Linear Response: Theory and Computation (Lecture 1)

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Overview

- Introduction
- Classical linear response theory
- Calculating transport coefficients from molecular dynamics
- Quantum linear response theory
- Numerical evaluation of the quantum Kubo conductivity
- Summary

Introduction

- Linear-response theory is one of the most understood topics in nonequilibrium statistical physics. It deals with systems not far from equilibrium, or particularly, systems at nonequilibrium **steady state**.
- We will study classical and quantum theories describing weakly perturbed systems. The weak perturbation will induce a response of the system which is linear in the perturbation. Hence the name **linear-response theory**.

References

- Mark E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation*, (Oxford University Press, 2010). **Chapters 1, 2, 3, 13, 14.**
- J. M. Haile, *Molecular Dynamics Simulation: Elementary Methods*, (Wiley, 1992). **Chapter 7.**
- R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, (Springer-Verlag, 1985). **Chapter 4.**
- M. Di Ventra, *Electrical Transport in Nanoscale Systems*, (Cambridge University Press, 2008). **Chapters 1, 2.**

Hamiltonian mechanics

- Hamilton's **equations of motion**:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{1}$$

- Any **physical quantity** a is a function of phase space point $x \equiv \{q_i, p_i\}_{i=1}^{3N}$ and possibly time t: $a = a(x, t)$.
- Time derivative of a phase space function $a(x)$:

$$\frac{da}{dt} = \sum_i \left[\dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i}\right] a \equiv \dot{x} \cdot \nabla_x a \equiv iLa, \tag{2}$$

where iL is the **Liouville operator**. For Hamiltonian systems:

$$iLa \equiv \{a, H\} \equiv \left[\frac{\partial a}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial a}{\partial p_i}\frac{\partial H}{\partial q_i}\right], \tag{3}$$

where $\{a, H\}$ is the **Poisson bracket** between $a(x)$ and $H(x)$.

Ensemble concept

- An **ensemble** is a collection of M (a huge number) systems described by the same set of microscopic interactions and sharing a common set of macroscopic properties. **Ensemble average** of a physical quantity $a(x)$ can be expressed as:

$$\langle a \rangle \equiv \frac{1}{M} \sum_{\lambda=1}^{M} a(x_\lambda). \tag{4}$$

- **Phase space distribution function**: $f(x, t)dx$ is the fraction of the total ensemble members contained in the phase space volume element dx at time t. It is a **probability density** satisfying

$$f(x, t) \geq 0; \quad \int dx f(x, t) = 1; \quad \langle a \rangle = \int dx f(x, t) a(x). \tag{5}$$

Equilibrium statistical mechanics

- **Liouville equation** (for a proof, see **Tuckerman, chapter 2**)

$$\frac{d}{dt}f(x,t) = \frac{\partial}{\partial t}f(x,t) + \{f(x,t), H(x,t)\} = 0. \tag{6}$$

- **Time-independent distribution**:

$$\frac{\partial}{\partial t}f(x,t) = 0 \Rightarrow \{f(x), H(x)\} = 0. \tag{7}$$

- A general solution is

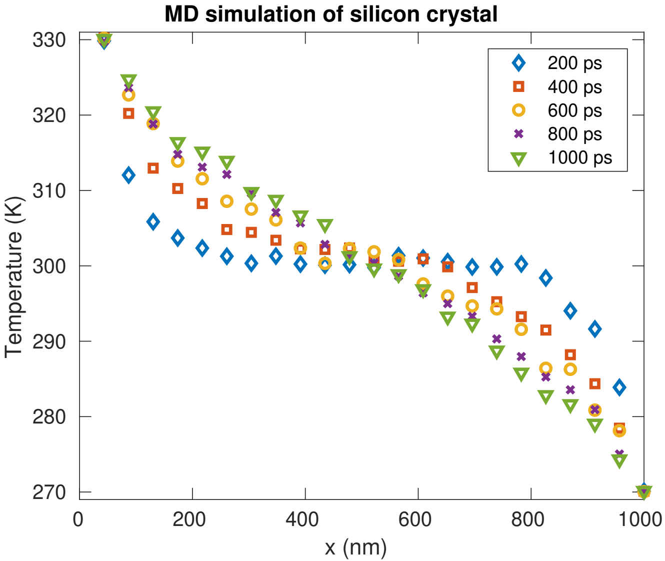
$$f(x) = \frac{1}{Z}f(H(x)); \quad Z = \int dxf(H(x)). \tag{8}$$

