

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

Home Work 08

Solutions

1. If a particle of radius a moves in a usual viscous (Newtonian) fluid, then it undergoes a simple diffusion with $\langle \Delta r^2(t) \rangle = 6Dt$ in the standard notation, where

$$\langle \Delta r^2(t) \rangle = 6Dt, \quad \underbrace{D = \frac{T}{\zeta}}_{\text{Einstein}}, \quad \underbrace{\zeta = 6\pi\eta a}_{\text{Stokes}}. \quad (1)$$

These relations give rise to the very efficient method of measuring viscosity, called microrheology (passive microrheology): the idea is to place a probe particle into a liquid, watch its random motion under the microscope, measure mean-square displacement, and thus find the value of η . For this purpose, the above relations are frequently combined as $D = T/6\pi\eta a$ (frequently referred to as Stokes-Einstein relation), or $\langle \Delta r^2(t) \rangle = 6Tt/\zeta$ (sometimes also called Einstein relations, or $\langle \Delta r^2(t) \rangle = Tt/\pi\eta a$ (sometimes called Stokes-Einstein relation). Technically, it turns out more convenient to perform microrheology analysis using the Laplace transformed relation¹

$$\underbrace{\langle \tilde{\Delta r}^2 \rangle_s = \frac{6T}{s^2\zeta}}_{\text{Einstein}} \implies \underbrace{\langle (\tilde{\Delta r})^2 \rangle_s = \frac{T}{\pi a s^2 \eta}}_{\text{Stokes-Einstein}}, \quad (2)$$

where a is the probe particle radius, and s is Laplace “frequency”.

The real advantage of microrheology is in dealing with more complex materials than just a Newtonian fluid, such as, e.g., viscoelastic materials, biological tissues, etc. Microrheology for a particle moving in a complex viscoelastic medium is based on the generalized Einstein and Stokes-Einstein relations

$$\langle \tilde{\Delta r}^2 \rangle_s = \frac{6T}{s^2 \tilde{\zeta}_s} \implies \langle (\tilde{\Delta r})^2 \rangle_s = \frac{T}{\pi a s^2 \tilde{G}_s}, \quad (3)$$

where a is particle radius, s is Laplace “frequency”, \tilde{G}_s is the Laplace transform of generalized (relaxation) modulus of the medium ($\tilde{G}_s = \int_0^\infty G(t)e^{-ts}dt$), and $\langle (\tilde{\Delta r})^2 \rangle_s$ is the Laplace transform of mean-squared displacement of the particle. Derive this relation.

I encourage you to work on this problem simultaneously with the next one.

Hints:

- (a) In solving this problem, it is very important (and unusually difficult!) to keep the notations clear enough to distinguish functions and their Laplace transforms. To emphasize it, I write, e.g., velocity as a function of time as $v(t)$, while its Laplace transform as \tilde{v}_s , indicating the argument as a subscript and, in addition, placing a tilde sign.
- (b) In this notation, $\langle (\tilde{\Delta r})^2 \rangle_s$ means the following: we imagine measuring particle displacement over time interval from 0 to t , $\Delta r(t)$; we then square this function of t and ensemble average, obtaining $\langle (\Delta r(t))^2 \rangle$; this is still a function of t . And this function we subject to Laplace transform, obtaining $\langle (\tilde{\Delta r})^2 \rangle_s$.
- (c) You should first obtain the first of the two relations (3), generalizing first of the two relations (2) (Einstein), and then the second (Stokes).
- (d) You may want to follow these steps:
 - i. Start with Langevin equation for a particle experiencing friction that has causal kernel $\zeta(t)$. Note: although we use the same letter, the kernel $\zeta(t)$ here is not the same as ζ in the usual, memory-free case; it has even a different dimension! However, Laplace (or Fourier) transform $\tilde{\zeta}_s$ has the same units as the usual ζ .

¹ In case you forgot, Laplace transform of a function $f(t)$ reads $\tilde{f}_s = \int_0^\infty f(t)e^{-st}dt$; I encourage you to make sure you understand why the Laplace transform of t is $1/s^2$.

