{ \AA}$$

$$K \sim \frac{\pi \lambda^3 \sigma^2}{4\epsilon} \approx 10^{-11} \text{ erg}$$

$$\chi_K \sim 4\chi \approx 4 \times 10^{-11} \text{ erg}$$

1. Poisson-Boltzmann equation in d=1

$$\frac{d^2\phi}{dx^2} - \frac{8\pi ce}{\epsilon} \sinh(\beta c\phi) = 0$$

↓

$$\boxed{\frac{d^2\psi}{d\xi^2} = \sinh \psi}$$

$$\text{let } \psi = \beta c\phi$$

$$\psi_0 = \beta c\phi_0$$

$$\xi = \frac{x}{\lambda}$$

$$\frac{1}{\lambda^2} = \frac{8\pi ce^2}{\epsilon k_B T}$$

$$\psi(0) = \psi_0$$

$$\psi(\infty) \rightarrow 0$$

1st integral (multiply by $\frac{d\psi}{d\xi}$)

$$\frac{1}{2} \left(\frac{d\psi}{d\xi} \right)^2 = \cosh \psi - 1 \quad \xleftarrow{\text{determined by bdy conditions at } \infty}$$

$$\rightarrow \frac{d\psi}{d\xi} = \sqrt{2(\cosh \psi - 1)} = -2 \sinh(\psi_0/2)$$

$$\text{or, } \frac{d\psi}{d\xi} = - (e^{\psi_0/2} - e^{-\psi_0/2})$$

$$\text{let } \alpha = e^{\psi_0/2}$$

choose this sign
so ψ drops to 0
as $x \rightarrow \infty$

$$d \ln(\alpha - 1) - d \ln(\alpha + 1) = -d\xi \Rightarrow \ln \frac{\alpha - 1}{\alpha + 1} = -\xi + \underbrace{\ln \frac{e^{\psi_0/2} - 1}{e^{\psi_0/2} + 1}}_{\text{by bdy condition}}$$



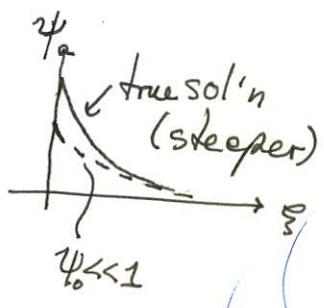
$$\boxed{e^{\psi_0/2} = \frac{e^{\psi_0/2} + 1 + (e^{\psi_0/2} - 1)e^{-\xi}}{e^{\psi_0/2} + 1 - (e^{\psi_0/2} - 1)e^{-\xi}}}$$

$$\text{check: } \xi = 0$$

$$\psi = \psi_0$$

$$\text{if } \psi_0 \ll 1 \Rightarrow \psi \approx \psi_0 e^{-\xi} \text{ which is correct.}$$

generally, ψ lies above the weak- ψ_0 limit



surface charge

$$\sigma = -\frac{\epsilon}{4\pi} \left. \frac{d\phi}{dx} \right|_{x=0} = \sqrt{\frac{2C\epsilon k_B T}{\pi}} \sinh(\psi_0/z)$$

$$\psi_0 \ll 1 \rightarrow \sqrt{\frac{2C\epsilon k_B T}{\pi}} \frac{\epsilon \phi_0}{z k_B T} = \frac{\epsilon}{4\pi z} \phi_0 \quad \text{correct.}$$

surface charge is always larger (from steeper drop in ϕ) than in weak- ψ_0 case

we say the increasing accumulation of charge (dilute) corresponds to an increase in the capacity of the double layer.

$$\begin{aligned} \text{Free energy (per unit area)} &= - \int_0^{\phi_0} \sigma(\phi') d\phi' \\ &= \boxed{-8Ck_B T \lambda \left[\cosh(\frac{\psi_0}{z}) - 1 \right]} \end{aligned}$$

