Estimations

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1 Diffusion on a parabolic peak

Let's say $\rho(t=0) = \rho_0(x)$. Then we can say

$$\rho_0(x) = \int \rho_0(y)\delta(x-y)\mathrm{d}y \tag{1}$$

We also know how a delta function evolves under a linear potential $f = -cx$:

$$\delta(x - x_{init})\Big|_{t=0} \to \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - x_{init} - vt)^2}{4Dt}\right] \tag{2}$$

where

$$v = -\frac{D}{T}\frac{\partial f}{\partial x}\Big|_x = c\frac{D}{T} \tag{3}$$

Now, we can say that if $v(x) \neq const$ and $D(x) \neq const$, then for small enough δt we can still say that each $\delta(x-y)$ in the initialintegral will transform approximately under liner force.

So, we define

$$P(x, \delta t | y, 0) = \frac{1}{\sqrt{4\pi D(x)\delta t}} \exp\left[-\frac{(x - y - v(x)t)^2}{4D(x)\delta t}\right], \quad v(x) = -\frac{D}{T}\frac{\partial f}{\partial x}\Big|_x \tag{4}$$

Then we can evolve each $\delta(x-y)$ and get

$$\rho_1(x) = \rho(t = \delta t, x) \approx \int \rho_0(y) P(x, \delta t | y, 0)\mathrm{d}y \tag{5}$$

If $v(x) = v_0 = const$ and $D(x) = D_0 = const$, then we can easily solve this because we basically have

$$\rho_1(x) = \int \rho_0(y) g(x - y, \delta t, D, ...)\mathrm{d}y \tag{6}$$

so for fourier images

$$\tilde{\rho}_1(k) = \tilde{\rho}_0(k) \cdot \tilde{P}(k, \delta t, D, ...) \tag{7}$$

so

$$\tilde{\rho}_n(k) = \tilde{\rho}_0(k) \cdot \tilde{P}^n(k, \delta t, D, ...) \tag{8}$$

therefore we get a convolution

$$\rho_{n=t/\delta t}(x) = \left\{\rho_0 * F^{-1}\left[\tilde{P}^n(k, \delta t, D, ...)\right]\right\}(x) \tag{9}$$

A typical case of $\rho_0(x) = \delta(x - x_{init})$ gives us

$$\rho_{n=t/\delta t}(x) = F^{-1}\left[\tilde{P}^n(k, \delta t, D, ...)\right](x - x_{init}) \tag{10}$$

However, our case is morecomplicated since we at least do not have $v(x) = const$. For us $f(x) = -\pi\Gamma^2(x - x_0)^2$, so $v(x) = 2\pi(x - x_0)\Gamma^2 D/T$. This does not allow us to write $P(x, \delta t|y, 0)$ as a function on $x - y$ so $\rho_1(x)$ is not a convolution of $\rho_0(x)$ with a function.

So, we have to go back to a more straighforward way of eq.(5). We also need to choose $D(x)$ and we choose the simplest thing $D(x) = D = const$.

After performing a few integrals of the form of eq.(5) we can notice that the density has the form of

$$\rho_n(x) = A_n \exp\left[-\frac{(\alpha_n x + \beta_n x_0 - x_i)^2}{\sigma_n^2}\right] \tag{11}$$

where $A_n = |\alpha_n/\sigma_n|/\sqrt{\pi}$.

We also notice

$$\begin{aligned} \alpha_n &= (1 - 2D\delta t\pi\Gamma^2)^n \\ \beta_n &= 1 - (1 - 2D\delta t\pi\Gamma^2)^n = 1 - \alpha_n \\ \sigma_n^2 - \sigma_{n-1}^2 &= \frac{\alpha_n^2}{\alpha_1^2}\sigma_1^2 \end{aligned} \tag{12}$$

Finally, we can notice $n = t/\delta t$ and take the limit $2\pi\Gamma^2 D\delta t \to 0$ to get

$$\begin{aligned} \alpha_t &= e^{-2Dt\pi\Gamma^2} \\ \beta_t &= 1 - \alpha_t \\ \sigma_t^2 &= \frac{1 - \alpha_t^2}{\pi\Gamma^2} \end{aligned} \tag{13}$$

Defining $\tau = 1/2\pi D\Gamma^2$ we can write

$$\rho_t(x) = \frac{1}{\sqrt{\pi s_t^2}} \exp\left[-\frac{[(x - x_0) - (x_{init} - x_0)e^{t/\tau}]^2}{s_t^2}\right], \quad s_t^2 = \frac{e^{2t/\tau} - 1}{\pi\Gamma^2} \tag{14}$$

where τ is the time at which $\Delta F(\sqrt{2D\tau})/T = -1$. This also makes the limit $\delta t \to 0$ from above to be natural : $\delta t/\tau \ll 1$.