- ii. Laplace transform all terms of Langevin equation (resorting to integration by parts in the term involving acceleration).
- iii. Solve for \tilde{v}_s , multiply by $v(0)$, and ensemble average. Take into account that Langevin random force is independent of velocity. Take into account the known result of equilibrium statistical physics for mean squared velocity, and then, at this stage (not earlier!), neglect the inertia term.
- iv. Now look at $\langle (\Delta r(t))^2 \rangle$. Write $\Delta r(t)$ as the integral of velocity, square it, and ensemble average, shifting velocity-velocity correlation function like $\langle v(t')v(t'') \rangle = \langle v(0)v(t'' - t') \rangle$.
- v. The usual Stokes formula $\zeta = 6\pi a\eta$. Show that it can be written as the statement at zero frequency: $\tilde{\zeta}_{s=0} = 6\pi a\tilde{G}_{s=0}$. Assume, as everybody does in the field, that this Stokes relation is valid for any frequency.

Solution

We start by writing Langevin equation with friction force which depends on the history of motion (for any one direction x , y , or z):

$$m\dot{v} = - \int_{-\infty}^t \zeta(t-t')v(t')dt' + \xi(t) . \quad (4)$$

Note: although we use the same letter, the kernel $\zeta(t)$ here is not the same as ζ in the usual, memory-free case; it has even a different dimension! Similarly, also random force $\xi(t)$ is not the same as in the memory-free case. Now multiply both sides of equation by e^{-st} and integrate over time from 0 to ∞ (in the left hand side, you have to integrate by parts):

$$-mv(0) + ms\tilde{v}_s = -\tilde{\zeta}_s\tilde{v}_s + \tilde{\xi}_s , \quad (5)$$

which is easily solved for \tilde{v}_s :

$$\tilde{v}_s = \frac{mv(0) + \tilde{\xi}_s}{ms + \tilde{\zeta}_s} . \quad (6)$$

Multiply this by $v(0)$ and ensemble average:

$$\langle v(0)\tilde{v}_s \rangle = \frac{m\langle v^2(0) \rangle + \langle v(0)\tilde{\xi}_s \rangle}{ms + \tilde{\zeta}_s} . \quad (7)$$

The first term in the numerator is known to us: $m\langle v^2(0) \rangle = T$ (equipartition theorem!). The second term in the numerator vanishes, because random force is independent of the velocity. Also neglecting the inertia-related term in the denominator, which is OK except at the very high frequencies, we get

$$\langle v(0)\tilde{v}_s \rangle = \frac{T}{\tilde{\zeta}_s} . \quad (8)$$

On the left, we have a weird object, correlation of velocity at a particular time with Laplace transform of velocity as a function of Laplace frequency s , which involves all times. As it turns out, it is related to $\langle (\Delta \tilde{r})^2 \rangle_s$.

To see this, write $\Delta r(t) = \int_0^t v(t')dt'$, square it, remembering factor 3 for 3 spatial dimensions, ensemble average, and then shift times under the integral:

$$\begin{aligned} \langle (\Delta r(t))^2 \rangle &= 3 \int_0^t \int_0^t \langle v(t')v(t'') \rangle dt' dt'' = \\ &= 3 \int_0^t \int_0^t \langle v(0)v(t'' - t') \rangle dt' dt'' = \\ &= 3 \left\langle v(0) \int_0^t \int_0^t v(t'' - t') dt' dt'' \right\rangle \end{aligned} \quad (9)$$

And now finally we Laplace transform $\int_0^t \int_0^t v(t'' - t') dt' dt''$. By properly changing the variables and flipping the order of integrations, we arrive at

$$\int_0^\infty dt \int_0^t dt' \int_0^t dt'' v(t'' - t') e^{-st} = \frac{2}{s^2} \tilde{v}_s . \quad (10)$$

Together (8) and (10) yield

$$\langle (\Delta \tilde{r})^2 \rangle_s = \frac{6T}{s^2 \tilde{\zeta}_s} . \quad (11)$$

This generalizes the Einstein relation.

