New York University
Physics Department
Class GA.2061 "Non-Equilibrium Statistical Physics", Fall 2021

1. In class, we derived the Fokker-Planck equation which describes diffusion of the particle in presence of an energy landscape. This equation is also sometimes called Smoluchowski equation, and can be simplistically called the diffusion equation:

$$\frac{\partial P_t(x)}{\partial t} = -\text{div} J \ , \quad J = -De^{-U/T}\nabla\left(e^{U/T}P_t(x)\right) \ . \tag{1}$$

Consider 1D diffusion of particles through a narrow channel connecting two large volumes where $U = $ const. Imagine that U in the channel is an asymmetric saw-tooth potential (see figure 1). In which direction diffusion transport is faster?

Hint: Imagine that at the present time concentration in one reservoir is c_1 and concentration in the other reservoir is c_2. Imagine further that these reservoirs are so big that their concentrations do not change appreciably during the time one particle diffuses through the channel. Then, comparing this with the "diffusion on a graph" problem, there will be some rate constant of going from 1 to 2 and another rate constant of going from 2 to 1. That means, fluxes $J_{1\to2} = c_1\omega_{1\to2}$ and $J_{2\to1} = c_2\omega_{2\to1}$. Your task is to find $\omega_{1\to2}$ and $\omega_{2\to1}$. The easiest way is to consider a steady transport. Namely, imagine that concentrations c_1 and c_2 are maintained by some external agent. Then $P_t(x)$ will be steady, time independent, with boundary conditions of $P = c_1$ at one end and $P = c_2$ at the other end.

Hint: Before doing calculations, think about the expected answer from the general physics point of view.
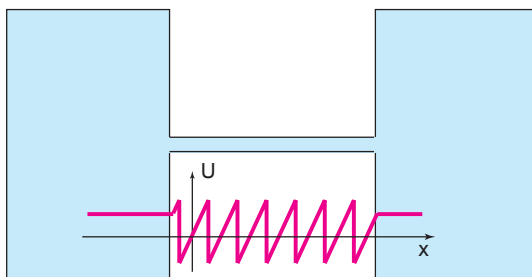

FIG. 1. Saw tooth potential.

Solution

Thermodynamics requires that the transport rate is the same in both directions. Otherwise, this system would violate the detailed balance and one could easily build a perpetual motion machine...

To confirm this by calculation, the easiest approach is to consider stationary transport. Suppose concentration on the one side of the channel is c_1 and on the other c_2 and $c_1 \neq c_2$. Then, there is a current in the channel, and the distribution in the channel is stationary, does not depend on time. This leads to the conclusion that current J does not depend on time and does not depend on x. Therefore,

$$e^{-U(x)/T}\nabla\left(e^{U(x)/T}P_t(x)\right) = -J/D \ , \tag{2}$$

where J is a constant current to be related later to the boundary conditions. This differential equation is easy to solve:

$$P_t(x) = -(J/D)e^{-U(x)/T}\left[\int_0^x e^{U(x')/T}dx' + A\right] \ , \tag{3}$$

where A is an integration constant. We now should remember that potential is zero at both ends and we should write the boundary conditions:

$$P_t(0) = -\frac{J}{D}A = c_1 \ ,$$

$$P_t(L) = -\frac{J}{D}\left[\int_0^L e^{U(x')/T}dx' + A\right] = c_2 \ .$$

We now exclude an unknown A from these two equations and determine the current:

$$J = \frac{(c_1 - c_2)D}{\int_0^L e^{U(x')/T} dx'} \ . \tag{4}$$

We considered the stationary transport, when concentrations on both sides are supported constant. In fact, if the outside concentrations change slowly on the time scale of single molecule translocation, then we can present current in the form $J = c_1\omega - c_2\omega$. That means, the current from the side 1 is $c_1\omega$ and current in the opposite direction is $c_2\omega$, and, importantly, the rate constant ω is the same in both directions:

$$\omega = \frac{D}{\int_0^L e^{U(x')/T} dx'} \ . \tag{5}$$

In particular, MFPT in either direction is $1/\omega$.

The dependence on the potential landscape is in the denominator. It is obvious that it does not depend on the direction. Notice that the integrated quantity is not the Boltzmann exponent, but rather its inverse. It means the main contribution will be given by the maximum of U, by the highest potential barrier - as we expect intuitively.

