

- In the previous plot, we already see that the self-diffusion constant of Brownian particles is determined through the long-time limit of the mean square displacements.

- In this plot, we derive the definition of the diffusion constant in an alternative way using the linear response theory.

- The result is an example of the so-called Green-Kubo formula, which can define transport coefficients in terms of equilibrium correlation functions of corresponding variables.

- Let us consider a Brownian particle under **the** influence of an external drift force in **the** x-direction.

- The Langevin equation we introduced in the previous plot is simply modified by adding **the** external force on the right hand side, as shown in Eq.(41).

- Understanding how a system “responds” to such an external force or perturbation provides valuable information on the dynamical properties of the system.

- This is precisely what linear response theory allows us to do.

- It measures the response of the system to an external perturbation, under **the** assumption that the response is linear in this perturbation.

- The first question we want to ask, is how does the system reach a steady state under this external force.

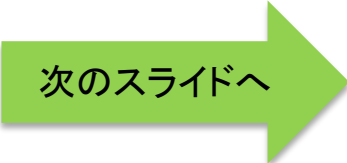
- Thus, we take the steady state average of Eq.(41), in the limit where the force is held constant for infinitely long time.

- The limit of each term in Eq.(41) is given by the following equations.
- By definition, the change in velocity should be zero in the steady state.

- This means that the velocity is constant, and it should be exactly zero along the y and z directions.

- Thanks to the properties of the random force, its average should also be zero.

- Finally, since **the** external force is constant, its average is simply F_0 in **the** x direction (zero along y and z).

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- Thus, we see that we only need to consider the dynamics along **the** x direction since motion along y and z will average out to zero.

- Taking the long time average of Eq.(41) on both sides, we see that the steady-state drift velocity is given by F_0 divided by the friction constant ζ .

- Then, using **the** Einstein relation, we can rewrite the steady state velocity in terms of the diffusion coefficient and the thermal energy, as shown in Eq.(42).

- Finally, solving for D we obtain Eq.(43).

- This tells us that the diffusion constant can also be obtained from the steady-state velocity of a particle driven by an external force through a fluid.

- In contrast, in the previous plot we derived the diffusion coefficient in terms of the mean-squared displacement of a particle diffusing in a fluid.

- Let us now introduce the basics of linear response theory.

- Its formal derivation is not treated in this course, but can be found in several text books including

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- “Basic concepts for simple and complex liquids”, and
- “Non-equilibrium statistical mechanics”

- In the linear response theory,
- we assume that the system is evolving in time with an equilibrium Hamiltonian H_0 .

- Then, an external force $F(t)$, is applied to the system, which gives rise to change in the Hamiltonian, from H_0 to $H_0 + H'(t)$.

- $H'(t)$ is **the** energy gain describing the coupling of **the** external force to the system.

- By definition, H' is written as $-A F(t)$, and A is said to be the conjugate variable to F .

- Now, consider how **the** average of a dynamical variable B changes under **the** external perturbation H' .

- Let **the** average of B at equilibrium, under H_0 , be denoted as B_0 .

- Under the perturbed Hamiltonian, $H_0 + H'$, the average of B at time t will deviate from B_0 by an amount $\propto \Delta B$.

- Here, we stress that B_0 is calculated as an average over **the** original Hamiltonian H_0 ,

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- whereas the deviation ΔB is calculated over the perturbed Hamiltonian.

- Using linear response theory, we can compute the time evolution of ΔB , provided that **the** external force is “small” enough.

- Then, to the first order in the perturbation, the time evolution of $\Psi_{\Delta B}$, under **the** external force F , is given by a convolution of $\Psi_{\Phi_{BA}}$ and F .

- Where $\Psi_{\text{Phi_BA}}$ is the response function, and **the** integral is taken from $-\infty$ to t .

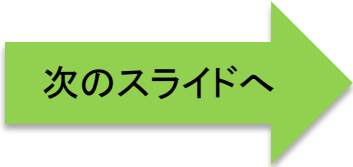
- This result is extremely useful, because Eq.(44) predicts the temporal value of B under **the** influence of an external force solely

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- from **the** equilibrium properties of the system in **the** absence of any external forces!

- Notice that, as given in Eq.(45), the response function is defined as the cross correlation function of A dot and B under equilibrium Hamiltonian.

- We see that linear response theory allows us to connect averages at equilibrium, under H_0 , with averages out of equilibrium, under $H_0 + H'$.

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- As an example, let us revisit the problem of calculating the self-diffusion constant of a particle, now using linear response theory.

- Assume that we have a single particle at equilibrium in a fluid.

- At time $t=0$, we turn on an external potential, which applies a constant external force on the particle.

- Without loss of generality, we can set the force to act along **the** x-direction and define the coordinates such that $R = 0$ at $t=0$.

- Mathematically, this force is represented as a constant amplitude F_0 multiplied with the Heaviside step function $\Upsilon\text{Theta}(t)$

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- which equals to 1 for t larger than 0, and 0 otherwise, as illustrated in the figure.

- The change in energy, the perturbation Hamiltonian H' , is given by the work done on the system by **the** external force.

- By definition this is equal to the force times the distance travelled.

- Thus, $A = R_x$.

- Since the response function depends on \dot{A} which is \dot{R} thus V , let's take B equals to V , to obtain the response in terms of the velocity autocorrelation function.

- From the linear response function Eqs.(44) and (45),

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- the drift velocity under the perturbed Hamiltonian $H_0 + H'$ is represented by the time integral of the velocity autocorrelation function from zero to t since $F=0$ for t less than 0.

- Even though we assumed a constant force along **the** x-direction, this can be generalized to an arbitrary direction, to give the general form in expression (46).

- In the figure we have illustrated the time evolution of the drift velocity after **the** application of external drift force at $t=0$.

- Finally, from Eqs.(43) and (46), the self diffusion constant of the Brownian particle is obtained by taking the limit when t goes to infinity.

- Linear response theory allows us to replace **the** average over the perturbed system, with a different average over **the** unperturbed system.

- The final result is shown as Eq.(47). This is an example of the so-called Green-Kubo formula,

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- which can define transport coefficients in terms of equilibrium correlation functions of corresponding variables.

- Here we have computed the Diffusion coefficient in terms of the velocity auto-correlation function of an equilibrium system!