Now the Stokes relation. Usually, it is written as $\zeta = 6\pi a\eta$. If velocity is a constant, then friction force is $-\int_{-\infty}^t \zeta(t-t')v(t')dt' = -v\int_{-\infty}^t \zeta(t-t')dt' = -v\zeta$, which means $\zeta = -\int_0^\infty \zeta(t)dt = \tilde{\zeta}_{s=0}$. Similarly, we know that $\eta = \int_0^\infty G(t)dt$ in terms of generalized modulus G , which means $\eta = \tilde{G}_{s=0}$. Thus, Stokes relation is $\tilde{\zeta}_{s=0} = 6\pi a\tilde{G}_{s=0}$. Assume that it is valid also at non-zero frequencies: $\tilde{\zeta}_s = 6\pi a\tilde{G}_s$. Plug this into the generalized Einstein relation above to get

$$\langle (\Delta \tilde{r})^2 \rangle_s = \frac{T}{\pi a s^2 \tilde{G}_s} . \quad (12)$$

2. Consider paper [1]. What did they measure using microrheology? In the derivation of generalized Stokes-Einstein relation, there is a typo; what is it?

Solution

This was mostly a methodical paper. They generalized a little bit the microrheology method to include angular motions and measured viscosity of a certain polymeric liquid by means of microrheology and compared it very successfully with the known results.

They mistakenly write $\langle \tilde{v}(0)\tilde{v}(s) \rangle$, while it should be $\langle v(t=0)\tilde{v}_s \rangle$.

3. Consider Smoluchowski equation (i.e., diffusion equation in an external potential field $U(x)$ (in any dimension you like). We usually say that the current there includes diffusion and drift. Show that it can be equivalently presented as containing drift only, except it is “drift” not in the regular potential $U(x)$, but in chemical potential $\mu(x)$. Show that “diffusion” in this interpretation means simply the drift driven by the “entropic force”.

Solution

Regular Smoluchowski equation reads

$$\dot{\pi}_t(x) = -\nabla J , \quad \text{with} \quad J = -D\nabla\pi_t(x) - \frac{1}{\zeta}\pi_t(x)\nabla U . \quad (13)$$

The diffusion term in this current can be re-written as $D\nabla\pi_t(x) = \frac{1}{\zeta}\pi_t(x)\nabla [T \ln \pi_t(x)]$. Thus,

$$J = -\frac{1}{\zeta}\pi_t(x)\nabla [T \ln \pi_t(x) + U(x)] , \quad (14)$$

where the expression in square brackets is nothing else but the chemical potential of an ideal gas with concentration $\pi_t(x)$. In this sense, diffusion is simply the drift in the field of force $\nabla\mu$, which includes the real external force and an entropic contribution.

4. (a) What is the expectation value, $\langle x \rangle$, of the amount of money left in possession of someone who was gambling (in an “honest casino” without a bias) for some time t and *has not lost his/her money* before t ?
 (b) You should have found $\langle x \rangle$ which depends on initial amount of money x_0 , on t (and D). Consider asymptotics in both small t and large t regimes (explain what “small” and “large” mean here).

Solution

As we discussed in class, the solution of the relevant diffusion equation reads

$$\mathcal{P}_t(x) = \frac{1}{\sqrt{4\pi Dt}} \left[e^{-(x-x_0)^2/4Dt} - e^{-(x+x_0)^2/4Dt} \right] . \quad (15)$$

This is the fraction of players who started at $t=0$ with the initial amount of money x_0 and have money x at the time t . The integral of this function over all positive x means the fraction of players who were not ruined (i.e., absorbed at $x=0$) by the time t .