2. Nuclear pores are wonderful devices, one of the wonders of the living nature, which selectively allow some particles (e.g., proteins) to go between the inside of cell nucleus and cytoplasm, while they do not pass other particles. How they do it is an open question and a subject of intense current research (see, e.g., [1]). Suppose pore is so narrow that it can be considered 1D. By modifying the pore side walls you can effectively imagine any potential $U(x)$ for the particle moving inside this 1D channel. Let x be the coordinate along the channel, and let the region $0 < x < (a + b)$ represent the bulk solution outside the pore; the region $(a + b) < x < (a + b + l)$ is the pore itself where potential is equal to $U(x)$; and region $(a + b + l) < x < (a + b + l + c)$ is the bulk inside the nucleus (see sketch in Fig. 2). Potential in the bulk is U_o, on both sides of the pore. Particles are input at $x = a$ and output at $x = a + b + l + c$. Potential is U_o in both bulk regions. If you take potential inside the pore to be below U_o, $U(x) < U_o$ (potential well), then the particle rapidly jumps down into the pore, but is slowed down at the exit, because it has to climb up the barrier; if you take $U(x) > U_o$ (barrier), then ... What profile would make the transport (MFPT) fastest? Analyze how it depends on distances a, b, c, l. For simplicity, you can assume potential inside the pore a constant U_i.

Hint: Do not forget about the time particle spends fruitlessly in $0 < x < a$.

Solution

For simplicity, I assume below that energy U is measured in the units of temperature, i.e., $T = 1$.

We face the problem that particles can diffuse from the input point in the wrong direction (see figures 2 and 3). In the auxiliary stationary process particles will have to fill in the "dead region" between $0 < x < a$. For the Smoluchowski equation in auxiliary stationary case we have $\partial_t P = -\partial_x J = 0$; as usually, this means $J = \text{const}$ independent of x – except it can be different on the two sides of the input point $x = a$. Given the reflection boundary condition at $x = 0$, we have $J = 0$ at $0 < x < a$ and J is equal to the input current everywhere else, at $x > a$. Then, at $x < a$ the Smoluchowski equation
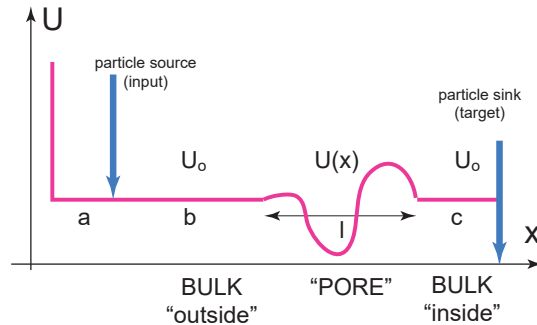
$$J = -De^{-U(x)} \nabla \left(P(x) e^{U(x)} \right) \tag{6}$$

FIG. 2. For problem 2. Particles are input at a, output at sink $a + L$, and cannot go to $x < 0$.
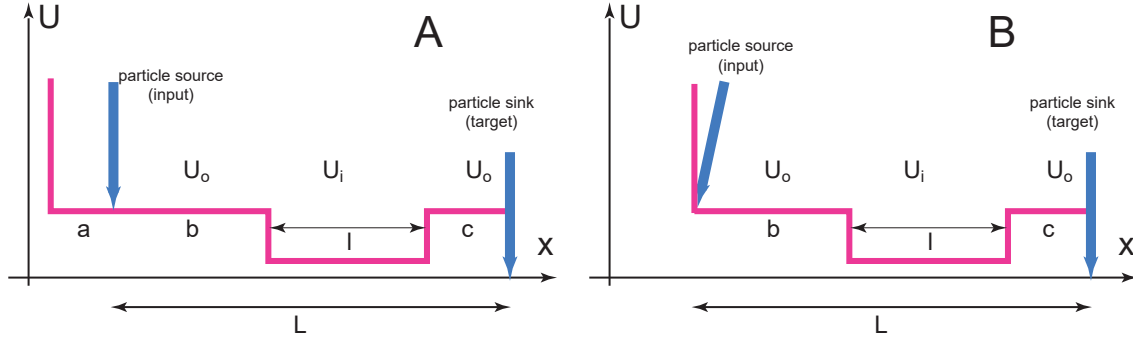
FIG. 3. Example of rectangular potential with (A) and without (B) dead end region.