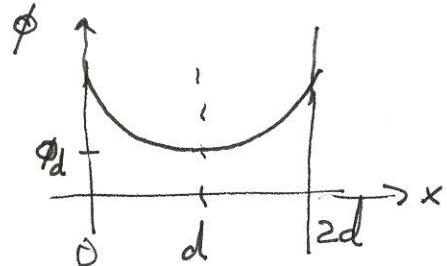
$$\text{when } \psi_0 \ll 1 \rightarrow -\frac{C\epsilon^2 \phi_0^2 \lambda}{k_B T} = -\frac{\epsilon \phi_0^2}{8\pi \lambda} \quad \text{correct}$$

increases faster than weak- ψ_0 case.
(in magnitude)

Harder calculation - 2 interacting double layers:

using the previous techniques, the 1st integral becomes

$$\frac{d\psi}{ds} = - \sqrt{2 \cosh \psi - 2 \cosh \psi_d} \quad \text{where } \psi_d = \frac{e\phi_d}{k_B T}$$



for a plate-spacing $2d$
so ϕ_d is potential mid-way
between 2 plates

$$\text{so } \int_{\psi_0}^{\psi_d} \frac{d\psi}{\sqrt{2(\cosh \psi - \cosh \psi_d)}} = -\frac{d}{\lambda} \quad \text{an elliptic integral.}$$

the essence of the interaction result can be obtained by approximate superposition of the potentials from the two plates, assuming $\frac{d}{\lambda} \gg 1$ but still keeping ψ_0 arbitrary then the potential in the middle is $\approx 2 \cdot$ separate contributions

$$\psi_d \approx 4 \left(\frac{e^{\psi_0/2} - 1}{e^{\psi_0/2} + 1} \right) e^{-d/\lambda}$$

larger prefactor than bare, weak ψ_0 result.

Finally, in a similar spirit, the free energy of interaction at large distances is approximately

$$\underline{32Ck_BT} \lambda \left(\frac{e^{\psi_{12}-1}}{e^{\psi_{12}+1}} \right)^2 (1 - \tanh(d/2))$$

again an enhanced prefactor

A more complete calculation can be found in

E.J.W. Verwey and J.Th.G. Overbeek,
"Theory of the stability of lyophobic Colloids,"
Elsevier, New York, 1948

A true classic

$$E = \frac{1}{2} A \int_0^L ds \lambda^2 - f z$$

$$z = \int_0^L ds \cos(\theta(s)) \approx \int_0^L ds \left(1 - \frac{1}{2} \theta^2 + \dots\right)$$

$$\tilde{t}_\perp \sim \theta$$

$$\approx L - \frac{1}{2} \int_0^L ds \tilde{t}_\perp^2$$

$$\text{so, } E \approx \frac{1}{2} \int_0^L ds \left\{ A \left(\frac{\partial \tilde{t}_\perp}{\partial s} \right)^2 + f \tilde{t}_\perp^2 \right\} - f L \quad \leftarrow \text{unimportant constant}$$

$$\text{define } \tilde{t}_\perp(s) = \sum_g e^{-igs} \hat{t}_{+g}$$

$$\text{then } E = \frac{1}{2} \int_0^L ds \left\{ \sum_g \sum_{g'} e^{-i(g+g')s} [-g g' A + f] \hat{t}_{+g} \hat{t}_{+g'} \right\} \quad \int_0^L ds e^{-i(g+g')s} = L \delta_{g,g'}$$

$$= \frac{1}{2} \sum_g L (A g^2 + f) |\hat{t}_{+g}|^2 \quad \langle |\hat{t}_{+g}|^2 \rangle = \frac{k_B T}{L(A g^2 + f)}$$