Introducing first the variables $\xi = x/\sqrt{4Dt}$ and $\xi_0 = x_0/\sqrt{4Dt}$, and then later introducing $\eta = \xi - \xi_0$ in one integral and $\eta = \xi + \xi_0$ in the other, we arrive at the following expression for the number of players not eliminated by the time t :

$$\begin{aligned} \int_0^{+\infty} \mathcal{P}_t(x) dx &= \\ &= \frac{1}{\sqrt{\pi}} \left[\int_0^\infty e^{-(\xi-\xi_0)^2} d\xi - \int_0^\infty e^{-(\xi+\xi_0)^2} d\xi \right] = \\ &= \frac{1}{\sqrt{\pi}} \left[\int_{-\xi_0}^\infty e^{-\eta^2} d\eta - \int_{\xi_0}^\infty e^{-\eta^2} d\eta \right] = \\ &= \frac{1}{\sqrt{\pi}} \int_{-\xi_0}^{\xi_0} e^{-\eta^2} d\eta = \text{Erf} \left(\frac{x_0}{\sqrt{4Dt}} \right), \end{aligned} \quad (16)$$

where Error function is defined as: $\text{Erf}(y) = (2/\sqrt{\pi}) \int_0^y e^{-s^2} ds$. Therefore, *conditional* probability distribution of the amount of money owned by those who did not loose by the time t reads

$$p_t(x) = \frac{\mathcal{P}_t(x)}{\int_0^\infty \mathcal{P}_t(x) dx}, \quad (17)$$

where the integral downstairs does not depend on x , and so, to answer the problem, we have to address $\int_0^\infty x \mathcal{P}_t(x) dx$. This is done in the same style as normalization integral before, by introducing ξ and η , and the result reads:

$$\int_0^\infty x \mathcal{P}_t(x) dx = \sqrt{\frac{4Dt}{\pi}} \left\{ \underbrace{\int_{-\xi_0}^{\xi_0} \eta e^{-\eta^2} d\eta}_0 + \xi_0 \underbrace{\left[\int_{-\xi_0}^\infty e^{-\eta^2} d\eta + \int_{\xi_0}^\infty e^{-\eta^2} d\eta \right]}_{\int_{-\infty}^\infty e^{-\eta^2} d\eta = \sqrt{\pi}} \right\} = x_0. \quad (18)$$

Thus,

$$\langle x \rangle = \int_0^\infty x p_t(x) dx = \frac{x_0}{\text{Erf} \left(\frac{x_0}{\sqrt{4Dt}} \right)}. \quad (19)$$

That is a good example where you may want to know the asymptotics. Indeed, how does this quantity behave with time? Knowing the asymptotics of the error function, we conclude:

- At early times, $t \ll x_0^2/4D$, when initial amount of money dominates and chances to have already lost it are small, the argument of error function is large, and we get $\langle x \rangle \simeq x_0$ (not surprisingly!). If one wants to know how does $\langle x \rangle$ depart from x_0 , one has to use the next term in asymptotics of the error function, yielding

$$\langle x \rangle \simeq x_0 \left[1 + \sqrt{\frac{Dt}{\pi x_0^2}} e^{-x_0^2/4Dt} \right]. \quad (20)$$

Thus, $\langle x \rangle$ grows with time, but, at the beginning, extremely slowly.

- Late in the game, at $t \gg x_0^2/4D$, when majority of players have already lost and only most lucky ones remain, the argument of error function is small, and we get

$$\langle x \rangle \simeq \sqrt{\pi Dt}. \quad (21)$$

Thus, while vast majority of players loose everything, the remaining minority becomes increasingly rich!

5. Read the paper [2] about bacteria swimming at a surface. Authors state that internal dynamics of bacteria can be reasonably approximated in terms of three distinct states, with the dynamics described by equations 1. Why is there no term $+k_{21}p_2$ in the right hand side of equation 1B? Is it a mistake? Do authors discuss this issue?

Do you find their arguments convincing? Construct your own argument based on survival probability plots in fig. 1g. Does the internal dynamics of these bacteria obey the detailed balance?

Solution

Figure 1g shows that survival probability of state 2 (Running state) decays as a simple exponential in time, that means there is only one outgoing current from this state. At the same time, survival probability of the state 0 is clearly non-exponential, consists of two distinct exponentials. Together this implies the set of states and transitions shown in figure 2e. This definitely does not obey the detailed balance, which of course is not so surprising for a live bacteria..

