Long-range forces: F+S Chapter 12

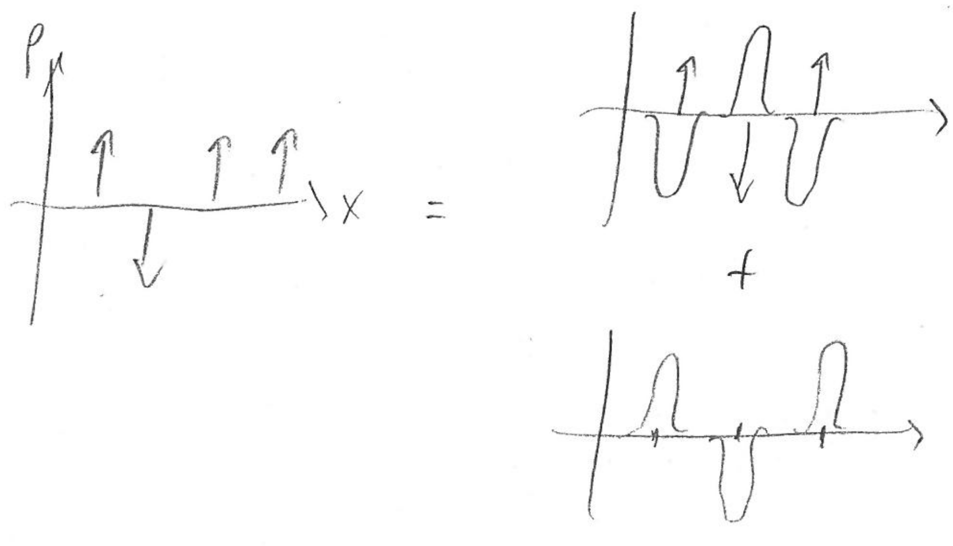
charges $\{q_i\} \rightarrow \varphi(\underline{r}) = \sum_i \frac{1}{4\pi\varepsilon_0} \frac{q_i}{|\underline{r}-\underline{r}_i|}$

$\xrightarrow[\text{system}]{\text{periodic}} \sum_i \sum_{\underline{n}} \frac{1}{4\pi\varepsilon_0} \frac{q_i}{|\underline{r}-\underline{r}_i-\underline{n}L|}$ $\left\{ \begin{array}{l} \underline{n} = \text{integer vector} \\ L = \text{box size} \end{array} \right.$

Sum is conditionally convergent at best.

Ewald summation: $\frac{1}{r} = \underbrace{\frac{1-f(r)}{r}}_{\text{converges}} + \underbrace{\frac{f(r)}{r}}_{\text{converges in Fourier space}}$ $\quad f(r) \xrightarrow[r\to\infty]{} 1$

$f(r)$ = screening function $= \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha \underline{r}^2}$



point + screen charge
"real" term

"compensating" charge
$\sum_{\underline{r}} \frac{f(r)}{r} \rightarrow \sum_{\underline{k}} F(\underline{k})$

Coulomb Energy $U = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{4\pi\varepsilon_0 |\underline{r}_i - \underline{r}_j|} = \frac{1}{2} \sum_i q_i \varphi(r_i)$

write $\varphi(\underline{r}_i) = \sum_{j \neq i} \left(\varphi_{point} + \varphi_{screen} + \varphi_{long} \right)$