yields equilibrium concentration profile, $P(x) \sim e^{-U(x)}$ in the dead end region, where there is no current (this region is in equilibrium with the system which flows past its entrance), and the non-equilibrium profile in the flowing region:

$$P(x) = \begin{cases} Ae^{-U(x)} & \text{for } 0 < x < a \\ \frac{J}{D(x)} \int_x^{\text{sink}} e^{U(x')} dx' e^{-U(x)} & \text{for } a < x \end{cases} \tag{7}$$

The coefficient A (i.e., the number of particles in the dead end region, or the fraction of time spent there fruitlessly by every particle) is determined from the condition that $P(x)$ is continuous at $x = a$; then total current is found from the condition that total number of particles in the system, N, is given (for instance, one). This yields the following general formula in 1D:

$$\tau = \frac{1}{N} \int_{\text{input}}^{\text{sink}} e^{-U(x)} \left[\int_x^{\text{sink}} e^{U(x')} dx' \right] dx$$
$$+ \frac{1}{N} \underbrace{\left[\int_0^{\text{input}} e^{-U(x)} dx \right]}_{capacitance} \times \underbrace{\left[\int_{\text{input}}^{\text{sink}} e^{U(x')} dx' \right]}_{resistance} \tag{8}$$

Now let us specify the results for the case of rectangular potential as shown in figure 3:

$$\tau = \underbrace{\frac{L^2}{2D_o} + \frac{La}{D_o}}_{\tau_0, flat\ landcsape} + l(b+a) \left[\frac{e^{U_i - U_o}}{D_i} - \frac{1}{D_o} \right] + lc \left[\frac{e^{U_o - U_i}}{D_o} - \frac{1}{D_o} \right] + \frac{l^2}{2} \left[\frac{1}{D_i} - \frac{1}{D_o} \right] \tag{9}$$

For generality, I assumed here that diffusion coefficient inside the channel, D_i, may be different from that outside, D_o.

Consider now some examples.

- **Symmetric case: $D_o = D_i$, and $a = 0$, and $b = c$** The $a = 0$ means there is no dead end region, as in figure 3 B, while $b = c$ means symmetric situation:

$$\tau = \tau_0 + 2lb \cosh [U_i - U_o] \geq \tau_0 \tag{10}$$

  Thus, it is a loose-loose situation: the time is always longer due to any non-flat potential, well or barrier. The optimal transport is achieved by flat potential.

- **Asymmetric case: $D_o = D_i$, and $a = 0$, but $b \neq c$**

$$\tau = \tau_0 + \frac{l}{D_o} \left[b \left(e^{U_i - U_o} - 1 \right) + c \left(e^{U_o - U_i} - 1 \right) \right] \ . \tag{11}$$

- $U_i < U_o$ (well): b-term accelerates, c-term slows down.
- $U_i > U_o$ (barrier): b-term slows down, c-term accelerates.

- **Optimization of potential at $D_i = D_o$, $a \neq 0$ and $b \neq c$**

$$\tau = \tau_0 + \frac{l}{D_o} \left[(b+a)\left(e^{U_i-U_o} - 1\right) + c\left(e^{U_o-U_i} - 1\right) \right] \ . \tag{12}$$

- At fixed lengths a, b and c, the largest possible speed-up is achieved at $e^{U_i-U_o}\big|_{\text{optimal}} = \sqrt{\frac{c}{a+b}}$
  * If $a+b > c$, then optimal is well;
  * If $a+b < c$, then optimal is barrier.
- $\tau_{\text{optimal}} = \frac{1}{2D_o}\left[(a+b+l+c)(b+l+c) - 2l\left(\sqrt{a+b} - \sqrt{c}\right)^2 \right]$

3. Smoluchowski "coagulation" theory in 3 dimensions tells that if particles of concentration c diffuse and get absorbed by a target of radius b, then the absorption rate (inverse first passage time) is $k = 4\pi bcD$.

   (a) Re-derive this result using a different method, i.e., considering an auxiliary steady diffusion process between two concentric spheres. Imagine that the target of radius b is located in the center of a bigger sphere of radius R, with particles fed into the system through the outer sphere and absorbed on the target of the inner sphere. Show that in the limit $R \gg b$ the result is identically the same as that of Smoluchowski, where you have to properly identified c.