  An example is the **canonical ensemble** ($\beta = 1/k_B T$):

$$Z = \int dxe^{-\beta H(x)}. \tag{9}$$

- How about if $\frac{\partial}{\partial t}f(x,t) \neq 0$?

An example of driven system



Transport phenomena

- Diffusion (mass/particle is transported)
- Thermal conduction (heat/energy is transported)
- Viscosity (momentum is transported)
- Electrical conduction (charge/spin is transported)
- ...

Driven systems – Equations of motion

- Introduce a time-dependent driving force $F_e(t)$:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} + C_i(x)F_e(t) \tag{10}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} + D_i(x)F_e(t) \tag{11}$$

- The phase space distribution function $f(q, p, t) = f(x, t)$ is time dependent and we need to solve the Liouville equation:

$$\frac{\partial}{\partial t} f(x, t) + iLf(x, t) = 0. \tag{12}$$

Driven systems – Perturbation expansion

- Assume that the **perturbation is weak**, we can write

$$f(x,t) = f_0(H(x)) + \Delta f(x,t). \tag{13}$$

- The equilibrium phase space distribution function $f_0(H(x))$ satisfies the equilibrium Liouville equation:

$$iL_0 f_0(H(x)) = 0, \tag{14}$$

where iL_0 is the Liouville operator for the unperturbed system.

- The total Liouville operator can also be written as a sum:

$$iL = iL_0 + i\Delta L(t). \tag{15}$$

- The Liouville equation now becomes:

$$\frac{\partial}{\partial t}\left[f_0(x) + \Delta f(x,t)\right] = \left[iL_0 + i\Delta L(t)\right]\left[f_0(x) + \Delta f(x,t)\right]. \tag{16}$$

Driven systems – Linear approximation and formal solution

- **Neglecting** the second-order term, we have

$$\left(\frac{\partial}{\partial t} + iL_0\right)\Delta f(x,t) = -i\Delta L(t) f_0(H(x)). \tag{17}$$

- This equation can be formally solved as

$$\Delta f(x,t) = -\int_0^t ds e^{-iL_0(t-s)} i\Delta L(s) f_0(x). \tag{18}$$

- **Mathematical background**. For a first-order inhomogeneous differential equation $\dot{y}(t) + p(t)y(t) = q(t)$, we have a general solution $y(t) - y(0) = \frac{1}{u(t)}\int_0^t dsu(s)q(s)$, where $u(t) = e^{\int_0^t dsp(s)}$, where $u(t)$ is called the integrating factor.

Driven systems – Dissipative flux

- Consider the factor in the above equation

$$i\Delta L(s)f_0(H(x)) = iL(s)f_0(H(x)) = \dot{x}(s)\cdot\nabla_x f_0(H(x)). \tag{19}$$

- Using the equations of motion for the driven system, we have

$$i\Delta L(s)f_0(H(x)) = \frac{\partial f_0(H(x))}{\partial H}\dot{x}(s)\cdot\frac{\partial H}{\partial x} = -\frac{\partial f_0(H(x))}{\partial H}j(x)F_e(s), \tag{20}$$

where $j(x)$ is the **dissipative flux**:

$$j(x) = -\sum_i\left[D_i(x)\frac{\partial H}{\partial p_i} + C_i(x)\frac{\partial H}{\partial q_i}\right]. \tag{21}$$