$\underline{U_{comp}}$: get φ_c from Poisson eq. $\nabla^2 \varphi_c = -\rho_c/\varepsilon_0 \rightarrow \hat{\varphi}_c = \hat{\rho}_c/\varepsilon_0 \underline{k}^2$

$$\rho_c(\underline{r}) = \sum_i \sum_{\underline{n}} q_i \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\underline{r}-\underline{r}_i-\underline{n}L)^2}$$

so $$\hat{\rho}_c(\underline{k}) \equiv \frac{1}{V}\int_V d^3r\, e^{-i\underline{k}\cdot\underline{r}} \rho_c(\underline{r}) = \frac{1}{V} \underbrace{\int_V d^3r \sum_{\underline{n}}}_{=\int_\infty} \cdots$$

$$= \frac{1}{V}\sum_i q_i e^{-i\underline{k}\cdot\underline{r}_i - \underline{k}^2/4\alpha}$$

$$+\ \hat{\varphi}_c(\underline{k}) = \frac{1}{\varepsilon_0 V \underline{k}^2} \sum_i q_i e^{-i\underline{k}\cdot\underline{r}_i - \underline{k}^2/4\alpha}$$

$$\xrightarrow[\underline{k}\to 0]{} \underbrace{\sum_i q_i}_{=0 \text{ here}} - i\underline{k}\cdot \underbrace{\sum_i q_i \underline{r}_i}_{\text{related to exterior BC}} + O(\underline{k}^2)$$

related to exterior BC $\Rightarrow 0$ for perfect conductor surr.

$$\rightarrow \varphi_c(\underline{r}) = \sum_{\underline{k}\neq 0} \hat{\varphi}_c(\underline{k})\, e^{i\underline{k}\cdot\underline{r}} \quad . \ ! \text{ convergent due to } e^{-\underline{k}^2/4\alpha}$$

Write $$U_{comp} = \underbrace{\frac{1}{2}\sum_{i=1}^{N} q_i \cdot \underbrace{\sum_{j=1}^{N} q_j \varphi_c(r_{ij})}_{\varphi_c(r_j)}}_{=U_{comp,x}} - \underbrace{\frac{1}{2}\sum_i q_i \varphi_c(0)}_{=U_{self}}$$

$$U_{comp,x} = \frac{1}{2}\sum_{\underline{k}\neq 0} \sum_{ij=1}^{N} \frac{q_i q_j}{\varepsilon_0 V \underline{k}^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j) - \underline{k}^2/4\alpha}$$

$$= \frac{V}{2\varepsilon_0} \sum_{\underline{k} \neq 0} \frac{1}{\underline{k}^2} |\tilde{\rho}(\underline{k})|^2 e^{-\underline{k}^2/4\alpha}$$

↑ ρ not ρ_c, $\tilde{\rho} = \frac{1}{V} \sum_i q_i e^{-i\underline{k}\cdot\underline{r}_i}$

Converges due to $e^{-\underline{k}^2/4\alpha}$

<u>U_{self}</u> : $\varphi_c(\underline{0})$ = potential at $\underline{r}=0$ due to Gaussian charge dist centred at $\underline{r}=0$

solve $\nabla^2 \varphi_c = -\frac{1}{\varepsilon_0} \cdot q_i \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha \underline{r}^2} = \frac{1}{r} \frac{\partial^2}{\partial r^2}(r\varphi_c)$

⋮

$$\varphi_c(r) = \frac{q_i}{4\pi\varepsilon_0 r} \operatorname{erf}(\sqrt{\alpha} r) \xrightarrow[r \to 0]{} \frac{q_i}{4\pi\varepsilon_0} \cdot 2\sqrt{\frac{\alpha}{\pi}}$$

↳ $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z dT\, e^{-T^2}$

So $U_{self} = \frac{1}{2} \sum_i q_i \varphi_c(0) = \frac{1}{4\pi\varepsilon_0} \sqrt{\frac{\alpha}{\pi}} \sum_i q_i^2$

— x —

<u>U_{real}</u> :

$$= \frac{1}{2} \sum_i q_i \sum_{j \neq i} \sum_{\underline{n}} \left(\frac{q_j}{4\pi\varepsilon_0 r_{ij\underline{n}}} - \frac{q_j}{4\pi\varepsilon_0 r_{ij\underline{n}}} \operatorname{erf}(\sqrt{\alpha}\, r_{ij\underline{n}}) \right)$$

