Advanced Topics in Physics

Lecturer: Prof. Eric Akkermans
(Notes by Yaroslav Don)

Spring 2016

Contents

4 Lesson 4

4.1 Stochastic Processes

4.1.1 Relation between γ and the mobility μ

Where $\gamma^{-1} = \mu$

Let's look on a stochastic process $\vec{v}(t)$. Let's define a (1D) relation

$$r(t) = \int_0^{t'} v(t')\,\mathrm{d}t' \tag{4.1}$$

This is well defined (thanks to Ito calculus). We, therefore, can write the correlation

$$\left\langle r^2(t)\right\rangle = \int_0^{t'}\int_0^{t''} \underbrace{\langle v(t')\,v(t'')\rangle}_{\text{new correlation } K_{vv}\left(t',t''\right)} \tag{4.2}$$

such that

$$K_{\xi\xi}(t,t') = \underbrace{\langle \xi(t)\,\xi(t')\rangle}_{\tau^*} \tag{4.3}$$

and we can:

Anticipate the result

$$t \gg \tau, \qquad \left\langle r^2(t)\right\rangle = 6Dt. \tag{4.4}$$

Note that the correlation time of the velocity, $K_{vv}(t',t'') = \tau = \frac{m}{\gamma}$ is different than $\tau* \to 0$.

Show that (as in the last week)

$$v(t) = v(0)\,\mathrm{e}^{-t/\tau} + \mathrm{e}^{-t/\tau}\frac{1}{m}\int_0^t \mathrm{d}t'\,\mathrm{e}^{t'/\tau}\xi(t') \tag{4.5}$$

such that the correlation

$$\langle v(t+s)\,v(t)\rangle \simeq v^2(0)\,\mathrm{e}^{-(2t+s)/\tau} + \mathrm{e}^{-(2t+s)/\tau}\frac{1}{m^2}C_{\xi\xi}\int_0^{t+s}\mathrm{d}t'\int_0^t \mathrm{d}t''\,\mathrm{e}^{\left(t'+t''\right)/\tau}\delta(t'-t'') \tag{4.6}$$

using $K_{\xi\xi}(t,t') = C_{\xi\xi}\delta(t-t')$. Therefore

$$\langle v(t+s)\,v(t)\rangle \xrightarrow{t\gg\tau} \frac{k_\mathrm{B}T}{m}\mathrm{e}^{|s|/\tau}, \tag{4.7}$$

where

$$\begin{cases} C_{\xi\xi} = 2k_\mathrm{B}T\gamma \qquad (D=1) \\ \tau = \frac{m}{\gamma} \end{cases}. \tag{4.8}$$

Hence

$$\left\langle r^2(t)\right\rangle \xrightarrow{t\to\infty} t\int_{-\infty}^{\infty}\mathrm{d}s\,\langle v(t'+s)\,v(t')\rangle \equiv tC_{vv} = 2Dt \tag{4.9}$$

and when we plug $C_{vv} = 2\frac{k_\mathrm{B}T}{m}\tau$, we get the Einstein relation:

$$D = \frac{k_\mathrm{B}T}{\gamma} \tag{4.10}$$

and

$$C_{vv} = \int_{-\infty}^{\infty}\mathrm{d}s\,\langle v(s)\,v(0)\rangle = 2\frac{k_\mathrm{B}T}{\gamma} \tag{4.11}$$

4.1.2 Correlation Functions

Following the previous discussion, we have three correlation functions:

1. The Noise Correlation Function

$$\frac{1}{\mu} = \gamma = \frac{1}{2k_\mathrm{B}T} \int_{-\infty}^{\infty} \mathrm{d}s \, \langle \xi(s)\, \xi(0) \rangle \tag{4.12}$$

   which describes the white noise;

2. The Velocity Correlation Function

$$\mu = \frac{1}{2k_\mathrm{B}T} \int_{-\infty}^{\infty} \mathrm{d}s \, \langle v(s)\, v(0) \rangle \tag{4.13}$$

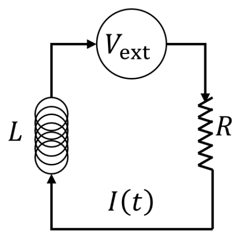
   which is derived from the noise, but has different correlation argument;

3. The Diffusion

$$D = \int_{-\infty}^{\infty} \mathrm{d}s \, \langle v(s)\, v(0) \rangle \tag{4.14}$$

4.1.3 Nyquist theorem — Kubo formula

Let's look on the following circuit:



which is described by the simple formula

$$L\frac{\mathrm{d}I}{\mathrm{d}t} = \underbrace{V_\mathrm{ext}}_{\text{"gravity"}} - RI(t) + \underbrace{V'(t)}_{\substack{\text{underlying}\\ \text{stochastic process}}} \tag{4.15}$$

such that the noise is *thermal*:

$$\langle I \rangle = \frac{1}{R} V_\mathrm{ext} \tag{4.16}$$

and the resistance of the stochastic process[1] abides

$$R = \frac{1}{2k_\mathrm{B}T} \int_{-\infty}^{\infty} \mathrm{d}s \, \langle V'(t+s)\, V'(t) \rangle = \frac{C_{VV}(0)}{2k_\mathrm{B}T} \tag{4.17}$$

Hence, we can write a correlation function

$$C_{VV}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}s \, \mathrm{e}^{\mathrm{i}\omega s} \, \langle V'(s)\, V'(0) \rangle \simeq 2k_\mathrm{B}T\, R. \tag{4.18}$$

This is the Nyquist-Johnson theorem[2].

[1] The equipartition assumption we use is due to the kinetic term in the Hamiltonian, $\frac{1}{2}L\left\langle I^2 \right\rangle = \frac{1}{2}k_\mathrm{B}T$, similarly to the mechanical $\frac{1}{2}m\left\langle v^2 \right\rangle = \frac{1}{2}k_\mathrm{B}T$.

[2] This is true only in the classical case; in the quantum case the formulae break, since $T \to 0$.

We can also write it in terms of the conductance:

$$\frac{1}{R}=G=\frac{1}{2k_{\mathrm{B}}T}\int_{-\infty}^{\infty}\mathrm{d}s\,\langle I\left(t+s\right)I\left(t\right)\rangle \tag{4.19}$$

It is usually more convenient to write it in terms of the conductivity σ, where $G=\sigma L^{d-2}$ (using $R=\rho\frac{L}{S}$):

$$G=\frac{1}{2k_{\mathrm{B}}T}\int_{-\infty}^{\infty}\mathrm{d}s\,\langle j\left(s\right)j\left(0\right)\rangle\,. \tag{4.20}$$

This is the KUBO formula[3].

Corollary. *Any time we have some "viscosity", we must seek the noise.*

Remark. When we have several sources of noise (classical), each characterized by its own viscosity η_i, then we can add all of them linearly $H=\sum_i\eta_i$ (The Mathison rule). In quantum case it is not true: due to entanglement we cannot separate them (this is the quantum mesoscopic physics).

4.2 Fluctuation-Dissipation Theorem (FDT) – Linear Response

Idea & objective: Formalize all the previous results.

4.2.1 Basic Idea

Each time we have a system out of equilibrium we can express its properties (viscosity, etc.) using the properties of the system in equilibrium (correlation function). This result is attributed to CALLEN & WELTON (PR, 1951)[4].

The basic idea behind (ONSAGER regression hypothesis, 1930): If you take a system out of equilibrium, in order to return back to equilibrium there will be fluctuations. However, there isn't any difference between those fluctuations and the fluctuations *at equilibrium.*

The derivation of CALLEN & WELTON is quantum mechanical, but it ought not to be so.

4.2.2 Classical description

1. Hamiltonian Mechanics. Let there be a system S and microscopic states (point in phase space) $\{p_1,p_2\ldots p_n\}\cup\{q_1,q_2\ldots q\}\equiv(p,q)$.

   At $t=0$ we have $(p\left(0\right),q\left(0\right))$. The state of S at time t is completely determined by initial conditions $+\mathcal{H}\left(p\left(0\right),q\left(0\right)\right)$, where we have defined the time evolution $\mathcal{T}_t:\left(p\left(t\right),q\left(t\right)\right)=\mathcal{T}_t\left(p\left(0\right),q\left(0\right)\right)$. We also assume statistical mechanics: the microstates of S *at equilibrium* are distributed with

$$P\left(p,q\right)=\frac{1}{Q}\mathrm{e}^{-\beta\mathcal{H}(p,q)},\qquad Q=\int\mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}(p,q)} \tag{4.21}$$

2. Time Setup. $t\to-\infty$.

   S is perturbed $\to$ new equilibrium at $t=0$ characterized by $\mathcal{H}'\left(p,q\right)$. At $t=0$ turn off the perturbation $\mathcal{H}\left(p,q\right)$.

   Relaxation: physical variable $A\left(p,q\right)$.

[3] In the quantum case, we have the same formula without the $\frac{1}{2k_{\mathrm{B}}T}$ factor, after deriving the KUBO formula using another source of noise (not thermal).

[4] Before that, EINSTEIN (1905), NYQUIST (1928).

3. Linear response: Perturbation is weak enough such that

$$\mathcal{H}' = \mathcal{H} + \Delta\mathcal{H} \tag{4.22}$$

where

$$\Delta\mathcal{H} = -fA \tag{4.23}$$

and f is the perturbing field. With this definition,

$$f = \frac{\partial F}{\partial A} \tag{4.24}$$

and F is the free energy.