   (b) Consider a similar problem in 2D. How is the result similar, and how is it different from 3D?

Solution

   (a) For steady state problem $c(r) = A\left(1 - \frac{b}{r}\right)$, which satisfies absorbing boundary condition at $r = b$, and now coefficient A has to be identified such that there is one particle in the system, $\int_b^R c(r)4\pi r^2 dr = 1$. After that, current into the target, $J = 4\pi b^2 \left.\partial c\right|_{r=b}$ gives the inverse mean first passage time. Going through the algebra, the answer is $\tau = \frac{2R^3 - 3bR^2 + b^3}{6bD} \simeq \frac{R^3}{3bD}$, where the last formula is for $R \gg b$ limit. This is exactly $\tau = \frac{1}{4\pi bcD}$, where $c = \frac{1}{(4/3)\pi R^3}$ – one particle per volume $(4/3)\pi R^3$.

   (b) Similar steady concentration profile in 2D reads $c(r) = A\ln\frac{r}{b}$ and then $\tau = \frac{2R^2\ln(R/b) - R^2 + b^2}{4D} \simeq \frac{R^2\ln(R/b)}{2D}$. If we eliminate R in favor of c, according to $c = 1/\pi R^2$, then $\tau = \frac{\ln 1/\pi b^2 c}{4\pi cD}$. Thus, the dependence on the target size, b, is very weak, only logarithmic. This is all because random walks in 2D are denser and less likely to miss past the target.

4. For a system with quadratic Hamiltonian

$$\mathcal{H}\{m(\mathbf{x})\} = \int d^d\mathbf{x} \left[\frac{a}{2}m^2 + \frac{g}{2}(\nabla m)^2\right] \ , \tag{13}$$

which can be diagonalized in terms of Fourier modes, find relaxation times of every mode, $\tau_{\mathbf{q}}$, for both types of dynamics, model A and model B. Which relaxation time is longer, and why?

Solution

In terms of Fourier modes, given Hamiltonian reads

$$\mathcal{H} = \int \frac{d\mathbf{q}}{(2\pi)^d} \frac{a + gq^2}{2} |m_{\mathbf{q}}|^2 \ . \tag{14}$$

For the model A, in which order parameter is not conserved, the generalized force driving relaxation is $-\frac{\delta\mathcal{H}}{\delta m_{\mathbf{q}}} = -(a + gq^2)m_{\mathbf{q}}$. Therefore, the dynamics equation reads

$$\partial_t m_{\mathbf{q}} = -\gamma(a + gq^2)m_{\mathbf{q}} + \eta_{\mathbf{q}} \ , \tag{15}$$

where $\eta_{\mathbf{q}}$ is the noise (which must be balanced with kinetic coefficient γ by a proper fluctuation-dissipation Einstein relation. Independently, just from the dynamic equation above we read out the requisite relaxation time for every mode:

$$\frac{1}{\tau_{\mathbf{q}}} = \gamma(a + gq^2) \quad \text{for} \quad \text{model A.} \tag{16}$$

Given that equilibrium correlation length for this model is $r_c = \sqrt{g/a}$, our result can be re-written as $\tau_{\mathbf{q}} = \frac{1}{\gamma a}\left(1 + (qr_c)^2\right)$. We see that relaxation time on distances larger than correlation length, i.e., at $q \ll 1/r_c$, relaxation time saturates to scale-independent maximal value $1/\gamma a$, while at shorter distances relaxation time goes as $\tau_{\mathbf{q}} \sim \frac{1}{\gamma a}(qr_c)^{-2}$.

For the model B, in which order parameter is conserved, the dynamic equation looks like

$$
\begin{aligned}
\partial_t m_{\mathbf{q}} &= -\nabla \cdot \left(-\nabla\left(-\frac{\delta\mathcal{H}}{\delta m_{\mathbf{q}}}\right)\right) + \nabla \cdot \sigma_{\mathbf{q}} \\
&= -\gamma q^2 \left(a + gq^2\right) m_{\mathbf{q}} + \nabla \cdot \sigma_{\mathbf{q}} \ ,
\end{aligned}
\tag{17}
$$

where σ is noise. This time, we read out relaxation time as

$$
\frac{1}{\tau_{\mathbf{q}}} = \gamma a q^2 \left(1 + (qr_c)^2\right) \ .
\tag{18}
$$

Thus, on very long length scales, at $qr_c \ll 1$, relaxation time does not saturate, but behaves like in diffusion, $\tau_{\mathbf{q}} \sim q^{-2}$. This is because the order parameter is conserved, and it has to diffuse a long distance of order $1/q$ to equilibrate.