↳ $|\underline{r}_j - \underline{r}_i - \underline{n}L|$

$$= \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} q_i q_j \sum_{\underline{n}} \frac{\operatorname{erfc}(\sqrt{\alpha}\, r_{ij\underline{n}})}{r_{ij\underline{n}}}$$

$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty dT\, e^{-T^2} \xrightarrow[z \to \infty]{} \frac{e^{-z^2}}{\sqrt{\pi} z}$ ∴ series in $\underline{n}$ converges

Convergent result; choose α to optimize

operations in U_{real} $= O\left(N \cdot \rho r_c^3 \right) = O\left(\frac{N^2}{\alpha^{3/2} V} \right)$

N: from $\sum_i$; ρr_c^3: neighbors; $r_c \to \frac{1}{\sqrt{\alpha}}$

" $U_{recip,\alpha}$ $= O\left(N \cdot \alpha^{3/2} V \right) = O\left(\alpha^{3/2} N V\right)$

N: compute $\rho(k)$; $\alpha^{3/2} V$: $e^{-k^2/4\alpha}$, $\underline{k} = \frac{2\pi}{V}\underline{n}$

Total # ops $= c_1 \cdot \frac{N^2}{\alpha^{3/2} V} + c_2\, \alpha^{3/2} N V$

max when $\frac{\partial}{\partial \alpha}(\,) = 0 \to \alpha^{3/2 *} \to$ # ops $\propto N^{3/2}$

Better: particle-mesh Ewald = "P^3M"

$U_{recip} \leftrightarrow$ smoothed charges

high accuracy not needed $\to$ finite diff solution

width of Gaussian $\sim \frac{1}{\sqrt{\alpha}}$ $\to$ grid spacing $\sim \frac{\text{width}}{10} \sim \frac{1}{\sqrt{\alpha}}$

grid points $= \frac{V}{\text{spacing}^3} \sim \alpha^{3/2} V$

Solve Poisson using FFT, # ops $= O(n \log n)$ # pts.

$\to$ # ops $= c_1 \frac{N^2}{\alpha^{3/2} V} + c_2' \alpha^{3/2} V \log\left(\alpha^{3/2} V\right) + c_3 \underbrace{N}_{\text{from } \tilde{\rho}(k)}$

$\xrightarrow{\text{optimize}}$ $O(N \log N)$.

Correlation functions + linear response FS, § 4.4, App. C
AT, Ch 8, 11

example - diffusivity

direct method : defn is $\langle (\underline{r}(t)-\underline{r}(0))^2\rangle \xrightarrow[t\to\infty]{} 6Dt$ (3d)

in the lj code, arrays dax(i), day(i), daz(i)

updated via dax = dax + $x_{new} - x_{old}$, etc.

→ dax = physical displacement of particle i (no PBC)

so $D = \frac{1}{N}\sum_i \left(dax(i)^2 + day(i)^2 + daz(i)^2\right) / 6 \times$ #steps × delta

CF method: $x(t) = x(0) + \int_0^t dt' v_x(t')$; also $y(t), z(t)$

$$\to D = \lim \frac{1}{6t}\langle(\underline{r}(t)-\underline{r}(0))^2\rangle$$

$$= \lim \frac{1}{6t}\left\langle\left(\int_0^t dt'\underline{v}(t')\right)^2\right\rangle$$

$$= \lim \frac{1}{6t}\int_0^t dt'\int_0^t dt''\underbrace{\langle\underline{v}(t')\cdot\underline{v}(t'')\rangle}$$

$C(t,t')$ = VACF

vel. auto-corrl. fcn.

In equil:

$C(t',t'') = C(t'+\Delta, t''+\Delta)$: time translation inv.