Let's solve. At $t = 0$

$$P'(p,q) = \frac{1}{Q'} \mathrm{e}^{-\beta\mathcal{H}'(p,q)}, \tag{4.25}$$

and the relaxation

$$\langle A \rangle = \frac{1}{Q'} \int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}'(p,q)} A(p,q)\,. \tag{4.26}$$

At $t > 0$, we have $f \to 0$ and the system S evolves with $\mathcal{H}$. Therefore

$$\langle A(t) \rangle = \frac{1}{Q'} \int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}'(p,q)} A(\mathcal{T}_t(p,q))\,. \tag{4.27}$$

Now we expand to the 1st order (because f is small)

$$\langle A(t) \rangle \simeq \frac{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}} (1 - \beta\Delta\mathcal{H})\; A(\mathcal{T}_t(p,q))}{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}} (1 - \beta\Delta\mathcal{H})}. \tag{4.28}$$

After some algebra,

$$\begin{aligned}\langle A(t) \rangle \simeq{}& \frac{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}} A(\mathcal{T}_t(p,q))}{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}}} + \beta f \frac{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}} A(p,q)\, A(\mathcal{T}_t(p,q))}{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}}} \\ &- \beta f \frac{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}} A(p,q)}{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}}} \frac{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}} A(\mathcal{T}_t(p,q))}{\int \mathrm{d}p\,\mathrm{d}q\,\mathrm{e}^{-\beta\mathcal{H}}}.\end{aligned} \tag{4.29}$$

This is equivalent to

$$\langle A(t) \rangle \simeq \langle A(t) \rangle_0 + \beta f \left(\langle A(0)\, A(t) \rangle_0 - \langle A \rangle_0^2 \right) \tag{4.30}$$

where $\langle \cdot \rangle_0$ is equilibrium w.r.t. $\mathcal{H}$. The last term in the equation is because equilibrium at 0 is equal to equilibrium at t.

Let us define $\delta A(t) = A(t) - \langle A \rangle_0$. We get

$$\Delta A = \langle A(t) \rangle - \langle A(t) \rangle_0 = \beta f \langle \delta A(0)\, \delta A(t) \rangle_0\,. \tag{4.31}$$

This is another form of the Fluctuation Dissipation Theorem.

4.2.3 Generalize

Let's take some perturbation $f(t)$ (not constant). Using the same calculation, we'd get

$$\Delta A(t) = \int \mathrm{d}t'\, \chi(t,t')\, f(t') \tag{4.32}$$

Therefore, the relaxation at time t is related to all the relaxations (possible equilibrium correlations) at all the times prior to t. But, we cannot drive the system with times $t' > t$ (causality). Therefore

$$\chi(t,t') = 0 \quad @ \quad t' > t \tag{4.33}$$

5 Lesson 5

5.1 Linear Response (Classical Approach)

5.1.1 The last time

We looked on the perturbed Hamiltonian

$$\mathcal{H}' = \mathcal{H} - fA, \tag{5.1}$$

and got the Onsager Fluctuation-Dissipation theorem

$$\Delta A = \beta f \left\langle \delta A\left(0\right) \delta A\left(t\right) \right\rangle_0 , \tag{5.2}$$

which states that the response of the system is indistinguishable from the fluctuations in equilibrium.

5.1.2 Calculation of χ

We have also generalized the calculation to the case of $f\left(t\right)$:

$$\Delta A\left(t\right) = \int \mathrm{d}t' \, \chi\left(t,t'\right) f\left(t'\right). \tag{5.3}$$

In order to have causality, $\chi\left(t,t'\right) = 0$ for $t' > t$.

Remark. The susceptibility χ depends on the system S only and *not* on f.

For a system S at equilibrium (stationary)

$$\chi\left(t,t'\right) = \chi\left(t-t'\right), \tag{5.4}$$

therefore,

$$\chi\left(t,t'\right) = \begin{cases} \chi\left(t-t'\right), & t > t' \\ 0, & t' > t \end{cases} \tag{5.5}$$

Take, for example, a step-wise f

$$f\left(t\right) = \begin{cases} f, & t > t' \\ 0, & t' > t \end{cases} \tag{5.6}$$

therefore

$$\Delta A\left(t\right) = \int_{-\infty}^{0} \mathrm{d}t' \, \chi\left(t,t'\right) f \underset{\chi\left(t-t'\right)}{=} f \int_{t}^{\infty} \mathrm{d}t' \, \chi\left(t'\right). \tag{5.7}$$

Hence

$$\beta \left\langle \delta A\left(0\right) \delta A\left(t\right) \right\rangle_0 = \int_{t}^{\infty} \mathrm{d}t' \, \chi\left(t'\right), \tag{5.8}$$

and we obtain

$$\chi\left(t\right) = \begin{cases} -\beta \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \delta A\left(0\right) \delta A\left(t\right) \right\rangle_0 & t > 0 \\ 0 & \text{otherwise} \end{cases}. \tag{5.9}$$

We could generalize this to any f.

5.1.3 Generalization

Let's generalize the Hamiltonian to any perturbation B

$$\mathcal{H}' = \mathcal{H} - fB, \tag{5.10}$$

and measure the response of A. We'd get

$$\Delta A(t) = \beta f \langle \delta B(0)\, \delta A(t) \rangle_0 \tag{5.11}$$

and the susceptibility depends on both A and B,

$$\chi_{AB}(t) = \begin{cases} -\beta \frac{\mathrm{d}}{\mathrm{d}t} \langle \delta B(0)\, \delta A(t) \rangle_0 & t > 0 \\ 0 & \text{otherwise} \end{cases}. \tag{5.12}$$

5.1.4 Example: Brownian of a Particle in a Fluid

When we apply a force f_0 to the system (particle), the conjugate coordinate to the force (position x) changes, and we measure the velocity v. In this case,

$$\mathcal{H}' = \mathcal{H} - f_0 x, \tag{5.13}$$

and

$$v(t) = \int_{-\infty}^{0} \mathrm{d}t'\, \chi_{vx}(t - t')\, f(t') = f_0 \int_t^{\infty} \mathrm{d}t'\, \chi_{vx}(t'). \tag{5.14}$$

Apply f_0 from $-\infty$ to 0 and $f = 0$ at $t = 0$; expect

$$v(0) = \mu f_0 \tag{5.15}$$

where μ is the mobility,

$$\mu = \frac{1}{k_\mathrm{B} T} \int_0^{\infty} \underbrace{\langle v(t)\, v(0) \rangle_0}_{K_{vv},\,\text{symmetric}} \mathrm{d}t, \tag{5.16}$$

hence

$$v(0) = \underbrace{f_0 \int_0^{\infty} \mathrm{d}t'\, \chi_{vx}(t')}_{\text{out of equilibrium}} = \underbrace{\frac{f_0}{k_\mathrm{B} T} \int_0^{\infty} \langle v(t)\, v(0) \rangle_0 \,\mathrm{d}t}_{\text{in equilibrium}}. \tag{5.17}$$

This suggest a relation between the fluctuation out of equilibrium (linear response theory) and the correlation functions in equilibrium:

$$\boxed{\chi_{xv}(t) = \beta K_{vv}(t).} \tag{5.18}$$

This is the Onsager relation hypothesis.

5.1.5 Proof of (5.18)

Claim.

$$\chi_{xv}(t) = -\beta \frac{\mathrm{d}}{\mathrm{d}t} \langle x(0)\, v(t) \rangle_0. \tag{5.19}$$

Proof. In the stationary case,

$$\langle x(0)\, v(t) \rangle_0 = \langle x(t')\, v(t' + t) \rangle_0. \tag{5.20}$$

Now, derive with respect to t',

$$0 = \frac{\mathrm{d}}{\mathrm{d}t'} \langle x(t') v(t'+t) \rangle_0 = \langle \dot{x}(t') v(t'+t) \rangle_0 + \left\langle x(t') \tfrac{\mathrm{d}}{\mathrm{d}t'} v(t'+t) \right\rangle_0 . \tag{5.21}$$

Also,

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \langle x(t') v(t'+t) \rangle_0 = \langle x(t') \dot{v}(t'+t) \rangle_0 &= - \langle \dot{x}(t') v(t'+t) \rangle_0 \\ &= - \langle v(t) v(0) \rangle_0 = -K_{vv}(t) \end{aligned} \tag{5.22}$$

hence

$$\chi_{xv}(t) = K_{vv}(t) = \tfrac{1}{m} \mathrm{e}^{-t/\tau}. \tag{5.23}$$

This is the Onsager Regression Hypothesis. □

5.2 Fluctuation-Dissipation Theorem in Fourier Space

5.2.1 Brownian Particle

Let us look on the susceptibility,

$$x(t) = \int \mathrm{d}t' \, \chi(t-t') f(t') . \tag{5.24}$$

We can automatically write the the correlation function,

$$\chi_{xx}(t) = -\beta \tfrac{\mathrm{d}}{\mathrm{d}t} \langle x(t) x(0) \rangle_0 = -\beta \tfrac{\mathrm{d}}{\mathrm{d}t} K_{xx}(t) . \tag{5.25}$$

Now, take a Fourier transform and get a *wrong* result

$$\tilde{\chi}_{xx}(\omega) \neq -\beta \mathrm{i} \omega \tilde{K}_{xx}(\omega) . \tag{5.26}$$

Because

$$\begin{cases} \chi_{xx}(t) & \text{is defined for } t<0 \text{ only!} \\ K_{xx}(t) & \text{is defined for all } t. \end{cases} \tag{5.27}$$