5. Regular diffusion equation

$$
\partial_t c = D\nabla^2 c + D\nabla\left(c\nabla\frac{U}{T}\right)
\tag{19}
$$

describes diffusion of a single particle, or diffusion of a cloud of non-interacting particles (i.e., an ideal gas). Re-derive this equation by identifying the appropriate "Hamiltonian" for the field $c(x)$ and deciding whether model A or model B should be used to describe its dynamics.

Solution

Free energy, or "Hamiltonian" of the system is that of an ideal gas, i.e.,

$$
\mathcal{H}\{c(x)\} = \int \left[Tc(x)\ln\frac{vc(x)}{e} + c(x)U(x)\right] d^d x \ ,
\tag{20}
$$

where v is some molecular volume, which plays no role in the final equations. Dynamics must be described by the model B, because particles are definitely conserved. So, we find variational derivative $\frac{\delta\mathcal{H}}{\delta c} = T\ln c(x) + U(x)$, and then dynamics is described by

$$
\partial_t c = -\mathrm{div}\, J \ , \text{with} \quad J = -\mu c(x)\nabla\frac{\delta\mathcal{H}}{\delta c}
\tag{21}
$$

, yielding

$$
\partial_t c = \mu T\nabla^2 c(x) + \mu\nabla\left(c(x)\nabla U\right) \ ,
\tag{22}
$$

exactly as expected.

The problems below are not required and will not be graded, but recommended to those students who want to improve their knowledge and performance.

6. Consider a sedimentation experiment. If there is just one particle of, radius a and with weight (corrected for buoyancy) P, then this particle sediments in a liquid with speed $v = P/6\pi\eta a$, where η is liquid viscosity.

What happens if two such particles sediment together, distance r apart? Do they fall faster or slower than $v = P/6\pi\eta a$? Consider at least two cases, when particles are on the same horizontal level, and when they are on the same vertical line. Assume $r \gg a$. Is the effect significant under realistic experimental circumstances?

What happens if you have a cloud of some N particles falling as a cloud of the size about R; does this cloud sediments faster or slower than v?

Solution

General formula for Oseen tensor is $H_{\alpha\beta}(\mathbf{r}) = \frac{1}{8\pi\eta r}\left[\delta_{\alpha\beta} + \frac{r_\alpha r_\beta}{r^2}\right]$. If one particle moves with the speed $v_\alpha^{(1)}$ with respect to the surrounding liquid, then it exerts force on the liquid $f_\beta^{(1)} = \xi v_\beta^{(1)}$, and this causes liquid to get an

additional velocity $H_{\alpha\beta}(\mathbf{r})f_\beta^{(1)}$ in the place where second particle is located, and this velocity has to be added to the velocity $v_\alpha^{(2)}$ of the second particle with respect to the surrounding liquid. Thus,

$$V_\alpha^{(2)} = v_\alpha^{(2)} + H_{\alpha\beta}(\mathbf{r})\xi v_\beta^{(1)} . \tag{23}$$

Small v are just the velocities of sedimentation for each particle, P/ξ, oriented vertically, along z: $v_\alpha^{(1)} = v_\alpha^{(2)} = \frac{P}{\xi}\delta_{\alpha z}$. Therefore,

$$\begin{aligned}
V_\alpha^{(1)} = V_\alpha^{(2)} &= \frac{P}{\xi}\left[\delta_{\alpha z} + \xi H_{\alpha z}(\mathbf{r})\right] \\
&= \frac{P}{\xi}\left[\delta_{\alpha z}\left(1 + \frac{\xi}{8\pi\eta r}\right) + \frac{\xi}{8\pi\eta r}\frac{r_\alpha r_z}{r^2}\right] .
\end{aligned} \tag{24}$$

First consider two particles on the same vertical line. In this case, $\mathbf{r}$ has only z-component, as well as sedimentation velocities. Therefore, particles fall down with the speed

$$V = \frac{P}{\xi}\left[1 + \frac{3a}{2r}\right] . \tag{25}$$

Second, for particles on the same horizontal plane, $\mathbf{r}$ has only horizontal components, so $r_z = 0$, and we get

$$V = \frac{P}{\xi}\left[1 + \frac{3a}{4r}\right] . \tag{26}$$

Particles help each other on both cases, but in the horizontal case twice weaker.