$= C(t'-t'') = C(t''-t')$: time reversal inv

so $\int_0^t dt'\int_0^t dt'' C(t',t'') = 2\int_0^t dt'\int_0^{t'} dt'' C(t''-t')$

square

Continuum method: $\frac{\partial c}{\partial t} = D\nabla^2 c$

1. $\int_\infty d^3r\, c(\underline{r},t) = K(t)$ = amount of diffusing material at time t

$$\frac{dK}{dt} = \int_\infty d^3r \frac{\partial c}{\partial t} = D\int_\infty d^3r\, \nabla^2 c$$

$$= D\int_{\partial S} d\underline{S}\cdot\nabla c = 0 \text{ if material is localized}$$

↳ surface at ∞

(e.g. pt. source $c(\underline{r},t) = (4\pi Dt)^{-3/2} e^{-r^2/4Dt} \xrightarrow[t\to 0]{} \delta^3(\underline{r})$)

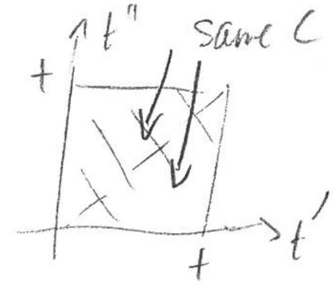
so $K(t) = K(0)$

2. $\langle(\underline{r}(t)-\underline{r}(0))^2\rangle = \int d^3r\, (\underline{r}-\underline{r}(0))^2 c(\underline{r},t) \Big/ \underbrace{\int d^3r\, c(\underline{r},t)}_{=K_0}$

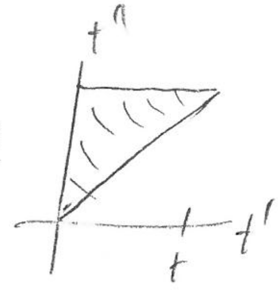
$$\frac{d}{dt}\langle \text{"} \rangle = \frac{1}{K_0}\int d^3r\, (\underline{r}-r_0)^2 \frac{\partial c}{\partial t} = \frac{D}{K_0}\int d^3r\, (\underline{r}-r_0)^2\nabla^2 c$$

$$= \frac{D}{K_0}\int d^3r \left\{ \nabla\cdot\left[(\underline{r}-r_0)^2\nabla c - \nabla(\underline{r}-r_0)^2\cdot c\right] + \nabla^2(\underline{r}-r_0)^2\cdot c\right\}$$

$$= \frac{D}{K_0}\underbrace{\int_{\partial S}\left[\text{"}\right]}_{0} + \frac{D}{K_0}\int d^3r\, 6c = 6D$$



$$= 2$$



Let $\tau = t'' - t'$ $\quad \dots = 2\int_0^t d\tau\, C(\tau) \int_\tau^t dt''$

$$= 2t \int_0^t d\tau \left(1 - \frac{\tau}{t}\right) C(\tau)$$

$C(\tau)$ decays with τ $\quad \xrightarrow[t\to\infty]{} 2t \int_0^\infty d\tau\, C(\tau)$

So $D = \frac{1}{3}\int_0^\infty d\tau\, C(\tau)$: example of a "Green Kubo" formula

transport coefficient $= \int dt$ (correlation fn.)

Recall Langevin eq $m\ddot{x} = -\gamma \dot{x} + \sqrt{2\gamma k_B T}\, \xi(t)$

$$\rightarrow \quad v_x(t) = v_x(0) e^{-\gamma t/m} + \sqrt{\cdot} \int_0^t dt'\, \eta(t') e^{-\frac{\gamma}{m}(t-t')}$$

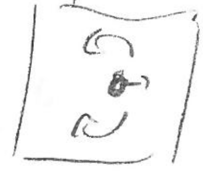
$$C_x(t) = \langle v_x(t)\, v_x(0) \rangle = \underbrace{v_x(0)^2}_{kT/m} e^{-\gamma t/m}$$

$$\rightarrow \quad D = \int_0^\infty d\tau\, C_{xx}(\tau) = kT/\gamma \quad \text{(Stokes-Einstein)}$$

Alder + Wainwright (1957) measured C_{xx} in 2d, got $C_{xx} \sim \frac{1}{t}$

($C_{xx} \sim t^{-d/2}$ in d-dim, later) !