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 particle diffusing inside some domain Ω , and suppose $\tau(y)$ is mean first passage time for this particle to start from point y inside Ω and to arrive to some part of the boundary, ω . Show that $\tau(y)$ satisfies

$$\underbrace{e^{U(\vec{y})} \nabla_y e^{-U(\vec{y})} D(\vec{y}) \nabla_y}_{\hat{\mathcal{L}}} \tau(\vec{y}) = -1 . \quad (22)$$

The function $\tau(\vec{y})$ is also subject to boundary conditions which it inherits from the Green's function: namely, $\tau = 0$ on the absorbing boundary ω and normal component of gradient of τ vanishes at the reflecting boundary $\bar{\omega}$.

Solution

Consider first the Green's function of the diffusion equation

$$\begin{aligned} \frac{\partial G(\vec{x}, \vec{y}, t)}{\partial t} &= \nabla_x e^{-U(\vec{x})} D(\vec{x}) \nabla_x e^{U(\vec{x})} G(\vec{x}, \vec{y}, t) \\ &\quad + \delta(\vec{x} - \vec{y}) \delta(t) , \end{aligned} \quad (23)$$

giving the time-evolution of the probability density (or 'concentration') $G(x, y, t)$ provided that at $t = 0$ particles are brought in into the point \vec{y} . Here, $D(\vec{x})$ is the diffusion coefficient, which might be coordinate-dependent; for instance, it might be equal D_1 within a narrow tube surrounding a line (representing DNA) and D_3 outside of this tube. Further, $U(\vec{x})$ is the externally applied potential, and we have set $k_B T = 1$.

We consider diffusion in some region Ω and will be interested in the first passage time into some boundary ω . That means, we impose absorbing boundary conditions on ω , $G(\vec{x}, \vec{y}, t)|_{\vec{x} \in \omega} = 0$, while on other parts of the boundary, $\bar{\omega}$ boundary conditions prohibit flow in or out of the domain Ω : $\nabla_n G(\vec{x}, \vec{y}, t)|_{\vec{x} \in \bar{\omega}} = 0$. For instance, ω might be the 'internal' surface, e.g., a sphere surrounding the target site, while $\bar{\omega}$ is the outer surface of the domain.

In calculations involving the first passage time, it would be convenient to consider the probability for the particle to still be 'alive' at time t , also called the survival probability $S(t)$, it is given by $S(t) = \int_{\Omega} c(\vec{x}, t) d\vec{x}$. The distribution of first passage times $F(t)$ is calculated from $S(t)$ via $F(t) = -\frac{\partial S(t)}{\partial t}$. This gives the following expression for the mean first passage time $\tau(\vec{y})$ [3]:

$$\begin{aligned} \tau(\vec{y}) &= \int_{0+}^{\infty} t F(t) dt \\ &= \int_{0+}^{\infty} S(t) dt \\ &= \int_{0+}^{\infty} \int_{\Omega} G(x, y, t) d\vec{x} dt , \end{aligned} \quad (24)$$

where \vec{y} is the initial position of the particle, $G(x, y, 0) = \delta(x - y)$. The lower limit of time integration is denoted $0+$ to emphasize impossibility of return in zero time, which means point 0 should not be included in the integration; it will become relevant later, when we will see a $\delta(t)$ under the integral - it will give the zero contribution.