Now consider a cloud of many, $N \gg 1$, particles. Penetration depth is estimated as $\lambda \sim (ac)^{-1/2} \sim \left(aN/R^3\right)^{-1/2}$. Look at $\lambda/R \sim (R/Na)^{1/2}$. If $\lambda/R \ll 1$, then the whole cloud is hardly penetrated by the flow, and therefore sedimentation speed is given by the formula similar to $v = P/6\pi\eta a$, except P has to be replaced by NP and radius a has to be replaced by R: $V \sim NP/6\pi\eta R$. This is valid if $\lambda/R \ll 1$, which means $R \ll Na$, which means then $V \gg v$: particles in the cloud co-operate and help each other very strongly.

7. Consider a poor clock which makes a random error of $\pm\delta$ every 12 hours. Suppose you look at it only at noon (astronomical time), so the first day it shows $12:00$, second day $12:00 \pm \delta$, etc. Day by day, it forms a random walk of some sort. Assuming your observation time is much-much longer than one day, write down the Fokker-Planck equation describing the position of clock hand at astronomic noon after some t days. Find the solution of this equation, given the initial condition ($12:00$ on first day) and properly formulated boundary condition.

Solution

The angle θ after time t has distribution $P_t(\theta)$ which obeys regular diffusion equation $\partial_t P = D\partial_\theta^2 P$, where diffusion coefficient is $D = \delta^2$. Since this is diffusion around the circle, the boundary conditions are periodic, i.e., $P(\theta) = P(\theta + 2\pi)$. Therefore, Green's function of this diffusion equation (which is what we need to find given the initial condition) is most conveniently written down using bilinear expansion. Corresponding eigenfunctions of the $\partial_\theta^2 \psi_n = \lambda_n \psi_n(\theta)$ satisfying periodic boundary conditions and symmetric around zero are $\psi_n(\theta) = \frac{1}{\sqrt{\pi}}\cos(n\theta)$ with $\lambda_n = -n^2$ for $n \neq 0$ and $\psi_0(\theta) = \frac{1}{\sqrt{2\pi}}$ with $\lambda_0 = 0$. Thus,

$$\begin{aligned}
P_t(\theta) &= \psi_0(\theta)\psi_0(0) + \sum_{n=0}^\infty e^{\lambda_n t}\psi_n(\theta)\psi_n(0) \\
&= \frac{1}{2\pi} + \frac{1}{\pi}\sum_{n=1}^\infty e^{-n^2\delta^2 t}\cos(n\theta) .
\end{aligned} \tag{27}$$

8. We considered first passage problem for a half-line. Consider now diffusion (or random walk) in a space of dimension d. Suppose there is a trap in the origin, and we start some distance x_0 from the origin, and want to know the first passage time to the trap. Since the direction from the origin to the starting point is irrelevant, we can imagine that initial distribution at $t = 0$ was smeared along the sphere of radius x_0. Then diffusing cloud

will remain spherically symmetric in the process of diffusion, $c(\mathbf{x}) = c(|\mathbf{x}|)$. That means, we can write down the diffusion equation in spherical coordinates, and deal with diffusion along radius only. But then it looks (or seems to look?) exactly like diffusion on a semi-infinite line! Write down the radial diffusion equation and check the correctness of the following idea.

Instead of smearing the initial distribution around the sphere, you can imagine that diffusion along radius happens slowly, while diffusion around the sphere of constant radius happens very fast. Then at every value of radius r the system comes to equilibrium at this particular radius r where it has entropy $S(r) = \ln A(r)$, where $A(r)$ is "surface area" of a sphere of radius r (it depends of course on space dimension d; in $d = 3$, $A = 4\pi r^2$, and in $d = 2$, $A(r) = 2\pi r$; you can find or derive $A(r)$ for any d). Is it possible to write down Smoluchowski equation using the "potential" profile related to $S(r)$?