Driven systems – Solution for the distribution function

- Suppose that $f_0(H(x))$ is given by a canonical distribution:

$$f_0(H(x)) = \frac{e^{-\beta H(x)}}{Z(N,V,T)}. \tag{22}$$

Then, we have

$$i\Delta L(s) f_0(H(x)) = \beta f_0(H(x)) j(x) F_e(s). \tag{23}$$

- Finally, we get the distribution function

$$\boxed{\Delta f(x,t) = -\beta \int_0^t ds e^{-iL_0(t-s)} f_0(H(x)) j(x) F_e(s).} \tag{24}$$

Driven systems – Expectation values of observables

- For any quantity $a(x)$ as a function of the phase space, its ensemble average at time t is

$$\langle a(t)\rangle = \int dx a(x) f(x,t) = \langle a(0)\rangle + \int dx a(x) \Delta f(x,t), \tag{25}$$

where $\langle a(0)\rangle = \int dx a(x) f_0(H(x))$ is the average of $a(x)$ in the unperturbed ensemble described by $f_0(H(x))$.

- Using the expression of $\Delta f(x,t)$ from the last slide, we have:

$$\boxed{\langle a(t)\rangle = \langle a(0)\rangle - \beta \int_0^t ds F_e(s) \int dx f_0(H(x)) a(x_{t-s}) j(x).} \tag{26}$$

Time correlation function (1)

- The average in terms of the equilibrium distribution $f_0(H(x))$ forms the (equilibrium) time correlation function

$$\langle a(t-s)j(0)\rangle = \int dx f_0(H(x)) a(x_{t-s}) j(x). \tag{27}$$

- More generally, we define the **equilibrium time correlation function** $\langle a(0)b(t)\rangle$ between two phase space functions $a(x)$ and $b(x)$ with respect to a normalized equilibrium distribution function $f_0(x)$ and dynamics generated by a Liouville operator iL_0 as

$$\boxed{\langle a(0)b(t)\rangle \equiv \int dx f_0(x) a(x) e^{iL_0 t} b(x).} \tag{28}$$

- A special case is the **autocorrelation function** in which $a(x) = b(x)$.

Time correlation function (2)

- Invariance under time translation

$$\langle a(0)b(t)\rangle = \langle a(-t)b(0)\rangle \tag{29}$$

  Jargon: t is the **correlation time**.

- At zero correlation time:

$$\langle a(0)b(0)\rangle = \int dx f_0(x)a(x)b(x) \tag{30}$$

  is simply the equilibrium average of $a(x)b(x)$.

- Long-time limit (Onsager regression hypothesis):

$$\lim_{t\to\infty}\langle a(0)b(t)\rangle = \langle a\rangle\langle b\rangle \tag{31}$$

Diffusion constant – Hamiltonian

- Consider a system in an **external potential field**

$$H' = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + U(\{\vec{r}_i\}_{i=1}^{N}) - f \sum_{i=1}^{N} x_i \tag{32}$$

  where $-fx_i = \phi(x_i)$ is the external potential energy of particle i.
- The **equations of motion**:

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}; \quad \dot{\vec{p}}_i = \vec{F}_i + f\vec{e}_x. \tag{33}$$

  From these, we have

$$\vec{C}_i = 0; \quad \vec{D}_i = f\vec{e}_x; \quad F_e(t) = 1. \tag{34}$$

  Therefore, the **dissipative flux** is

$$j = -f \sum_{i=1}^{N} \frac{p_{ix}}{m_i} = -fN \left(\frac{1}{N} \sum_{i=1}^{N} \frac{p_{ix}}{m_i} \right) \equiv -fNu_x. \tag{35}$$

Diffusion constant – steady state

- **Fick's law**:

$$J_x^{int} = -D\frac{\partial c}{\partial x}. \tag{36}$$

- Assume that the concentration is $c(x) = c(0)e^{-\beta\phi(x)} = c(0)e^{\beta fx}$. In the linear approximation, we have $c(x) = c(0)(1 + \beta fx)$ and

$$\frac{\partial c}{\partial x} = c(0)\beta f. \tag{37}$$

- The internal particle flux at steady state

$$J_x^{int} = -J_x^{ext} = -c(0)\lim_{t\to\infty}\langle u_x(t)\rangle. \tag{38}$$