How to solve this problem? Recall that

$$\begin{cases} \mathcal{F}[\text{real \& symmetric}] & = \text{real \& symmetric} \\ \mathcal{F}[\text{real \& odd}] & = \text{purely imaginary \& odd} \end{cases} .$$

Therefore, break $\chi_{xx}(t)$ into even and odd functions

$$\chi_{xx}(t) = \chi_{\mathrm{e}}(t) + \chi_{\mathrm{o}}(t) \tag{5.28}$$

and call the Fourier parts

$$\begin{cases} \tilde{\chi}_{\mathrm{e}}(\omega) & = \chi'(\omega) \\ \tilde{\chi}_{\mathrm{o}}(\omega) & = \mathrm{i}\chi''(\omega) \end{cases} \tag{5.29}$$

such that

$$\chi_{xx}(\omega) = \chi'(\omega) + \mathrm{i}\chi''(\omega) . \tag{5.30}$$

Now,

$$\chi_{xx}(t) = 2\chi_{\mathrm{o}}(t) = -\beta \tfrac{\mathrm{d}}{\mathrm{d}t} \langle x(t) x(0) \rangle_0 = -\beta \tfrac{\mathrm{d}}{\mathrm{d}t} K_{xx}(t) \tag{5.31}$$

hence,

$$2\mathrm{i}\chi''(\omega) = \mathrm{i}\beta\omega \langle x_\omega x_{-\omega} \rangle_0 \tag{5.32}$$

and, finally,

$$\boxed{\chi''(\omega) = \tfrac{1}{2}\omega\beta \left\langle |x_\omega|^2 \right\rangle_0 .} \tag{5.33}$$

This is the FD theorem in Fourier space.

5.3 Onsager Reciprocity Relations

Assign our simple working horse, Brownian Particle, in order to make things a bit simpler. Our usual Hamiltonian,

$$\mathcal{H}' = \mathcal{H} - fx. \tag{5.34}$$

From now on f and x are not necessarily force and position, but any type of conjugated variables. We get the 'velocity',

$$v(t) = \dot{x}(t) = \frac{1}{k_{\mathrm{B}}T}\int_0^\infty \mathrm{d}\tau\, f(t-\tau)\left\langle \dot{x}(0)\,\dot{x}(\tau)\right\rangle_0. \tag{5.35}$$

Let's generalize to other velocities,

$$\mathcal{H}' = \mathcal{H} - f_i x_i \tag{5.36}$$

so that

$$\dot{x}_i(t) = \beta\int_0^\infty \mathrm{d}\tau\, f_j(t-\tau)\left\langle \dot{x}_j(0)\,\dot{x}_i(\tau)\right\rangle_0, \tag{5.37}$$

(where the order of i and j is similar to our previous discussion of A and B).

5.3.1 Principle of Dynamical Reversibility of Microscopic Processes

The macroscopic behaviour is irreversible (e. g., friction). The outlined microscopic process, however, is reversible. Any correlation can be written as

$$\left\langle \dot{x}_j(0)\,\dot{x}_i(\tau)\right\rangle_0 \underset{\text{reversibility}}{=} \left\langle \dot{x}_j(0)\,\dot{x}_i(-\tau)\right\rangle_0 \underset{\substack{\text{translation}\\ \text{in time}}}{=} \left\langle \dot{x}_j(\tau)\,\dot{x}_i(0)\right\rangle_0, \tag{5.38}$$

hence

$$\left\langle \dot{x}_j(0)\,\dot{x}_i(\tau)\right\rangle_0 = \left\langle \dot{x}_i(0)\,\dot{x}_j(\tau)\right\rangle_0. \tag{5.39}$$

5.3.2 Essential Ingredients of Onsager Relations

Onsager Relations. Let's write the Onsager relations,

$$\frac{\mathrm{d}v}{\mathrm{d}t} = -\gamma v \quad\Longrightarrow\quad \frac{\mathrm{d}\dot{x}_i}{\mathrm{d}t} = -\gamma_{ij}\dot{x}_j. \tag{5.40}$$

Remark. γ_{ij} has no reasons to be symmetric.

Define the mobility,

$$v = \dot{x} = \mu F \quad\Longrightarrow\quad \dot{x}_i = \mu_{ij}F_j. \tag{5.41}$$

Note that for a single particle, $\gamma = \mu^{-1}$. The Onsager relations state that μ_{ij} *has to be symmetric*. Therefore, $\gamma_{ij} \neq \mu_{ij}^{-1}$.

Thermodynamic Equilibrium. In equilibrium we can define any transformation through the entropy:

$$\frac{1}{k_{\mathrm{B}}}\mathrm{d}S = \beta\mathrm{d}U - \beta\sum_s f_s \mathrm{d}x_s, \tag{5.42}$$

at equilibrium,

$$U = x_0, \quad \beta = F_0. \tag{5.43}$$

Let's set some definitions,

$$F_s \equiv -\beta f_s$$
$$\Sigma \equiv S/k_{\mathrm{B}} \tag{5.44}$$

such that

$$\mathrm{d}\Sigma = \sum_s F_s \mathrm{d}x_s \quad \Longleftrightarrow \quad F_s = \frac{\partial \Sigma}{\partial x_s}. \tag{5.45}$$

At equilibrium $\Sigma = 0$ and $\bar{x}_s = 0$. Therefore, close to equilibrium,

$$\Sigma = -\frac{1}{2} S_{ij} x_i x_j \tag{5.46}$$

where S_{ij} is not necessarily symmetric, but must be *negative definite*.

Let's introduce some more terminology,

$$J_i \equiv \dot{x}_i = \frac{\mathrm{d}x_i}{dt} \qquad \text{fluxes (currents)} \tag{5.47}$$

$$F_i = \frac{\partial \Sigma}{\partial x_i} = -S_{ik} x_k \qquad \text{(forces)} \tag{5.48}$$

such that

$$J_i = \mu_{ij} F_j. \tag{5.49}$$

Let's define the probability

$$P\left(x_0, \ldots, x_n\right) \mathrm{d}x_0 \ldots \mathrm{d}x_n \propto \mathrm{e}^{\Sigma} \mathrm{d}x_0 \ldots \mathrm{d}x_n. \tag{5.50}$$

Hence, at equilibrium,

$$\left\langle x_i F_j \right\rangle_0 = \frac{\int \mathrm{d}x_i \mathrm{e}^{\Sigma} \frac{\partial \Sigma}{\partial x_j} x_j}{\int \mathrm{d}x_i \mathrm{e}^{\Sigma}} = \delta_{ij}, \tag{5.51}$$

and we get

$$\left\langle x_i F_j \right\rangle_0 = \delta_{ij}. \tag{5.52}$$

On the other hand,

$$\left\langle x_i\left(\tau\right) x_j\left(0\right)\right\rangle = \left\langle x_i\left(-\tau\right) x_j\left(0\right)\right\rangle, \tag{5.53}$$

hence

$$\left\langle x_i\left(\tau\right) x_j\left(0\right)\right\rangle = \left\langle x_i\left(0\right) x_j\left(\tau\right)\right\rangle, \tag{5.54}$$

but

$$\frac{\left\langle x_i\left(\tau\right) x_j\left(0\right)\right\rangle - \left\langle x_i\left(0\right) x_j\left(0\right)\right\rangle}{\tau} = \frac{\left\langle x_i\left(0\right) x_j\left(\tau\right)\right\rangle - \left\langle x_i\left(0\right) x_j\left(0\right)\right\rangle}{\tau}, \tag{5.55}$$

and when $\tau \to 0$,

$$\left\langle \dot{x}_i\left(0\right) x_j\left(0\right)\right\rangle = \left\langle x_i\left(0\right) \dot{x}_j\left(0\right)\right\rangle. \tag{5.56}$$

Put in Eq. (?) and get

$$\mu_{ik} \left\langle F_k x_j\left(0\right)\right\rangle = \mu_{jk} \left\langle x_i\left(0\right) F_k\right\rangle \tag{5.57}$$

or

$$-\mu_{ik}\delta_{kj} = -\mu_{jk}\delta_{ik}, \tag{5.58}$$

and we get the Onsager relations (only at equilibrium!)

$$\mu_{ij} = \mu_{ji} \tag{5.59}$$

Remark. Outside of equilibrium μ_{ij} is not symmetric.

Generally,

$$\gamma_{ij}\mu_{jk} = S_{ik} \tag{5.60}$$

and S_{ik} is not generally symmetric.

6 Lesson 6

We have talked about the fluctuation-dissipation relations, linear response, Kubo formula and Onsager reciprocal relations. All of these were done close to equilibrium. Today, we will talk about systems far from equilibrium.

6.1 Generalization of the F. D. Relations far from Equilibrium

6.1.1 Synopsis

- Notion of Equilibrium: detailed balance.
- Generalization of the F. D. Relations: fluctuation theorems.[5]
- Large deviations.