It can be shown that $\tau(\vec{y})$ satisfies an interesting differential equation [4–6] which we will now derive (see also English translation of the classical work [4] reprinted in [7]). The derivation is motivated by the observation

that equation (23) can be re-written in the nice symmetric form. To achieve this, we should multiply both sides of the equation (23) by

$$\exp \left[\frac{U(\vec{x})}{2} - \frac{U(\vec{y})}{2} \right] \quad (25)$$

and define the new unknown function to replace G :

$$H(\vec{x}, \vec{y}, t) = G(\vec{x}, \vec{y}, t) \times \exp \left[\frac{U(\vec{x})}{2} - \frac{U(\vec{y})}{2} \right] . \quad (26)$$

As one can see, H satisfies equation

$$\begin{aligned} \frac{\partial H(\vec{x}, \vec{y}, t)}{\partial t} &= e^{U(\vec{x})/2} \nabla_x e^{-U(\vec{x})} D(\vec{x}) \nabla_x e^{U(\vec{x})/2} H(\vec{x}, \vec{y}, t) \\ &\quad + \delta(\vec{x} - \vec{y}) \delta(t) . \end{aligned} \quad (27)$$

Unlike the original equation (23), the new equation (27) involves symmetric Hermitian operator

$$e^{U(\vec{x})/2} \nabla_x e^{-U(\vec{x})} D(\vec{x}) \nabla_x e^{U(\vec{x})/2} , \quad (28)$$

and, therefore, H is a symmetric function of its arguments:

$$H(\vec{x}, \vec{y}, t) = H(\vec{y}, \vec{x}, t) . \quad (29)$$

This motivates re-writing τ (24) in terms of H :

$$\tau(\vec{y}) = \int_{0+}^{\infty} \int_{\Omega} H(x, y, t) e^{U(\vec{y})/2} e^{-U(\vec{x})/2} d\vec{x} dt \quad (30)$$

Let us now act on both sides of this equation with the operator $e^{U(\vec{y})/2} \nabla_y e^{-U(\vec{y})} D(\vec{y}) \nabla_y$. Since it deals with y variable only, it goes freely inside the integral where together with the factor $e^{U(\vec{y})/2}$ it forms the operator similar to (28) except acting on y rather than on x ; given the symmetry property of H , we then find

$$\begin{aligned} &e^{U(\vec{y})/2} \nabla_y e^{-U(\vec{y})} D(\vec{y}) \nabla_y \tau(\vec{y}) \\ &= \int_{0+}^{\infty} \int_{\Omega} \left[\frac{\partial H}{\partial t} - \delta(\vec{x} - \vec{y}) \delta(t) \right] e^{-U(\vec{x})/2} d\vec{x} dt . \end{aligned} \quad (31)$$

In the first term, with $\partial H / \partial t$, the time integration yields $H(t \rightarrow \infty)$, which is zero, and $H(t \rightarrow 0)$, which is $\delta(\vec{x} - \vec{y})$; upon integration over x , this yields $e^{-U(\vec{y})/2}$. The second term, with $\delta(t)$ vanishes, because integration starts right *after* zero time. Therefore, we obtain our equation for τ in the form

$$\underbrace{e^{U(\vec{y})} \nabla_y e^{-U(\vec{y})} D(\vec{y}) \nabla_y}_{\hat{L}} \tau(\vec{y}) = -1 . \quad (32)$$

The function $\tau(\vec{y})$ is also subject to boundary conditions which it inherits from G : namely, $\tau = 0$ on the absorbing boundary ω and normal component of gradient of τ vanishes at the reflecting boundary $\bar{\omega}$.

7. Consider a 1D potential landscape which is generated by a random walker: $U(x)$ is a “displacement” of a “walker” in “time” x ; that means, $\langle U(x) - U(x') \rangle = 0$ and $\langle (U(x) - U(x'))^2 \rangle = k |x - x'|$, with some constant k . Consider now the diffusion of a real particle in such landscape and find root-mean-squared displacement $r(t)$. This is a famous problem, called Sinai diffusion.

Solution

A hand waving argument is as follows: to move distance r , particle has to overcome a barrier of a typical height \sqrt{kr} . It takes time proportional to $t \simeq t_0 \exp(C\sqrt{kr}/T)$, where C is some numerical constant. Inverting this relation, we find $r(t)$:

$$r(t) \sim \frac{T^2}{k} \left(\ln \frac{t}{t_0} \right)^2 . \quad (33)$$

The $(\ln t)^2$ is the right answer, but making a more sophisticated argument is quite tricky, and there is a big literature about it, for instance, see [8] and references therein.

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