Then the diffusion constant is

$$D = -\frac{J_x^{int}}{\partial c/\partial x} = \frac{\lim_{t\to\infty}\langle u_x(t)\rangle}{\beta f}. \tag{39}$$

Diffusion constant – Apply the linear response theory

- The ensemble average of $u_x(t)$ is

$$\langle u_x(t)\rangle = \langle u_x(0)\rangle + \beta N f \int_0^t d\tau u_x(\tau) u_x(0) \tag{40}$$

- Because $\langle u_x(0)\rangle = 0$, we have

$$\langle u_x(t)\rangle = \beta N f \int_0^t d\tau u_x(\tau) u_x(0) \tag{41}$$

- Finally, we have

$$D = \frac{\lim_{t\to\infty}\langle u_x(t)\rangle}{\beta f} = N \int_0^\infty dt \langle u_x(t) u_x(0)\rangle \tag{42}$$

Diffusion constant – Final expressions

- Because $\langle \dot{x}_i(t)\dot{x}_j(0)\rangle = 0$, we have

$$D_{xx} = \int_0^{\infty} dt \frac{1}{N}\sum_{i=1}^{N}\langle \dot{x}_i(t)\dot{x}_i(0)\rangle. \tag{43}$$

- The running diffusion constant is defined as

$$D_{xx}(t) = \int_0^{t} d\tau \frac{1}{N}\sum_{i=1}^{N}\langle \dot{x}_i(\tau)\dot{x}_i(0)\rangle. \tag{44}$$

- For 3D isotropic systems, we have

$$D(t) = \frac{D_{xx}(t) + D_{yy}(t) + D_{zz}(t)}{3} = \frac{1}{3}\int_0^{t} d\tau \frac{1}{N}\sum_{i=1}^{N}\langle \dot{\vec{r}}_i(\tau)\cdot\dot{\vec{r}}_i(0)\rangle. \tag{45}$$

Group discussion: Green-Kubo relation for shear viscosity

Read **Section 13.3.1 of Tuckerman or his lecture 21**. After you understand it, follow it to derive the Green-Kubo relation for the xy component of the **shear viscosity** tensor η_{xy}:

$$\eta_{xy} = \frac{V}{k_B T} \int_0^\infty dt \langle p_{xy}(0) p_{xy}(t) \rangle, \tag{46}$$

where

$$p_{xy} = \frac{1}{V} \sum_i \left[\frac{(\vec{p}_i \cdot \vec{e}_x)(\vec{p}_i \cdot \vec{e}_y)}{m_i} + (\vec{r}_i \cdot \vec{e}_x)(\vec{F}_i \cdot \vec{e}_y) \right] \tag{47}$$

is the xy component of the pressure tensor.

Thermal conductivity

- One can also derive the Green-Kubo formula for **lattice thermal conductivity** using the linear response theory. However, the derivation is very lengthy and we will not delve into it. If you are interested in it, you can check chapter 21 of *Statistical Mechanics* by D. A. McQuarrie.
- Here is the final result:

$$\kappa_{\mu\nu}(t) = \frac{1}{k_B T^2 V} \int_0^t d\tau \langle J_\mu(\tau) J_\nu(0) \rangle. \tag{48}$$

- $\vec{J}$ is the heat current vector defined as

$$\vec{J} = \frac{d}{dt} \sum_i \vec{r}_i E_i. \tag{49}$$

Summary

Green-Kubo relations from the linear response theory:

- **Diffusion constant** = time integral of **velocity** autocorrelation function
- **Shear viscosity** = time integral of **stress** autocorrelation function
- **Bulk viscosity** = time integral of **pressure** autocorrelation function
- **Thermal conductivity** = time integral of **heat current** autocorrelation function
- **Electrical conductivity** = time integral of **electric current** autocorrelation function
- ...