6.1.2 Thermal Equilibrium.

Definition. Thermal equilibrium is the # Ω of microscopic configurations C of energy $E(C)$. The probability is given by the Gibbs-Boltzmann distribution

$$P_{\mathrm{eq}}(C) = \frac{1}{Z}\mathrm{e}^{-E(C)/k_{\mathrm{B}}T} \tag{6.1}$$

The entropy is given by

$$S = -k_{\mathrm{B}}\sum_{C} P_{\mathrm{eq}}(C)\ln P_{\mathrm{eq}}(C) \tag{6.2}$$

6.1.3 Markov process

Lets examine the process from configuration C_i to C_j

$$\underset{t}{C_i} \to \underset{t+\mathrm{d}t}{C_j} \tag{6.3}$$

The Markov Assumption: Let $M(C_j, C_i, t)\,\mathrm{d}t$ the probability to have a transition $C_i \to C_j$ at t during $\mathrm{d}t$. And let's examine the network of transitions

$$\begin{array}{ccccc} C_i & \longrightarrow & C_j & \longrightarrow & \\ & & \uparrow & & \\ C_l & \longrightarrow & C_k & \longrightarrow & \end{array} \tag{6.4}$$

And let $P_t(C)$ be the probability to be at configuration C at tine t. We can write the master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}P_t(C) = \sum_{C'\neq C} \underbrace{M(C,C')P_t(C')}_{\text{arrives to } C} - \underbrace{M(C',C)P_t(C)}_{\text{leaving } C} \tag{6.5}$$

A stationary state is

$$\frac{\mathrm{d}}{\mathrm{d}t}P_t(C) = 0 \tag{6.6}$$

and it gives conditions on Ω.

[5] Gallavotti & Cohen, 1995

Shorter Constraint (Onsager)

$$\forall C, C' \quad : \quad M(C, C') P_t(C') = M(C', C) P_t(C) \tag{6.7}$$

and we have $\frac{1}{2}\Omega(\Omega - 1)$ constraints.

Eq. 6.7 is a necessary condition for equilibrium. A system that breaks Eq. 6.7 is necessarily out of equilibrium. This means, that in Detailed Balance we have absence of currents.

Time reversal

Theorem. *The equilibrium state of a system, which satisfies Eq. 6.7 is necessarily invariant by time reversal,*

$$P(C(t)) = P(\Theta C(t)) \tag{6.8}$$

where Θ is the time reversal operator.

6.1.4 Physical Consequences of Detailed Balance

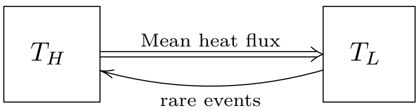
1. At equilibrium:

   Let $P(Q)$ is the probability that the system S gives heat Q to the reservoir R. Then, $P(-Q)$ is the same:

$$\frac{P(Q)}{P(-Q)} = 1 \tag{6.9}$$

2. Out of Equilibrium (far from equilibrium):

   Let us look on two reservoirs with temperatures $T_H > T_C$



(6.10)

   and the mean heat of flow is related to the system entropy

$$\frac{\langle Q \rangle}{T} = \langle S \rangle \tag{6.11}$$

   Thermodynamics says nothing about fluctuations. We would like to know, what is the probability to observe a rare event, such that a heat flows to the other direction.

   Claim. The probability distribution $P(Q_\tau)$ of exchanging with the reservoir C the heat Q_τ in a time τ is related to that of exchanging $-Q_\tau$. In simple words,

$$\ln\left(\frac{P(Q_\tau)}{P(-Q_\tau)}\right) = \Delta\beta Q_\tau \tag{6.12}$$

   where

$$\Delta\beta = \frac{1}{k_{\mathrm{B}}}\left(\frac{1}{T_C} - \frac{1}{T_H}\right) \tag{6.13}$$

   but

$$\Delta\beta Q_\tau = \underbrace{\sigma}_{\text{rate of entropy change}} \tau \tag{6.14}$$

   hence

$$\frac{P(\sigma)}{P(-\sigma)} = \mathrm{e}^{\sigma\tau} \tag{6.15}$$

   This is the Large Deviation Function (LDF).

Corollary. *The fluctuations always dissipate heat.*

Remark. The heat and entropy are extensive properties. Therefore, in very large systems (e. g., human body), $\mathrm{e}^{\sigma\tau} \ggg 1$. Therefore, $P(\sigma) \ggg P(-\sigma)$, and we don't see rare events. We need nanoscopic or mesoscopic systems to see such events.

6.1.5 Examples of Large Deviation Functions

Example 1. Consider a sum of independent random variables $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N$, where $\varepsilon_i = \begin{cases} +1 & \text{probability } p \\ -1 & \text{probability } q \end{cases}$. Then

1. Large Numbers Thm.: let $S_N = \sum_{i=1}^{N} \varepsilon_i$; then $\frac{S_N}{N} \xrightarrow{N\to\infty} \langle\varepsilon\rangle = p - q$.
2. Central Limit Thm.: $\frac{S_N - N(p-q)}{\sqrt{4pqN}}$ is the Gaussian

The behaviour of the probability $P\left(\frac{S_N}{N} = r\right)$ for large N and $r \in [-1, 1]$ is

$$\mathrm{Prob}\left(\frac{S_N}{N} = r\right) \underset{N\to\infty}{\sim} \mathrm{e}^{-N\phi(r)} \tag{6.16}$$

where

$$\phi(r) = \frac{1+r}{2} \ln\left(\frac{1+r}{2p}\right) + \frac{1-r}{2} \ln\left(\frac{1-r}{2q}\right) \tag{6.17}$$

and

$$\begin{cases} \phi(r = p - q) = 0 \\ \phi'(p - q) = 0 \end{cases}. \tag{6.18}$$

The function $\phi(r)$ is called the Large Deviation Function of this problem. It is a convex function with a minimum at $p - q$.

Example 2. Free Energy as an example of LDF. Consider N particles in a volume V with a density $r = \frac{N}{V}$. Let's look on some small volume $v \ll V$ inside the large one with particles n. Therefore,

$$\mathrm{Prob}\left(\frac{n}{v} = \rho\right) \sim \mathrm{e}^{-va(\rho)} \tag{6.19}$$

for some density ρ.

The free energy f per unit volume is

$$f(\rho) = \lim_{V\to\infty} -k_{\mathrm{B}}T \frac{\ln Z_V(\rho V)}{V} \tag{6.20}$$

with the partition function

$$Z = \mathrm{e}^{-\beta V f\left(\frac{N}{V}\right)} \tag{6.21}$$

and the probability

$$P\left(\frac{n}{v} = \rho\right) = \frac{Z_V(n)\, Z_{V-v}(N-n)}{Z_V(N)} = \mathrm{e}^{-va(\rho)} \tag{6.22}$$

and the LDF $a(\rho)$,

$$va(\rho) = \frac{1}{k_{\mathrm{B}}T}\left(vf(\rho) + (V-v)\, f\left(\frac{Vr - v\rho}{V-v}\right) - Vf(r)\right) \underset{v\ll V}{\simeq} \frac{v}{k_{\mathrm{B}}T}\left(f(\rho) - f(r) - (\rho - r)\, f'(r)\right). \tag{6.23}$$

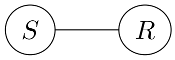
Remark. We can consider the free energy f itself as a LDF.

Remark. From the LDF we can calculate all the former fluctuation theorems (Onsager relations, etc.).

6.2 Fluctuation Theorems (Gallavotti and Cohen Relations)

6.2.1 Introduction

Let's look on some system coupled to a reservoir



(6.24)

with $E \equiv \Delta T, \Delta\rho, \Delta V, \ldots$ and $x(t)$ particles are transferred between S and R. Then the probability for some current j is

$$\mathrm{Prob}\left(\frac{x(t)}{t} = j, C \to C'\right) \underset{t\to\infty}{\sim} \mathrm{e}^{tG(j,E)}. \tag{6.25}$$

Note that in some cases this formula may not hold. The LDF $G(j,E)$ is independent of C and C' (prefactors can). Also $G(\bar{\jmath},E) = 0$ for the most probable current $\bar{\jmath}$.

We will prove the Gallavotti and Cohen Relation:

$$G(j,E) - G(-j,E) = \frac{Ej}{k_\mathrm{B}T} \tag{6.26}$$

and show that in order to break the detailed balance, we must follow a certain procedure. In other words, not every process can break DB.

7 Lesson 7

7.1 Fluctuation Theorems (Cont.)

7.1.1 Reminder

- We were talking about classical (non-quantum) description.
- We have described the Large Deviation Functions (LDFs).
- We have also stated the Gallavotti-Cohen relation between the values the LDF takes and the applied field. We have shown the response of the system, and saw that
$$\text{Prob}\left(\frac{x(t)}{t}=j\middle|C\to C'\right)\sim \mathrm{e}^{tG(j,E)} \tag{7.1}$$
where G is the LDF and E the applied field.
- We have shown the Detailed balance condition (in equilibrium):
$$M_x(C,C')\,P_{\text{eq}}(C')=M_{-x}(C',C)\,P_{\text{eq}}(C) \tag{7.2}$$
- We saw that one cannot break the detailed balance condition at will, but several constraints must be applied.

7.1.2 Out of Equilibrium

Out of equilibrium, $E\neq 0$ and Eq. (7.2) is changed into
$$\bar{M}_x(C,C')\,P_{\text{eq}}(C')=\bar{M}_{-x}(C',C)\,P_{\text{eq}}(C)\exp\left(\frac{E\cdot x}{k_{\text{B}}T}\right). \tag{7.3}$$
There exists a proof of (7.3) (not shown).

