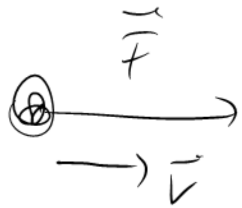
$$p\left(\vec r, t + \frac{a^2}{6D}\right) = \frac{1}{6}\sum_i p(\vec r + a\vec c_i, t)$$

$$\partial_t p = D\nabla^2 p$$

---

what happens if we introduce an external force $\vec F(\vec r, t)$?



$$\underbrace{\vec v}_{\text{drift velocity}} = \underbrace{\mu}_{\text{mobility}} \vec F$$

overdamped motion, no inertia $\rightsquigarrow$ mass unimportant!

New Mastereq.

$$p\left(\vec{r}, t + \frac{a^2}{6D}\right) = \frac{1}{6} \sum_i p(\vec{r} + a\vec{c}_i, t)$$

$$+ \sum_i T_i(\vec{r} + a\vec{c}_i, t)\, p(\vec{r} + a\vec{c}_i, t)$$

"transfer coefficient", encodes the effect of $\vec{F}$

$$\sum_i T_i(\vec{r}, t) = 0$$ conservation of probability

$T_i = ???$ <u>require</u>: - T_i dimensionless

- T_i scalar

- $T_i \propto \breve{F}$ linear response

$\Rightarrow T_i \propto \breve{F} \cdot$ (some vector) $\rightarrow \breve{c}_i$

$T_i \propto \breve{F} \cdot \breve{c}_i$

$\breve{c}_i \rightarrow$ dimensionless

$\breve{F} \rightarrow$ unit: $\frac{kg\,m}{s^2}$

get rid of kg: divide by $k_B T$, or multiply by $\beta = 1/k_B T$

$\hookrightarrow$ unit: $\frac{kg\, m^2}{s^2}$

$\Rightarrow T_i \propto \beta \breve{\vec{F}} \cdot \vec{c}_i$ unit: $\frac{1}{m}$ [meter]

$\Rightarrow T_i \propto a \beta \breve{\vec{F}} \cdot \vec{c}_i$ (a is only length)

$\rightarrow T_i = A a \beta \breve{\vec{F}} \cdot \vec{c}_i$ A numerical prefactor

$\hookrightarrow \sum_i T_i = 0$ conservation law

$$p\left(\vec{r}, t + \frac{a^2}{6D}\right) = \frac{1}{6} \sum_i p(\vec{r} + a\vec{c}_i, t)$$

$$+ A a \beta \sum_i c_{i\alpha} F_\alpha(\vec{r} + a\vec{c}_i, t)\, p(\vec{r} + a\vec{c}_i, t)$$

$$F_\alpha(\vec{r} + a\vec{c}_i, t)\, p(\vec{r} + a\vec{c}_i, t) \simeq$$

$$F_\alpha(\vec{r}, t)\, p(\vec{r}, t) + a c_{i\gamma} \partial_\gamma F_\alpha(\vec{r}, t)\, p(\vec{r}, t) + \underbrace{O(a^2)}_{\text{not needed}}$$

$$\sum_i c_{i\alpha} F_\alpha(\vec{r} + a\vec{c}_i, t)\, p(\vec{r} + a\vec{c}_i, t) \simeq$$

$$a \cdot 6 \cdot \frac{1}{3} \delta_{\alpha\gamma} \partial_\gamma F_\alpha(\vec{r}, t)\, p(\vec{r}, t) = 2a\, \partial_\alpha F_\alpha(\vec{r}, t)\, p(\vec{r}, t)$$

$$\frac{a^2}{6D}\,\partial_t\, p(\vec{r},t) = \frac{a^2}{6}\,\vec{\nabla}^2 p(\vec{r},t) + 2\,A\,a^2\beta(\vec{\nabla}\cdot\vec{F})\,p(\vec{r},t)$$

$$\partial_t\, p(\vec{r},t) = D\,\vec{\nabla}^2 p(\vec{r},t) + 12\,A\,D\beta(\vec{\nabla}\cdot\vec{F})\,p(\vec{r},t) \quad \Big|\ \frac{1}{a^3}$$

$$\boxed{\partial_t P = D\,\vec{\nabla}\cdot\left[\vec{\nabla} + 12\,A\beta\vec{F}\right] P(\vec{r},t)}$$

Smoluchowski equation

$A = ???$

force $\vec{F}$ $\leftrightarrow$ potential U $\quad \vec{F} = -\vec{\nabla} U$

(t-independent)

$t \to \infty \quad P \longrightarrow \text{const.} \cdot \exp(-\beta U)$

$$0 = \vec{\nabla} \cdot \left[\vec{\nabla} + \eta A \beta \vec{F} \right] \exp(-\beta U)$$

$$\vec{\nabla} \exp(-\beta U) = \exp(-\beta U)(-\beta) \vec{\nabla} U = \beta \vec{F} \exp(-\beta U)$$

$$0 = \vec{\nabla} \cdot \left[1 + \eta A \right] \beta \vec{F} \exp(-\beta U) \qquad \boxed{A = -\frac{1}{\eta}}$$

$$\Rightarrow \underbrace{\partial_t P = D\,\vec{\nabla}\cdot\left[\vec{\nabla} - \beta\vec{F}\right]P}_{\text{final Smoluchowski equation}}$$

interpretation as a continuity equation

$$\partial_t P + \vec{\nabla}\cdot\vec{j} = 0$$

$$\vec{j} = \underbrace{-D\nabla P}_{\text{diffusive current}} + \underbrace{D\beta\vec{F}P}_{\text{drift current}}$$

on the other hand: $\swarrow$ drift velocity

$$\text{drift current} = \bar{v}\, p$$

$$\leadsto \bar{v} = D \beta \bar{F} \qquad \text{def. mobility: } \bar{v} = \mu \bar{F}$$

$$\mu = D\beta \qquad \boxed{D = k_B T \mu}$$

$\hookrightarrow$ Einstein relation (example of the fluctuation-dissipation theorem)