One can plug this solution into the original Smoluchowski diffusion equation $\boldsymbol{\nabla}\cdot\Big[D(\vec{\nabla}+\vec{\nabla}f(x))P(x,t|y,0)\Big]=\partial_t P(x,t|y,0)$

In principle, one can choose any form for $f(x)$ and $D(x)$ and perform the procedure similar to eq.(5). The answer should be exact in the limit of small δt.

We can also estimate the thing we are getting in the simulation:

$$\left\langle (x-x_{init})^2\right\rangle = s_t^2+(x_{init}-x_0)^2(e^{t/\tau}-1)^2 \tag{15}$$

For $t/\tau \ll 1$ we get

$$\left\langle (x-x_{init})^2\right\rangle \approx 2Dt\left[1+\frac{t}{\tau}+\frac{(x_{init}-x_0)^2}{2D\tau}\frac{t}{\tau}\right] \tag{16}$$

So

$$\frac{\langle (x-x_{init})^2\rangle}{2Dt}-1\approx\frac{t}{\tau}\big(1+\pi\Gamma^2(x_{init}-x_0)^2\big)=\frac{t}{\tau}\left(1+\left|\frac{\Delta F(x_{init})}{T}\right|\right) \tag{17}$$

or specifically for $x_{init}=x_0$ we get

$$\frac{\langle (x-x_{init})^2\rangle}{2Dt}-1\approx\frac{t}{\tau}=2Dt\pi\Gamma^2 \tag{18}$$

If we choose t_{max} such that a normal diffusion would have reached $\Delta F_{max}/T$, i.e. $t_{max}/\tau = 2Dt_{max}\pi\Gamma^2 = |\Delta F_{max}/T|$, then we can see that the error depends only on the ΔF values at important points:

$$\frac{\langle (x(t_{max})-x_{init})^2\rangle}{2Dt_{max}}-1\approx\left|\frac{\Delta F_{max}}{T}\right|\left(1+\left|\frac{\Delta F(x_{init})}{T}\right|\right) \tag{19}$$

or, more precisely

$$\frac{\langle (x-x_{init})^2\rangle}{2Dt}-1\approx\frac{2Dt}{l^2}\left(1+\frac{(x_{init}-x_0)^2}{l^2}\right) \tag{20}$$

where $l^2=1/\pi\Gamma^2$.

2 NVT CNT

We know for 2D

$$\begin{aligned} \Delta G_{\mu VT} &= \pi r^2 \rho_\beta + 2\pi r \sigma \\ S &= e^{-\Delta\mu/T} \approx \rho/\rho_c \\ N^* &= \pi \left(\frac{\sigma}{\Delta\mu}\right)^2 \end{aligned} \tag{21}$$

where ρ_β is the density of the nucleated phase, ρ is the density of the nucleating component in the bulk and ρ_c is the coexistance density of the nucleating component,

We can write $\Delta\mu \approx -T\ln(\rho/\rho_c)$ and notice that ρ changes in the process of nucleation for a finite system at NVT:

$$\rho = \frac{\rho_0 L^2 - \pi r^2 \rho_\beta}{L^2 - \pi r^2} = \rho_0 \frac{1 - N_{cl}/N_\Sigma}{1 - (N_{cl}/N_\Sigma)(\rho_0/\rho_\beta)} \tag{22}$$

so

$$S(N_{cl}) = S_0 \frac{1 - N_{cl}/N_\Sigma}{1 - S_0(\rho_c/\rho_\beta)(N_{cl}/N_\Sigma)} \tag{23}$$

and therefore

$$g_{NVT} = \frac{\Delta G_{NVT}}{T} = \frac{\Delta G_{\mu VT}}{T} - N_{cl} \ln\left(\frac{1 - N_{cl}/N_\Sigma}{1 - S_0 \frac{\rho_c}{\rho_\beta}\frac{N_{cl}}{N_\Sigma}}\right) \tag{24}$$

The condition for small disturbance is

$$\frac{\Delta S}{S_0 - 1} = \frac{S_0}{S_0 - 1}\left[1 - \frac{1 - N_{cl}/N_\Sigma}{1 - S_0 \frac{\rho_c}{\rho_\beta}\frac{N_{cl}}{N_\Sigma}}\right] \ll 1 \tag{25}$$

We can also directly mimic simulation results by plotting

$$P_n = Z^{-1} \sum_{k=1}^{n-1} e^{g_k} k^{-2/3}, \quad Z = \sum_{k=1}^{N-1} e^{g_k} k^{-2/3} \tag{26}$$

Then one can (numerically) solve for $P(n) = 1/2$ for different $(\sigma/T,\ \rho_c)$ and choose such σ/T and ρ_c that minimize χ^2 from the simulation data.