We therefore can calculate the outcome of the Detailed Balance probability:
$$\text{Prob}\left(C(t)|C\to C'\right)=\text{Prob}\left(\Theta C(t)|C\to C'\right)\frac{P_{\text{eq}}(C')}{P_{\text{eq}}(C)}\exp\left(\frac{E\cdot x(t)}{k_{\text{B}}T}\right) \tag{7.4}$$
where $x(t)$ is the total number of particles that has been exchanged after time t. Next, we sum over all the trajectories $C(t)$; a fixed $x(t)$ is transformed to
$$\text{Prob}\left(x(t)|C\to C'\right)=\exp\left(\frac{E\cdot x(t)}{k_{\text{B}}T}\right)\text{Prob}\left(-x(t)|C'\to C\right)\frac{P_{\text{eq}}(C')}{P_{\text{eq}}(C)}. \tag{7.5}$$

We now apply the LDF assumption, $\frac{x(t)}{t}=j$, to obtain
$$\boxed{\frac{P\left(\frac{x}{t}=j\right)}{P\left(\frac{x}{t}=-j\right)}=\exp\left(\frac{tjE}{k_{\text{B}}T}\right).} \tag{7.6}$$

Apply LDF's $P\left(\frac{x(t)}{t}=j\right)\sim \mathrm{e}^{tG(j,E)}$ and get
$$tG(j,E)=tG(-j,E)+\frac{tjE}{k_{\text{B}}T}. \tag{7.7}$$
Hence, we have the Gallavotti-Cohen relations
$$\boxed{G(j,E)-G(-j,E)=\frac{jE}{k_{\text{B}}T}.} \tag{7.8}$$
The temperature T is the temperatures of the reservoirs (recall that it cannot be defined out of equilibrium).

7.1.3 Implications

The G&C relations implies the Fluctuation-Dissipation Theorem (FDT) and the Onsager relations.

Reminder: FDT states that for

$$\Delta = \left. \frac{\left\langle x^2(t) \right\rangle - \langle x(t) \rangle^2}{t} \right|_{E=0} \tag{7.9}$$

and a linear response of the applied field E

$$\sigma E = \frac{\langle x(t) \rangle}{t} \tag{7.10}$$

one has

$$\boxed{\Delta = 2 k_{\mathrm{B}} T \sigma.} \tag{7.11}$$

Another reminder: for two fields j_x and j_y one has the Onsager relations,

$$\boxed{\sigma_{xy} = \sigma_{yx}.} \tag{7.12}$$

To prove FDT, we expand G close to equilibrium has a up to second order,

$$G(j, E) = aj + BE + cj^2 + djE + eE + \dots \tag{7.13}$$

And since $G = 0$ for $j = \bar{j} = \sigma E$ one has

$$G(j, E) = -\frac{(j - \bar{j})^2}{2\Delta}. \tag{7.14}$$

From G&C we have

$$-\frac{(j - \sigma E)^2}{2\Delta} = -\frac{(j + \sigma E)^2}{2\Delta} + \frac{Ej}{k_{\mathrm{B}} T} \tag{7.15}$$

hence

$$\Delta = 2 k_{\mathrm{B}} T \sigma. \tag{7.16}$$

To prove Onsager relations, we need at least two fields E_x, E_y to have

$$G(j_x, j_y, E_x, E_y) = G(-j_x, -j_y, E_x, E_y) + \frac{E_x j_x}{k_{\mathrm{B}} T} + \frac{E_y j_y}{k_{\mathrm{B}} T} \tag{7.17}$$

and after some algebra one has

$$\boxed{\sigma_{xy} = \sigma_{yx}.} \tag{7.18}$$

7.2 Quantum Statistical Mechanics

In this chapter we will try to describe the statistical mechanics of a pure quantum system.

7.2.1 KMS (Kubo-Martin-Schwinger) Condition

Let A be a quantum system. We define the thermal average of A by

$$\left\langle \hat{A} \right\rangle = \frac{\mathrm{Tr}\left(\hat{A} \mathrm{e}^{-\beta \hat{H}} \right)}{\mathrm{Tr}\left(\mathrm{e}^{-\beta \hat{H}} \right)} \tag{7.19}$$

and let us define the partition function

$$Z = \mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\right). \tag{7.20}$$

We now would like to look on the correlation functions

$$C_{AB}\left(t\right) \equiv \left\langle \hat{A}\left(t\right)\hat{B}\left(0\right)\right\rangle = \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{\beta\hat{H}}\hat{A}\left(t\right)\hat{B}\left(0\right)\right), \tag{7.21}$$

where we used the Heisenberg evolution

$$\hat{A}\left(t\right) = \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{A}\left(0\right)\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}. \tag{7.22}$$

Plug in and obtain

$$\begin{aligned}
C_{AB}\left(t\right) &= \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{A}\left(0\right)\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\hat{B}\left(0\right)\right)\\
&= \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\mathrm{e}^{-\beta\hat{H}}\hat{A}\left(0\right)\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\hat{B}\left(0\right)\right)\\
&= \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\hat{A}\left(0\right)\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\hat{B}\left(0\right)\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\right)\\
&= \left\langle \hat{A}\left(t\right)\hat{B}\left(-t\right)\right\rangle.
\end{aligned} \tag{7.23}$$

where in the 3rd line we used the cyclicity of the trace. So far, nothing surprising. On the other hand,

$$\begin{aligned}
C_{AB}\left(t\right) &= \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\hat{B}\left(0\right)\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\mathrm{e}^{-\beta\hat{H}}\hat{A}\left(0\right)\right)\\
&= \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\mathrm{e}^{+\beta\hat{H}}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\hat{B}\left(0\right)\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\mathrm{e}^{-\beta\hat{H}}\hat{A}\left(0\right)\right)\\
&= \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\mathrm{e}^{\mathrm{i}\frac{\hat{H}}{\hbar}\left(-t-\mathrm{i}\hbar\beta\right)}\hat{B}\left(0\right)\mathrm{e}^{-\mathrm{i}\frac{\hat{H}}{\hbar}\left(-t-\mathrm{i}\hbar\beta\right)}\hat{A}\left(0\right)\right)\\
&= \left\langle \hat{B}\left(-t-\mathrm{i}\hbar\beta\right)\hat{A}\left(0\right)\right\rangle.
\end{aligned} \tag{7.24}$$

We therefore have the KMS condition

$$\boxed{C_{AB}\left(t\right) = C_{BA}\left(-t-\mathrm{i}\hbar\beta\right).} \tag{7.25}$$

In other words, Quantum Mechanics is a game of imaginary time.

7.2.2 Remarks

In order to obtain the KMS results, we had to play with two operators. One is $\mathrm{e}^{-\beta\hat{H}}$, which is a Trace Class (a trace of a given operator, $\mathrm{Tr}\left(\hat{O}\right) < \infty$) and well defined. The other operator is $\mathrm{e}^{+\beta\hat{H}}$, which is ill-defined.

If we go to the complex t plane, where $z = t + \mathrm{i}s$, we have

$$C_{AB}\left(z\right) = \frac{1}{Z}\,\mathrm{Tr}\left(\mathrm{e}^{-\mathrm{i}\hat{H}z/\hbar}\hat{B}\left(0\right)\mathrm{e}^{-\mathrm{i}\frac{\hat{H}}{\hbar}\left(-z-\mathrm{i}\hbar\beta\right)}\hat{A}\left(0\right)\right). \tag{7.26}$$

In order to this quantity to be defined, we must have two conditions,

$$\begin{cases}\Re\left(-\mathrm{i}z\right) < 0\\ \Re\left(-\mathrm{i}\left(-z-\mathrm{i}\hbar\beta\right)\right) < 0\end{cases}, \tag{7.27}$$

or equivalently,

$$\boxed{-\hbar\beta < \Im(t) < 0.} \tag{7.28}$$

Similarly,

$$\tilde{C}_{AB} \equiv \left\langle \hat{B}(0)\,\hat{A}(t)\right\rangle$$

implies that

$$\boxed{0 < \Im(t) < \hbar\beta.} \tag{7.29}$$

7.2.3 The Opposite Direction

In other words, the KMS condition is very strong. It is a condition for a thermal equilibrium.

Now, let us assume the KMS and show thermal equilibrium. Let

$$\langle A\rangle = \mathrm{Tr}(\rho A), \tag{7.30}$$

where $\mathrm{Tr}(\rho) = 1$ and ρ is unknown. Some algebra gives

$$\begin{aligned}\left\langle \hat{B}(0)\,\hat{A}(t+\mathrm{i}\hbar\beta)\right\rangle &= \mathrm{Tr}\left(\rho\hat{B}(0)\,\hat{A}(t+\mathrm{i}\hbar\beta)\right) = \dots\\ &= \mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\hat{A}(t)\,\mathrm{e}^{\beta\hat{H}}\rho\hat{B}(0)\right)\\ &= \mathrm{Tr}\left(\rho\hat{A}(t)\,\hat{B}(0)\right).\end{aligned} \tag{7.31}$$

The last line is simply the KMS condition. Note that it is true for any t and any $\hat{A}$. It is possible only if $\rho\mathrm{e}^{\beta\hat{H}} = N$ for N some number. Hence

$$\rho = N\mathrm{e}^{-\beta\hat{H}} \tag{7.32}$$

7.2.4 Fourier Transforms

Let us define

$$\begin{cases} C_{AB}(t) = \left\langle \hat{A}(t)\,\hat{B}(0)\right\rangle = & \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\,\mathrm{e}^{\mathrm{i}\omega t}\tilde{C}_{AB}(\omega)\\ C_{AB}(t) = \left\langle \hat{B}(t)\,\hat{A}(0)\right\rangle = & \dots\end{cases} \tag{7.33}$$

KMS condition states that

$$\left\langle \hat{A}(t)\,\hat{B}(0)\right\rangle = \left\langle \hat{B}(-t-\mathrm{i}\hbar\beta)\,\hat{A}(0)\right\rangle = \left\langle \hat{B}(0)\,\hat{A}(t+\mathrm{i}\hbar\beta)\right\rangle, \tag{7.34}$$

hence

$$\boxed{\tilde{C}_{AB}(\omega) = \tilde{C}_{BA}(\omega)\,\mathrm{e}^{\beta\hbar\omega}.} \tag{7.35}$$

This is the Detailed Balance condition. Recall that KMS has

$$C_{AB}(t) = C_{BA}(-t-\mathrm{i}\hbar\beta). \tag{7.36}$$

8 Lesson 8

8.1 Quantum Statistical Mechanics

8.1.1 Reminder

We saw the equilibrium condition for a quantum system (the KMS condition),

$$C_{AB}\left(t\right)=C_{BA}\left(t\right)\left(-t-\mathrm{i}\hbar\beta\right). \tag{8.1}$$

for $-\hbar\beta<\Im\left(t\right)<\hbar\beta$. We then went to the Fourier space, where this equation reads,

$$\tilde{C}_{AB}\left(\omega\right)=\tilde{C}_{BA}\left(-\omega\right)\mathrm{e}^{\beta\hbar\omega}. \tag{8.2}$$

This is the Detailed Balance Condition.