$\vec{v} = \mu \vec{F}$ $\vec{F} = \xi \vec{v}$

$\hookrightarrow \xi = \frac{1}{\mu}$ friction coefficient

5.3. Langevin Equation

Back to the particle hopping on the lattice

$$\vec{r}(t+h) = \vec{r}(t) + a\vec{c}_i$$

position of the particle

random variable, just the direction that the particle has picked

$$\Delta \vec{r} = \vec{r}(t+h) - \vec{r}(t) = a\,\vec{c}_i$$

is a random variable

$\to \langle \Delta \vec{r} \rangle$ mean displacement

$\langle \Delta \vec{r}^2 \rangle$ " square "

$\langle \Delta \vec{r}^k \rangle$ mean kth displacement

$$\langle \Delta \vec{r}^k \rangle = a^k \underbrace{\langle \vec{c}_i^{\,k} \rangle}_{\text{order one!}} = O(a^k)$$

BUT for the asymptotic behavior we only need to be accurate up to $O(a^2)$

$\rightarrow$ only needed $\langle \breve{c} \rangle$, $\langle \breve{c}^2 \rangle$

$\langle \breve{c}^k \rangle = \sum_i \breve{c}_i^k \, p_i$

transition probability, or prob. to pick a jump in direction i

we know

$p_i = \frac{1}{6} - T_i$

jump in direction $-\breve{c}_i$!

$$A = -1/12$$

$$p_i = \frac{1}{6} - T_i = \frac{1}{6} - A\, a \beta \vec{F} \cdot \vec{c}_i =$$

$$= \frac{1}{6} + \frac{1}{12} a \beta \vec{F} \cdot \vec{c}_i$$

$a \to 0$

$(h \to 0)$:

diffusion dominates

$$\langle c_\alpha \rangle = \sum_i p_i c_{i\alpha} = \frac{1}{6} \underbrace{\sum_i c_{i\alpha}}_{=0}$$

$$+ \frac{1}{12} a \beta F_\gamma \underbrace{\sum_i c_{i\gamma} c_{i\alpha}}_{2\delta_{\alpha\gamma}} = \frac{1}{6} a \beta F_\alpha$$

$$\langle a\vec{c} \rangle = \frac{a^2}{6}\beta\vec{F}$$

$$\langle c_\mu c_\nu \rangle = \sum_i p_i \, c_{i\mu} c_{i\nu} =$$

$$= \underbrace{\frac{1}{6}\sum_i c_{i\mu} c_{i\nu}}_{\frac{1}{3}\delta_{\mu\nu}} + \frac{1}{12} a\beta F_\alpha \underbrace{\sum_i c_{i\alpha} c_{i\mu} c_{i\nu}}_{=0} =$$

$$= \frac{1}{3}\delta_{\mu\nu}$$

$$\langle (ac_\mu)(ac_\nu) \rangle = 2 \cdot \frac{a^2}{6}\delta_{\mu\nu}$$

Centered moment:

$$\left\langle \left[(ac_\mu) - \langle ac_\mu \rangle \right] \left[(ac_\nu) - \langle ac_\nu \rangle \right] \right\rangle =$$

$$\langle (ac_\mu)(ac_\nu) \rangle - \underbrace{\underbrace{\langle ac_\mu \rangle}_{\propto a^2} \underbrace{\langle ac_\nu \rangle}_{\propto a^2}}_{O(a^4) \to \text{neglect}} = 2 \cdot \frac{a^2}{6} \delta_{\mu\nu}$$

EQUIVENT update procedure

$$\vec{r}(t+h) = \vec{r}(t) + \frac{a^2}{6}\beta\vec{F} + \sqrt{2\cdot\frac{a^2}{6}}\,\vec{\rho}$$

random vector

$$\langle\vec{\rho}\rangle = 0$$

$$\langle\rho_\alpha\rho_\beta\rangle = \delta_{\alpha\beta}$$

ONLY properties that are needed

$$\left\langle\left(\sqrt{2\cdot\frac{a^2}{6}}\,\rho_\alpha\right)\sqrt{2\cdot\frac{a^2}{6}}\,\rho_\beta\right\rangle = 2\cdot\frac{a^2}{6}\,\delta_{\alpha\beta}$$

Now, $a^2 = 6Dh$ $\quad \frac{a^2}{6} = Dh$

$$\frac{a^2}{6}\beta = Dh\beta \underset{\uparrow}{=} \mu h$$

Einstein

$$\underbrace{\vec{r}(t+h) = \vec{r}(t) + \mu \vec{F} h + \sqrt{2Dh}\,\vec{\rho}}_{\text{Langevin in its discretized form}}$$

$$\underbrace{\frac{\vec{r}(t+h) - \vec{r}(t)}{h} = \mu \vec{F} + \sqrt{\frac{2D}{h}}\,\vec{\rho}}$$

$\Rightarrow \dfrac{d\vec{r}}{dt}$ does not exist

$\downarrow$ diverges for $h \to 0$!!

<u>FORMAL</u> way of writing the update scheme:

Langevin equation

$$\frac{d\vec{r}}{dt} = \mu \vec{F} + \vec{\eta}$$

noise variable

"Gaussian white noise"

$$\langle \vec{\eta} \rangle = 0$$

$$\langle \eta_\alpha(t)\, \eta_\beta(t') \rangle = 2D\, \delta(t-t')\, \delta_{\alpha\beta}$$

(not so obvious)