$\times \text{ or}$
 $y \text{ constant}$

$$\text{length change} = \frac{1}{2} \int_0^L ds \tilde{t}_\perp^2 = \frac{1}{2} \sum_g \frac{2 L k_B T}{L(A g^2 + f)} \rightarrow \int \frac{dg}{2\pi} \frac{L k_B T}{A g^2 + f} = \frac{L k_B T}{\sqrt{4fA}}$$

$$\text{so } \frac{L-z}{L} = \boxed{1 - z/L = \frac{k_B T}{\sqrt{4fA}}} \quad \text{or } f = \frac{(k_B T)^2}{A} \frac{1}{4(1-z/L)^2} \quad A = k_B T L p$$

$$\boxed{f = \frac{k_B T}{L p} \frac{1}{4(1-z/L)^2}}$$

Freely-jointed chain

$$\left. \begin{aligned} &\text{partition function of one link } Z_1 = \int_0^\pi d\phi \sin \phi e^{+\beta f b \cos \phi} = 2 \operatorname{sinh}(\beta f b) \\ &\langle \text{displacement} \rangle = \frac{\partial \ln Z_1}{\partial \beta f} = b \left\{ \coth(\beta f b) - \frac{1}{\beta f b} \right\} \end{aligned} \right.$$

$$\langle \text{full length} \rangle = Nb \left\{ \coth(\beta f b) - \frac{1}{\beta f b} \right\}; \text{ extended length} = Nb$$

$$\Delta \frac{\text{length}}{Nb} = 1 - z/L \approx 1 - \coth(\beta f b) + \frac{1}{\beta f b} \approx \frac{k_B T}{b f} \quad 1 - \frac{z}{L} \leftarrow \frac{k_B T}{f b}$$

$$\boxed{f \approx \frac{k_B T}{b} \frac{1}{(1-z/L)}}$$



6 (cont'd)

$$\begin{aligned}\text{Correlation function} &= \frac{1}{L} \int d\mathbf{r} \left\langle \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{\mathbf{t}}_1(\mathbf{q}) \sum_{\mathbf{q}'} e^{-i\mathbf{q}'\cdot(\mathbf{r}+\mathbf{s})} \hat{\mathbf{t}}_1(\mathbf{q}') \right\rangle \\ &= \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{s}} \langle |\hat{\mathbf{t}}_1(\mathbf{q})|^2 \rangle = \sum_{\mathbf{q}} \frac{k_B T}{L(Ag^2 + f)} e^{i\mathbf{q}\cdot\mathbf{s}} \cdot 2 \\ &= 2 \frac{k_B T}{A} \int \frac{dq}{2\pi} \frac{e^{i\mathbf{q}\cdot\mathbf{s}}}{q^2 + f/A} = \frac{k_B T}{\sqrt{fA}} e^{-s\sqrt{f/A}} \sim e^{-s/\xi} \quad \xi = \sqrt{A/f}\end{aligned}$$

by contour integration

$$m \frac{du}{dt} = -\gamma u + A(t) \quad , \quad \frac{du}{dt} = -\gamma u + A(t) \quad e^{\int_0^t dt' \frac{du}{dt'}} \underbrace{\left(\frac{du}{dt} + \gamma u \right)}_{\frac{d}{dt}(u e^{\int_0^t dt' \frac{du}{dt'}})} = A(t) e^{\int_0^t dt' \frac{du}{dt'}}$$

$$u(0) = u_0$$

$$\text{so } u(t) e^{\int_0^t dt' \frac{du}{dt'}} - u_0 = \int_0^t dt' e^{\int_0^{t'} dt'' \frac{du}{dt''}} A(t'')$$

$$U = \boxed{U(t) - u_0 e^{-\gamma t} = e^{-\gamma t} \int_0^t dt' e^{\int_0^{t'} dt'' \frac{du}{dt''}} A(t'')} \quad \langle U \rangle = e^{-\gamma t} \int_0^t dt' e^{\int_0^{t'} dt'' \frac{du}{dt''}} \cancel{\langle A(t'') \rangle} = 0$$

$$\langle U^2 \rangle = \langle U^2 \rangle - 2 \langle U \rangle u_0 e^{-\gamma t} + u_0^2 e^{-2\gamma t} = \langle U^2 \rangle - u_0^2 e^{-2\gamma t}$$

$$= e^{-2\gamma t} \int_0^t dt' \int_0^{t'} dt'' e^{\gamma(t'+t'')} \underbrace{\langle A(t') \cdot A(t'') \rangle}_{\phi(t'-t'')}$$

$$= \frac{1}{2} e^{-2\gamma t} \int_0^t \int_0^x dx \int_{-\infty}^{\infty} dy \underbrace{\phi(y)}_z$$