Remark. These results (previous and forthcoming) hold irrespective of the exact statistics (e.g., Fermi-Dirac or Bose-Einstein).

8.1.2 Quantum Version of the F-D Theorem[6]

We have an Hamiltonian $\mathcal{H}$ and a perturbation $f\left(t\right)\hat{B}\left(t\right)$. We are interested in the quantity

$$\left\langle \hat{A}\left(t\right)\right\rangle =\frac{1}{Z}\operatorname{Tr}\left(\mathrm{e}^{-\beta\mathcal{H}}\hat{U}_{t}\left(f\right)A\left(0\right)\hat{U}_{t}^{-1}\left(f\right)\right). \tag{8.3}$$

Note that unlike the classical case, we do not start at $\mathcal{H}$ and stop and $t=0$; nevertheless, the calculation will be the same.

The evolution operator $\hat{U}_{t}\left(f\right)$ holds

$$-\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{U}_{t}\left(f\right)=\left(\mathcal{H}+f\left(t\right)\hat{B}\left(t\right)\right)\hat{U}_{t}\left(f\right), \tag{8.4}$$

hence,

$$\begin{aligned}\hat{U}_{t}\left(f\right)=U\left(t\right)&+\frac{\mathrm{i}}{\hbar}\int_{0}^{t}\mathrm{d}\tau\,U\left(\tau\right)f\left(\tau\right)B\left(\tau\right)U\left(t-\tau\right)\\&-\frac{1}{\hbar^{2}}\int_{0}^{t}\mathrm{d}\tau_{1}\int_{0}^{\tau_{1}}\mathrm{d}\tau_{2}\,U\left(\tau_{2}\right)f\left(\tau_{2}\right)B\left(\tau_{2}\right)U\left(\tau_{1}-\tau_{2}\right)f\left(\tau_{1}\right)B\left(\tau_{1}\right)U\left(t-\tau_{1}\right)+O\left(f^{3}\right).\end{aligned} \tag{8.5}$$

More compactly, we can write this equation with $\mathcal{T}$ the time ordering operator:

$$\hat{U}_{t}\left(f\right)=\mathcal{T}\left[\exp\left(\frac{\mathrm{i}}{\hbar}\int_{0}^{t}\mathrm{d}\tau\left(\mathcal{H}+f\left(t\right)\hat{B}\left(t\right)\right)\right)\right]. \tag{8.6}$$

After we inserted this expression to $\left\langle \hat{A}\left(t\right)\right\rangle$ we obtain

$$\left\langle \hat{A}\left(t\right)\right\rangle =\left\langle \hat{A}\left(0\right)\right\rangle +\int_{0}^{t}\mathrm{d}\tau\,R_{AB}\left(t-\tau\right)f\left(\tau\right)+O\left(f^{2}\right), \tag{8.7}$$

with

$$\boxed{R_{AB}\left(t-\tau\right)=-\frac{\mathrm{i}}{\hbar}\left\langle \left[A\left(t\right),B\left(\tau\right)\right]\right\rangle =-\frac{\mathrm{i}}{\hbar}\frac{1}{Z}\operatorname{Tr}\left(\mathrm{e}^{-\beta\mathcal{H}}\left[A\left(t\right),B\left(\tau\right)\right]\right),\quad t>\tau.} \tag{8.8}$$

[6] We will mostly follow the paper of Callen & Welton, PR., 1951

8.1.3 A Massage and Games

We'd like to play with various functions. Let's begin with the correlation function

$$\begin{aligned} C_{[A,B]}\left(t\right) \equiv \left\langle \left[A\left(t\right), B\left(0\right)\right]\right\rangle &= \left\langle A\left(t\right) B\left(0\right) - B\left(0\right) A\left(t\right)\right\rangle \\ &= \left\langle A\left(t\right) B\left(0\right) - B\left(-t\right) A\left(0\right)\right\rangle . \end{aligned} \tag{8.9}$$

Now write the Fourier transform as

$$C_{[A,B]}\left(t\right) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\mathrm{i}\omega t}\tilde{C}_{[A,B]}\left(\omega\right), \tag{8.10}$$

to obtain

$$\tilde{C}_{[A,B]}\left(\omega\right) = \tilde{C}_{AB}\left(\omega\right) - \tilde{C}_{BA}\left(-\omega\right) = \tilde{C}_{AB}\left(\omega\right)\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right), \tag{8.11}$$

where in the last equation we used (8.2).

Now, let's inspect the correlation function of the anti-commutator

$$C_{\{A,B\}}\left(t\right) \equiv \left\langle \left\{A\left(t\right), B\left(0\right)\right\}_{+}\right\rangle . \tag{8.12}$$

The same massage gives

$$\tilde{C}_{\{A,B\}}\left(\omega\right) = \tilde{C}_{AB}\left(\omega\right)\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right). \tag{8.13}$$

This gives us a direct relation between the two:

$$\tilde{C}_{[A,B]}\left(\omega\right) = 2\tanh\left(\tfrac{1}{2}\beta\hbar\omega\right)\tilde{C}_{\{A,B\}}\left(\omega\right). \tag{8.14}$$

We now can write (8.8) as

$$\boxed{R_{AB}\left(t\right) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\mathrm{i}\omega t}\,\frac{2}{\hbar}\tanh\left(\tfrac{1}{2}\beta\hbar\omega\right)\tilde{C}_{\{A,B\}}\left(\omega\right).} \tag{8.15}$$

This is sometimes called the Quantum Fluctuation-Dissipation Theorem (QFDT).

8.1.4 Linear Response – Definitions and Properties

Let us write

$$R_{AB}\left(t-\tau\right) \equiv -\frac{\mathrm{i}}{\hbar}\left\langle \left[A\left(t\right), B\left(\tau\right)\right]\right\rangle \Theta\left(t-\tau\right). \tag{8.16}$$

Usually in the literature we see the susceptibility

$$\tilde{\chi}_{AB}\left(t-t'\right) \equiv \frac{\mathrm{i}}{\hbar}\left\langle \left[A\left(t\right), B\left(t'\right)\right]\right\rangle \Theta\left(t-t'\right). \tag{8.17}$$

This is sometimes called the Response function, Retarded Green function, Retarded propagator, etc.

Let us now write the properties of $\mathcal{H}$. We expand it in its eigenfunctions,

$$\mathcal{H}\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle, \tag{8.18}$$

with the equilibrium population

$$\rho_{\mathrm{eq}} = \frac{1}{Z}\mathrm{e}^{-\beta\mathcal{H}}, \tag{8.19}$$

such that

$$\left\langle \varphi_n\middle|\rho_{\mathrm{eq}}\middle|\varphi_n\right\rangle \equiv \Pi_n\delta_{nn'} = \frac{1}{Z}\mathrm{e}^{-\beta E_n}\delta_{nn'}. \tag{8.20}$$

Therefore

$$\tilde{\chi}_{AB}(\tau) = \Theta(\tau)\,\frac{\mathrm{i}}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\,A_{nq}B_{qn}\mathrm{e}^{\mathrm{i}(E_n-E_q)\tau/\hbar}, \tag{8.21}$$

where $\Theta(\tau)$ ensures causality. We can now write its Fourier components,

$$\chi_{AB}(\omega) \equiv \int_0^\infty \mathrm{d}\tau\,\mathrm{e}^{\mathrm{i}\omega\tau}\tilde{\chi}_{AB}(\tau)\,. \tag{8.22}$$

Let us introduce a factor $\mathrm{e}^{\varepsilon\tau/\hbar}$ with $\varepsilon \to 0^+$ to have

$$\boxed{\chi_{AB}(\omega) = \frac{1}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\,A_{nq}B_{qn}\lim_{\varepsilon\to 0^+}\frac{1}{\omega_{qn}-\omega-\mathrm{i}\varepsilon},} \tag{8.23}$$

where $\hbar\omega_{qn} \equiv E_q - E_n$. This value $\chi_{AB}(\omega)$ is called the Susceptibility, Admittance, 1/Impedance.