Solution

Effective "potential" $U(r) = -TS(r) = -T \ln A(r)$, then Smoluchowski equation reads $\partial_t \tilde{c}(r,t) = D\partial_r \left(e^{\ln A(r)} \partial_r \left(e^{-\ln A(r)} \tilde{c}(\right.\right.$ or $\partial_t \tilde{c}(r,t) = D\partial_r \left(A(r)\partial_r \left(\tilde{c}(r,t)/A(r) \right) \right)$. As regards $A(r)$, it has dependence on r in the form r^{d-2} and there is some coefficient depending on d – but it cancels away, so we don't even have to find it. In the end we get

$$\partial_t \tilde{c}(r,t) = D\partial_r \left(r^{d-1}\partial_r \left(r^{-d+1}\tilde{c}(r,t) \right) \right) \ . \tag{28}$$

Why did we use special notation for concentration, $\tilde{c}(r,t)$? This quantity is the density in r-space, i.e., $\tilde{c}(r,t)dr$ is the number of particles (or the amount of probability) in the "peel" region between r and $r + dr$. Since the volume of this "peel" is $A(r)dr$, the number of particles there in terms of usual concentration c is $c(r,t)A(r)dr$, which means $\tilde{c}(r,t) = c(r,t)A(r)$. Therefore, equation (28) in terms of usual concentration reads

$$\partial_t c(r,t) = Dr^{-d+1}\partial_r \left(r^{d-1}\partial_r c(r,t) \right) \ . \tag{29}$$

What we obtained in the right hand side is exactly the radial part of Laplace operator in spherical coordinates in d dimensions, you can say we have derived it in a new way.

9.   • Show that Smoluchowski equation in phase space for many particles

$$\frac{\partial \Psi}{\partial t} = \sum_{m,n} \frac{\partial}{\partial x_m} L_{mn} \left[T\frac{\partial \Psi}{\partial x_n} + \Psi\frac{\partial U}{\partial x_n} \right] \tag{30}$$

can be presented as

$$\frac{\partial \Psi}{\partial t} = \sum_{m,n} \frac{\partial}{\partial x_m} \Psi L_{mn} \frac{\partial}{\partial x_n} \left[T\ln \Psi + U \right] \tag{31}$$

and explain the physical meaning of the later form. Here Ψ is the probability distribution of a "representative point", i.e., of the point in multidimensional phase space representing a given system that may include arbitrarily many real particles;

   • Identify flow (current) in phase space;

   • Show that Smoluchowski equation, assuming no flux in or out of the system, describes 'relaxation' dynamics, in the sense that the "free energy"

$$F\{\Psi\} = \int \Psi \left[T\ln \frac{\Psi}{e} + U \right] dx \tag{32}$$

never increases with time, and decreases in all cases except when Ψ is . . . what is the Ψ at which free energy does not decrease?

Solution

The later form of writing the Smoluchowski equation is nice because $T\ln \Psi + U$ is the chemical potential and therefore the flux $\mathbf{J} = -\Psi L_{mn}\frac{\partial}{\partial x_n} \left[T\ln \Psi + U \right]$ is proportional to the gradient of chemical potential.

If we differentiate the free energy with respect to time, use the Smoluchowski equation, and integrate by parts

(remembering that there is no flux through the boundaries) we get

$$
\dot{F} = \int \dot{\Psi}\, [T \ln \Psi + U]\, dx =
$$
$$
= \int \frac{\partial}{\partial x_m} \Psi L_{mn} \frac{\partial}{\partial x_n} [T \ln \Psi + U] \times [T \ln \Psi + U]\, dx =
$$
$$
= -\int \Psi L_{mn} \frac{\partial}{\partial x_n} [T \ln \Psi + U] \times \frac{\partial}{\partial x_m} [T \ln \Psi + U]\, dx =
$$
$$
= -\int \Psi L_{mn} \frac{\partial}{\partial x_n} \left[T \ln \frac{\Psi}{\Psi_{\mathrm{eq}}} \right] \times \frac{\partial}{\partial x_m} \left[T \ln \frac{\Psi}{\Psi_{\mathrm{eq}}} \right] dx \le 0 \; ,
$$

where $\Psi_{\mathrm{eq}} = e^{-U/T}$ is the equilibrium distribution. Thus, because of the positive definite property of matrix L_{mn}, we see that free energy decreases unless Ψ is equilibrated, in which case free energy does not change.

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[1] M. Beck and E. Hurt, The nuclear pore complex: understanding its function through structural insight, Nature Reviews Molecular Cell Biology **18**, 73 (2017).