↑ extend by virtue
of short-time feature of ϕ

$$\langle U^2 \rangle = \frac{1}{2} e^{-2\gamma t} \tau \cdot \frac{1}{3} (e^{2\gamma t} - 1) = \frac{\tau}{2\gamma} (1 - e^{-2\gamma t})$$

$$\text{as } t \rightarrow \infty \quad \langle U^2 \rangle \text{ satisfies } \frac{1}{2} m \langle U^2 \rangle = \frac{3}{2} k_B T \quad \langle U^2 \rangle = \frac{3k_B T}{m}$$

$$\text{so } \frac{\tau}{2\gamma} = \frac{3k_B T}{m} \quad \boxed{\langle U^2 \rangle = \frac{3k_B T}{m} (1 - e^{-2\gamma t})}$$

To evaluate higher moments we note that since $\langle A \rangle = 0$, all odd moments are = 0
For the even moments we'll have to evaluate an expression of the form

$$e^{-2n\gamma t} \int dt_1 \cdots \int dt_{2n} e^{\gamma(t_1 + \cdots + t_{2n})} \langle A(t_1) A(t_2) \cdots A(t_{2n}) \rangle$$

so doing this by pairs will give the same contribution per pair as $\langle U^2 \rangle$, yielding $\langle U^2 \rangle^n$, with a prefactor given by the number of distinct pairs we can choose from $2n$ labels t_1, \dots, t_{2n}



- contd

so, with $2n$ labels there are n pairs:

the # of ways is $\frac{(2n)!}{n! 2^n} = \frac{2n \cdot (2n-1)(2n-2)(2n-3)\dots}{n \cdot (n-1)(n-2)\dots 2^n} = (2n-1)!!$

\leftarrow switch within pairs
 \uparrow permuting pairs

$$\therefore \langle U^{2n} \rangle = 1 \cdot 3 \cdot 5 \cdots (2n-1) \langle U^2 \rangle^n = (2n-1)!! \langle U^2 \rangle^n$$

For a Gaussian distribution this is exactly
the case, so

$$\langle U^2 \rangle = 1! \langle U^2 \rangle$$

$$\langle U^4 \rangle = 3 \langle U^2 \rangle^2$$

$$\langle U^6 \rangle = 15 \langle U^2 \rangle^3$$

$$P(\underline{u}, t; \underline{u}_0, 0) = \left[\frac{m}{2\pi k_B T (1 - e^{-2St})} \right]^{3/2} \exp \left[-\frac{m |\underline{u} - \underline{u}_0|^2}{2k_B T (1 - e^{-2St})} \right]$$

since $\underline{u}(t) = \underline{u}_0 e^{-St} + \int_0^t dt' e^{-S(t-t')} \underline{A}(t') ; \underline{\zeta} - \underline{\zeta}_0 = \int_0^t dt' \underline{u}(t')$

$$\underline{\zeta} - \underline{\zeta}_0 = \int_0^t dt' \left[\underline{u}_0 e^{-St'} + \int_0^{t'} dt'' e^{-S(t''-t')} \underline{A}(t'') \right]$$

so
$$\underline{\zeta} - \underline{\zeta}_0 - \frac{1}{S} (1 - e^{-St}) \underline{u}_0 = \int_0^t dt' \int_0^{t'} dt'' e^{-S(t'+t'')} \underline{A}(t'')$$

integrate by parts $dv = dt' e^{-St'} \quad u = \int_0^{t'} dt'' e^{-St''} \underline{A}(t'')$

$$v = -\frac{1}{S} e^{-St'} \quad du = e^{St'} \underline{A}(t') dt'$$

$$-\frac{1}{S} e^{-St} \int_0^{t'} dt'' e^{St''} \underline{A}(t'') \Big|_0^t + \frac{1}{S} \int_0^t dt' e^{-St'} e^{St'} \underline{A}(t')$$