Remark. Note that we used simple quantum mechanics, and not quantum statistics. Quantum statistics came after introducing QFT into quantum mechanics: when you need to quantize a field (scalar or spinor), you need to know whether it is a Fermion or a Boson. The statistics we used when calculating, for example, black body radiation were not quantized. The FD or BE distributions are simply a matter of choice. Therefore all this derivation is valid.

8.1.5 Extension of $\chi_{AB}(\omega)$ to the Complex Plane

This is related to the Kramers-Krönig relations.

Let us look on the complex plane $z = x + \mathrm{i}y$,

$$\hat{\chi}_{AB}(z) = \int_{-\infty}^{\infty}\mathrm{d}\tau\,\mathrm{e}^{\mathrm{i}z\tau}\tilde{\chi}_{AB}(\tau) = \int_{-\infty}^{\infty}\mathrm{d}\tau\,\mathrm{e}^{-y\tau}\mathrm{e}^{\mathrm{i}x\tau}\tilde{\chi}_{AB}(\tau)\,, \tag{8.24}$$

on the upper half-plane $y = \Im(z) \geq 0$. Here the $\hat{\square}$ denotes a function on the complex plane. Note that $\hat{\chi}_{AB}(z)$ is well defined in the upper half-plane. It is analytic and given by $\chi_{AB}(\omega)$,

$$\chi_{AB}(\omega) = \lim_{\varepsilon\to 0^+}\hat{\chi}_{AB}(z = \omega + \mathrm{i}\varepsilon)\,. \tag{8.25}$$

Therefore,

$$\hat{\chi}_{AB}(z) = \frac{1}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\,A_{nq}B_{qn}\frac{1}{\omega_{qn}-z}. \tag{8.26}$$

Therefore, all the singularities of $\hat{\chi}_{AB}(z)$ come from the poles of $\frac{1}{\omega_{qn}-z}$. Since ω_{qn} are real, all singularities of $\hat{\chi}_{AB}(z)$ are poles along the real axis.

There is a discrete energy spectrum for $\mathcal{H}$. In the $V \to \infty$ limit, we'll obtain a cut in the complex plane along the real axis (the poles become a line).

Corollary. *A single isolated atom does not dissipate energy. You need a continuum in order to dissipate.*

8.1.6 Spectral Function (Dissipation)

Let us define

$$\xi_{AB}(\omega) \equiv \frac{\pi}{\hbar}\frac{1}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\,A_{nq}B_{qn}\delta(\omega_{qn}-\omega)\,. \tag{8.27}$$

It is usually denoted by $\chi''_{AB}(\omega)$. Hence,

$$\hat{\chi}_{AB}(z) = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\xi_{AB}(\omega)}{\omega - z}. \tag{8.28}$$

Therefore

$$\chi_{AB}(\omega) = \frac{1}{\pi}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\xi_{AB}(\omega')}{\omega' - \omega - \mathrm{i}\varepsilon}. \tag{8.29}$$

On the other hand,

$$\hat{\xi}_{AB}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{-\mathrm{i}\omega t}\xi_{AB}(\omega), \tag{8.30}$$

implies that

$$\hat{\xi}_{AB}(t) = \frac{1}{2\hbar}\langle[A(t), B(0)]\rangle. \tag{8.31}$$

Note that there is no Θ function; therefore $\hat{\xi}_{AB}(t)$ (the spectral / Green's function) does not preserve causality. The relation between the two reads

$$\tilde{\chi}_{AB}(t) = 2\mathrm{i}\Theta(t)\,\xi_{AB}(t). \tag{8.32}$$

We can now write

$$\xi_{AB}(\omega) = \frac{1}{2\mathrm{i}}\lim_{\varepsilon\to 0^+}\left[\hat{\chi}_{AB}(\omega + i\varepsilon) - \hat{\chi}_{AB}(\omega - i\varepsilon)\right], \tag{8.33}$$

where we used the Cauchy principal value relation,

$$\lim_{\varepsilon\to 0^+}\frac{1}{\omega' - \omega \mp \mathrm{i}\varepsilon} = \mathcal{P}\left(\frac{1}{\omega' - \omega}\right) \pm \mathrm{i}\pi\delta(\omega' - \omega). \tag{8.34}$$

Remark. The value $\hat{\chi}_{AB}(\omega - i\varepsilon)$ exists in the lower-half plane. Since $\chi_{AB}(\omega - i\varepsilon)$ was not shown to exist, it must preserve the hat $\hat{\chi}$. The hat on $\hat{\chi}_{AB}(\omega + i\varepsilon)$ is there for solidarity.

Let us continue. Causality

$$\begin{aligned}
\hat{\chi}_{AB}(\omega - i\varepsilon) &= \frac{1}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\frac{A_{nq}B_{qn}}{\omega_{qn} - \omega + \mathrm{i}\varepsilon}. \\
&= \frac{1}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\left(\frac{A^*_{nq}B^*_{qn}}{\omega_{qn} - \omega - \mathrm{i}\varepsilon}\right)^* \\
&= \frac{1}{\hbar}\sum_{n,q}(\Pi_n - \Pi_q)\left(\frac{B^\dagger_{nq}A^\dagger_{qn}}{\omega_{qn} - \omega - \mathrm{i}\varepsilon}\right)^* \\
&= \left(\hat{\chi}_{B^\dagger A^\dagger}(\omega + i\varepsilon)\right)^*,
\end{aligned} \tag{8.35}$$

and therefore well defined. Hence

$$\xi_{AB}(\omega) = \frac{1}{2\mathrm{i}}\left(\chi_{AB}(\omega) - \chi^*_{B^\dagger A^\dagger}(\omega)\right). \tag{8.36}$$

For $A^\dagger = B$ we have

$$\xi_{AA^\dagger}(\omega) = \Im\left(\chi_{AA^\dagger}(\omega)\right) \equiv \chi''_{AA^\dagger}(\omega) \tag{8.37}$$

9 Lesson 9

9.1 Quantum Statistical Mechanics

9.1.1 Reminder

We defined the retarded Green's function,

$$\tilde{\chi}_{AB}\left(t-t'\right) \equiv \frac{\mathrm{i}}{\hbar}\left\langle\left[A\left(t\right),B\left(t'\right)\right]\right\rangle_{\mathrm{eq}}\Theta\left(t-t'\right), \tag{9.1}$$

and showed that its analytic continuation,

$$\hat{\chi}_{AB}\left(z\right)=\int_{-\infty}^{\infty}\mathrm{d}\tau\,\mathrm{e}^{\mathrm{i}z\tau}\tilde{\chi}_{AB}\left(\tau\right), \tag{9.2}$$

is analytic for $\mathfrak{Im}\left(z\right)>0$. We then showed that the limit

$$\chi_{AB}\left(\omega\right)=\frac{1}{\pi}\lim_{\varepsilon\to0^{+}}\hat{\chi}_{AB}\left(z=\omega+\mathrm{i}\varepsilon\right) \tag{9.3}$$

is well defined.

We finished with the spectral function

$$\xi_{AB}\left(\omega\right)\equiv\frac{\pi}{\hbar}\frac{1}{\hbar}\sum_{n,q}\left(\Pi_{n}-\Pi_{q}\right)A_{nq}B_{qn}\delta\left(\omega_{qn}-\omega\right), \tag{9.4}$$

and showed that's its time-space counterpart is

$$\tilde{\xi}_{AB}\left(t\right)=\frac{1}{2\hbar}\left\langle\left[A\left(t\right),B\left(0\right)\right]\right\rangle. \tag{9.5}$$

Therefore,

$$\tilde{\chi}_{AB}\left(t-t'\right)=2\mathrm{i}\Theta\left(t-t'\right)\xi_{AB}\left(t-t'\right). \tag{9.6}$$

We will inspect the function

$$\xi_{AA^{\dagger}}\left(\omega\right)=\mathfrak{Im}\chi_{AA^{\dagger}}\left(\omega\right)\equiv\chi''_{AA^{\dagger}}\left(\omega\right) \tag{9.7}$$

9.1.2 What we will do today

We will show that this spectral function is related to the dissipation in the system. We will also show that these results can be elementary derived from the KMS condition. We will finally show that these results are not unique to Bosons. We will see how is related to the Kramers-Krönig relations.

9.1.3 Physical meaning of $\xi_{AA^{\dagger}}\left(\omega\right)$ — Dissipation

Reminder: we are looking on a perturbation $V\cos\omega t$. Let's recall Fermi Golden Rule: the probability per unit time to have a transition between a state $\left|\phi_{i}\right\rangle$ and a group of final states $\left|\phi_{f}\right\rangle$ is

$$\sum_{f}\frac{\pi}{2\hbar^{2}}\left|\left\langle\phi_{f}\right|V\left|\phi_{i}\right\rangle\right|^{2}\left[\delta\left(\omega_{fi}-\omega\right)+\delta\left(\omega_{if}-\omega\right)\right]. \tag{9.8}$$

If $E_{f}>E_{i}$, this is energy absorption; if $E_{f}<E_{i}$ this is emission.

