- 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.

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- 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.

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- 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 ¥zeta.

- 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 trough 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.

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- 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”

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- 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 Hamiltinan, 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.

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

- Let the average of B at equilibirum, 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 ¥Delta B.

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

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- whereas the deviation ¥Delta B is calculated over the perturbed Hamiltonian.

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

- Then, to the first order in the perturbation, the time evolution of ¥Delta B, under the external force F, is given by a convolution of ¥Phi_BA and F.

- Where ¥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 ¥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 A-dot which is R-dot thus V, lets take B equals to V, to obtain the response in terms of the velocity autocorrelation function.

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- 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 $t=0$.

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- 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!

静止してください