$$= -\frac{1}{S} e^{-St} \int_0^t dt' e^{St'} \underline{A}(t') + 0 + \frac{1}{S} \dots = \left| \frac{1}{S} \int_0^t dt' \left[1 - e^{-S(t-t')} \right] \underline{A}(t') \right|$$

change label

$$\langle \underline{\zeta} - \underline{\zeta}_0 \rangle = \underline{u}_0 \frac{(1 - e^{-St})}{S}$$

cont'd'

$$\text{calculate variance: } \langle I - I_0 \rangle - \frac{u_0^2}{5} (1 - e^{-5t}) = \frac{1}{5} \int_0^t dt' [1 - e^{-5(t-t')}] A(t')$$

$$|\langle I - I_0 \rangle|^2 - 2 \langle I - I_0 \rangle \cdot \frac{u_0^2}{5} (1 - e^{-5t}) + \frac{u_0^2}{5^2} (1 - e^{-5t})^2 = \frac{1}{5^2} \int_0^t dt' \int_0^t dt'' [1 - e^{-5(t-t')}] [1 - e^{-5(t-t'')}] A(t') A(t'')$$

$$\langle \rangle \Rightarrow 1 - e^{-5t+5t'} - e^{-5t+5t''} + e^{-25t+5(t'+t'')}$$

$$\langle |I - I_0|^2 \rangle - \frac{u_0^2}{5^2} (1 - e^{-5t})^2 = \underbrace{\frac{1}{5^2} \int_0^t dt' \int_0^t dt'' \langle A(t') A(t'') \rangle}_{\frac{1}{2} \int_0^{2t} dx x = t\tau} - \underbrace{e^{-5t} \int_0^t dt' \int_0^t dt'' e^{5t'} \langle AA \rangle}_{e^{-5t} \cdot \frac{1}{2} \int_0^{2t} dx e^{5x/2} \int_0^x dy y}$$

$$- e^{-5t} \int_0^t dt' \int_0^t dt'' e^{5t''} \langle AA \rangle + e^{-25t} \int_0^t dt' \int_0^t dt'' e^{5(t'+t'')} \langle AA \rangle = - \frac{2}{5} (1 - e^{-5t})$$

as previously $= - \frac{2}{5} (1 - e^{-5t})$

$$\frac{2}{25} (1 - e^{-25t})$$

$$\begin{aligned} \text{so } \left| \langle |I - I_0|^2 \rangle - \frac{u_0^2}{5^2} (1 - e^{-5t})^2 \right| &= \frac{2}{5^2} \left(t - \frac{2}{5} (1 - e^{-5t}) + \frac{1}{25} (1 - e^{-25t}) \right) \quad \tau = \frac{3k_B T}{m} \cdot 25 \\ &= \frac{3k_B T}{m 5^2} \{ 25t - 4(1 - e^{-5t}) + 1 - e^{-25t} \} \\ &= \boxed{\frac{3k_B T}{m 5^2} (25t - 3 + 4e^{-5t} - e^{-25t})} \end{aligned}$$

for small t

$$25t - 3 + 4(1 - 5t + \frac{1}{2} 5^2 t^2 - \frac{1}{6} 5^3 t^3 + \dots) \sim 1 + 25t - \frac{1}{2} \cdot 45^2 t^2 + \frac{1}{6} 85^3 t^3 \dots$$

$$= O(5^3 t^3)$$

$$\text{so } \langle |I - I_0|^2 \rangle \simeq \frac{u_0^2}{5^2} \cdot 5^2 t^2 \simeq u_0^2 t^2 \quad \boxed{\text{ballistic}} \quad \text{initial condition remembered}$$

large t

$$\langle |I - I_0|^2 \rangle \sim \frac{6k_B T}{m 5} t \quad m 5 = \gamma \quad \text{so } \frac{6k_B T}{m 5} = 6D.$$

$\sim 6Dt$ diffusion.