Why? correlations in the fluid motion :

if $v_x(0) > 0$, say, then  moving particle pushes others out of the way, → dipole flow 

→ look at point source of vorticity

$$\underline{\omega} = \nabla \times \underline{u}, \qquad \frac{\partial \underline{\omega}}{\partial t} = \nu \nabla^2 \underline{\omega} \qquad \nu = \text{kinematic visc.}$$

$$\underline{\omega}(0) = \underline{\omega}_0\, \delta(\underline{r}) \to \underline{\omega}(\underline{r},t) = \underline{\omega}_0 (4\pi\nu t)^{-d/2} e^{-r^2/4\nu t}$$

$$\to \underline{\omega}(0,t) \propto t^{-d/2}$$

See T. Franosch et al. Nature $\underline{478}$, 85 (2011)

— x —

General method - linear response

$A(\{x_i, p_i\})$ = some fcn. of position + velocity

in equil $\langle A \rangle_0 = \frac{1}{Z_0} \int d\Gamma\, e^{-H_0/kT} A(\Gamma)$

Often $A \sim$ current/flux of something so $\langle A \rangle_0 = 0$,
but if extra interaction added, get $\langle A \rangle \neq 0$.

Add perturbation $B(\{x_i, p_i\})$ to H: $H \to H_0 - B$.

$$\langle A \rangle = \frac{1}{Z} \int d\Gamma\, e^{-(H_0 - B)/kT} \cdot A$$

$$= \frac{\int d\Gamma\, e^{-H_0/kT} (1 + B/kT + \dots) A}{\int d\Gamma\, e^{-H_0/kT} (1 + B/kT + \dots)}$$

$$= \langle A \rangle_0 + \frac{1}{kT}\left(\langle BA \rangle_0 - \langle A \rangle_0 \langle B \rangle_0 \right)$$

or $\langle A \rangle = \frac{1}{kT} \langle AB \rangle_0$

Example: dipoles in an electric field

atomic dipole moment

instantaneous dipole moment $\underline{P}(t) = \sum_i \underline{p}_i \, \delta(\underline{r} - \underline{r}_i(t))$

total dipole moment / volume $\underline{P} = \frac{1}{V} \int d^3r \, \underline{P}(\underline{r}, t) = \frac{1}{V} \sum \underline{p}_i(t)$

expect $\underline{P} = \underline{\underline{\Sigma}} \cdot \underline{E}$ $\quad \underline{\underline{\Sigma}}$ = polarizability tensor

"perturbation" = interaction energy $\Delta H = -\sum_i \underline{p}_i \cdot \underline{E}$

$= -V \underline{P} \cdot \underline{E}$

use linear response $\underline{A} = \underline{P}$, $B = \Delta H$

$$\rightarrow \langle \underline{P} \rangle_t = \frac{1}{kT} \langle \underline{P} (V \underline{P} \cdot \underline{E}) \rangle$$

$$= \underbrace{\frac{V}{kT} \langle \underline{P}\, \underline{P} \rangle}_{\underline{\underline{\Sigma}}} \cdot \underline{E}$$

computed from equil fluctuations

Electrical conductivity $\begin{cases} \text{detailed treatment} - \text{F \& S} \\ \text{non-rigorous} - \text{here} \end{cases}$

current density $\underline{j}(\underline{r}, t) = \sum_i q_i \dot{\underline{r}}_i \, \delta(\underline{r} - \underline{r}_i(t))$

want avg $\langle \underline{J} \rangle = \frac{1}{V} \int d^3r \, \underline{j}(\underline{r}, t) \xrightarrow[\text{const } \underline{E}]{} \underline{\underline{\Sigma}} \cdot \underline{E}$

cond. tensor

tricky part : currents dissipate energy
not natural in Hamiltonian formalism

energy dissipation rate $= "\underline{F} \cdot \underline{v}" = \sum_i q_i \underline{E}(\underline{r}_i) \cdot \dot{\underline{r}}_i\, \delta(\underline{r}-\underline{r}_i)$

$= \int d^3r\, \underline{J}(\underline{r},t) \cdot \underline{E}$

if $\underline{E}$ is turned on at $t=0$,
energy loss $= - \int_0^\infty dt' \int d^3r\, \underline{J}(\underline{r},t') \cdot \underline{E}$

= perturbation in linear response

$\rightarrow \quad \langle \underline{J} \rangle = \frac{1}{kT} \langle \underline{J}(\underline{r},0) \cdot \int_0^\infty dt' \int d^3r\, \underline{J}(\underline{r},t') \cdot \underline{E} \rangle$

$\hookrightarrow \frac{1}{V} \int d^3r'\, \underline{J}(\underline{r}',0)$

$= \frac{1}{kTV} \int d^3r\, d^3r' \int_0^\infty dt' \langle \underline{J}(\underline{r},t')\, \underline{J}(\underline{r}',0) \rangle \cdot \underline{E}$

$\underline{\underline{\Sigma}}$

$\underline{\underline{\Sigma}} = \frac{1}{kTV} \int_0^\infty dt \langle \sum_{ij} q_i q_j\, \dot{\underline{r}}_i\, \dot{\underline{r}}_j \rangle$

— x —

Same reasoning for viscous stress tensor
direct method – simulate Couette or Poisseuille flow
semi-direct – Lees-Edwards BC
CF method : want $\langle \underline{\underline{\sigma}} \rangle = \frac{1}{V} \int d^3r \langle \underline{\underline{\sigma}}(r,t) \rangle$
$\uparrow$ Irving Kirkwood expr.

rate of energy loss $= -\int d^3r\, \underline{\underline{\sigma}} : \underline{\underline{e}}$ $\quad e_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i)$

viscosity, defined by $\langle \underline{\underline{\sigma}} \rangle = 2\mu \langle \underline{\underline{e}} \rangle$

pert in H is $\Delta H = -\int_0^\infty dt \int d^3r\, \underline{\underline{\sigma}} : \underline{\underline{e}}$

so $\quad \langle \underline{\underline{\sigma}} \rangle = \frac{1}{kT} \langle \underline{\underline{\sigma}}\, \Delta H \rangle_0$

$$= \underbrace{\frac{1}{kTV} \int_0^\infty dt \int d^3r\, d^3r' \langle \underline{\underline{\sigma}}(\underline{r},0)\, \underline{\underline{\sigma}}(\underline{r}'t') :}_{\text{4th rank tensor, used in elasticity}} \underline{\underline{e}} \rangle_0$$

Specialize to simple shear flow, $\underline{u} = \dot{\gamma} y \hat{x}$

$$e_{ij} = \begin{cases} \dot{\gamma}/2 & i=x,\ j=y \text{ or v.v.} \\ 0 & \text{otherwise} \end{cases}$$

? $\int d^3r\, d^3r'$ kills the $\delta(\underline{r}-\underline{r}_i)$ factors in IK

$\rightarrow \quad \mu = \frac{1}{VkT} \int_0^\infty dt' \langle \sigma_{xy}(0)\, \sigma_{xy}(t') \rangle$

$\quad \hookrightarrow \sum_i m_i \dot{x}_i \dot{y}_i + \sum_{i \neq j} x_{ij} F_{y,ij}$

better equil statistics: $\frac{1}{3} \sum_{\alpha = (xy),(yz),(zx)} \langle \sigma_\alpha(t)\, \sigma_\alpha(0) \rangle$

"Real" proof is very gory due to "anisotropy in NS", $\underline{k} \cdot \underline{v}(k) = 0$

$\rightarrow$ longitudinal + transverse CFs.

See Hansen + McDonald, Th. of Simple Liquids