Let us define $a\left(t\right)=a\cos\omega t$. Then, the total energy *absorbed* per unit time is

$$\frac{\mathrm{d}W_{\mathrm{abs}}}{\mathrm{d}t}=\frac{\pi a^{2}}{2\hbar^{2}}\sum_{nq}\Pi_{n}\hbar\omega\left|A_{nq}\right|^{2}\delta\left(\omega_{qn}-\omega\right), \tag{9.9}$$

and the total energy *emitted* per unit time is

$$\frac{\mathrm{d}W_{\mathrm{ems}}}{\mathrm{d}t} = \frac{\pi a^2}{2\hbar^2} \sum_{nq} \Pi_n \hbar\omega \left|A_{nq}\right|^2 \delta\left(\omega_{nq} - \omega\right) = \frac{\pi a^2}{2\hbar^2} \sum_{nq} \Pi_q \hbar\omega \left|A_{nq}\right|^2 \delta\left(\omega_{qn} - \omega\right). \quad (9.10)$$

At thermal equilibrium the lowest levels are more populated, or $\Pi_n > \Pi_q$. Therefore, combining these last two equations we obtain

$$\boxed{\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\pi a^2}{2\hbar^2} \sum_{nq} \left(\Pi_n - \Pi_q\right) \hbar\omega \left|A_{nq}\right|^2 \delta\left(\omega_{qn} - \omega\right)} = \frac{a^2}{2} \xi_{AA^\dagger}\left(\omega\right). \quad (9.11)$$

9.1.4 Symmetrized version of FDT

Let's inspect again the correlation

$$\tilde{C}_{AB}\left(t\right) = \left\langle A\left(t\right) B\left(0\right)\right\rangle, \quad (9.12)$$

that define the statistical fluctuations in a quantum way. It is not real, since

$$\left\langle A\left(t\right) B\left(0\right)\right\rangle^* = \left\langle B\left(0\right) A\left(t\right)\right\rangle. \quad (9.13)$$

In order to symmetrize, we define

$$\begin{aligned} \tilde{S}_{AB}\left(t\right) &\equiv \tfrac{1}{2} \left\langle A\left(t\right) B\left(0\right) + B\left(0\right) A\left(t\right)\right\rangle \\ &= \tfrac{1}{2} \left\langle \left\{A\left(t\right) B\left(0\right)\right\}_+ \right\rangle. \end{aligned} \quad (9.14)$$

Taking its Fourier transform we have

$$S_{AB}\left(\omega\right) = \pi \sum_{nq} \left(\Pi_n + \Pi_q\right) A_{nq} B_{qn} \delta\left(\omega_{qn} - \omega\right). \quad (9.15)$$

Let's massage it a bit:

$$\begin{aligned} \Pi_n + \Pi_q &= \left(\Pi_n - \Pi_q\right) \frac{\Pi_n + \Pi_q}{\Pi_n - \Pi_q} \\ &= \left(\Pi_n - \Pi_q\right) \frac{1 + \mathrm{e}^{-\beta\left(E_q - E_n\right)}}{1 - \mathrm{e}^{-\beta\left(E_q - E_n\right)}} \\ &= \left(\Pi_n - \Pi_q\right) \frac{1 + \mathrm{e}^{-\beta h\omega}}{1 - \mathrm{e}^{-\beta h\omega}}, \end{aligned} \quad (9.16)$$

where we used the direct Gibbs factors of $\Pi_{n,q}$. Therefore,

$$S_{AB}\left(\omega\right) = \hbar \frac{1 + \mathrm{e}^{-\beta h\omega}}{1 - \mathrm{e}^{-\beta h\omega}} \xi_{AB}\left(\omega\right), \quad (9.17)$$

or,

$$\boxed{S_{AB}\left(\omega\right) = \hbar \coth\left(\frac{\beta\hbar\omega}{2}\right) \xi_{AB}\left(\omega\right).} \quad (9.18)$$

This is the symmetrized FDT.

Exercise: Show that for $\hbar \to 0$ we get the classical version.

9.1.5 Einstein's relations

Let's return to the correlations.

$$C_{AB}(\omega) = \frac{2\hbar}{1-\mathrm{e}^{-\beta\hbar\omega}}\xi_{AB}(\omega) = 2\hbar\left(1+n_B(\omega)\right)\xi_{AB}(\omega), \tag{9.19}$$

where

$$n_B(\omega) = \frac{1}{1-\mathrm{e}^{-\beta\hbar\omega}}. \tag{9.20}$$

People like to say: "Oh, look! We have the Bose-Einstein factor. Therefore it proves the Bosonic nature of the photons". However, our derivation had nothing to do with Bosons! Therefore, it has no relation with the Bose-Einstein statistics.

9.1.6 Another derivation based on KMS

Let's inspect

$$\tilde{\xi}_{AB} = \frac{1}{2\hbar}\left\langle\left[A(t), B(0)\right]\right\rangle = \frac{1}{2\hbar}\left(\tilde{C}_{AB}(t) - \tilde{C}_{BA}(-t)\right). \tag{9.21}$$

From KMS we have

$$\tilde{C}_{AB}(t) = \tilde{C}_{BA}(-t-\mathrm{i}\hbar\beta). \tag{9.22}$$

It implies that

$$\tilde{C}_{BA}(-t) = \tilde{C}_{AB}(t-\mathrm{i}\hbar\beta). \tag{9.23}$$

It implies, in turn, that its Fourier transform reads

$$\begin{aligned}\int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t}\tilde{C}_{AB}(t-\mathrm{i}\hbar\beta)(t) &= \int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega(t+\mathrm{i}\hbar\beta)}\tilde{C}_{AB} \\ &= \mathrm{e}^{-\beta\hbar\omega}\int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t}\tilde{C}_{AB}.\end{aligned} \tag{9.24}$$

Therefore,

$$\xi_{AB}(\omega) = \frac{1}{2\hbar}\left(C_{AB}(\omega) - \mathrm{e}^{-\beta\hbar\omega}C_{AB}(\omega)\right) \tag{9.25}$$

or,

$$\boxed{C_{AB}(\omega) = 2\hbar\left(1+n_B(\omega)\right)\xi_{AB}(\omega).} \tag{9.26}$$

QED. □

Remark. In order to prove the quantum nature of photons (meaning, the radiation is quantized), one does not need the black body radiation. In fact, all one needs is the FDT. Einstein, in his 1905 proof, used thermodynamic arguments to show that light has to be quantized. However, the first real need of the quantum nature was Haroche's demonstration of single photons, on which he got the Nobel prize.

9.1.7 Another look on causality – Kramers-Krönig relations

Here the causality is manifested in $\Theta(\tau)$. We need a small set of assumptions:

1. $\tilde{\chi}_{AB}(\tau)$ is real (response function);
2. $|\chi_{AB}(\tau)|$ is bound ($< M$); and
3. $\chi_{AB}(\tau)$ is causal (meaning, it is 0 for $\tau < 0$).

Assumptions (2) and (3) imply that $\chi_{AB}(\omega)$ is well defined and does not have poles for $\mathfrak{Im}(z) > 0$ $(z = x + \mathrm{i}y)$. Therefore,

$$\chi_{AB}(x + \mathrm{i}y) = \int_{-\infty}^{\infty} \mathrm{d}z\, \tilde{\chi}_{AB}(\tau)\, \mathrm{e}^{\mathrm{i}x\tau}\mathrm{e}^{-y\tau} < \frac{M}{y}. \tag{9.27}$$

Remark. Physical system has poles only in the lower half of the complex plane. For example, for the Harmonic oscillator

$$m\ddot{z} + m\gamma\dot{z} + m\omega_0^2 z = F(t), \tag{9.28}$$

we have solutions of the form

$$z(t) = -\int_{-\infty}^{t} \mathrm{d}t'\, \underbrace{G(t - t')}_{\text{retarded Green's function}} f(t'), \tag{9.29}$$

where $f(t) = F(t)/m$. In other words,

$$\ddot{G}(\tau) + \gamma\dot{G}(\tau) + \omega_0^2 G(\tau) = -\delta(\tau), \tag{9.30}$$

such that

$$G(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, g(\omega)\, \mathrm{e}^{-\mathrm{i}\omega t}, \tag{9.31}$$

where

$$g(\omega) = \frac{1}{\omega^2 + \mathrm{i}\gamma\omega - \omega_0^2}. \tag{9.32}$$

We have poles at $\pm\omega_1 - \frac{\mathrm{i}\gamma}{2}$, where $\omega_1 = \left(\omega_0^2 - \frac{\gamma^2}{4}\right)^{1/2}$.

Now, we want to calculate this retarded Green's function.

- For $\tau < 0$, $G(\tau) = 0$. Hence, $\omega = \alpha + \mathrm{i}\beta$, $\beta > 0$ and $\mathrm{e}^{-\mathrm{i}\omega t} = \mathrm{e}^{\beta\tau}\mathrm{e}^{-\mathrm{i}\alpha\tau}$.
- For $\tau > 0$, $\omega = \alpha - \mathrm{i}\beta$, $\beta > 0$ and

$$G(\tau) = -2\mathrm{i}\pi \sum_{\text{resid.}} \frac{1}{2\pi} \frac{\mathrm{e}^{-\mathrm{i}\omega\tau}}{\left(\omega - \omega_1 + \mathrm{i}\frac{\gamma}{2}\right)\left(\omega + \omega_1 + \mathrm{i}\frac{\gamma}{2}\right)} = -\mathrm{e}^{-\gamma\tau/2}\frac{\sin\omega_1\tau}{\omega_1} \tag{9.33}$$

Note that in the Harmonic oscillator example we needed the γ in order to get poles in the lower half of the plane. However, we already showed in this course that this γ always exists in fluctuating systems. Equivalently, we could say that a response to a Harmonic perturbation cannot be infinite in time. [*remark end*]

Example. Let's inspect

$$\chi(\omega) \equiv \sum_n \frac{1}{\omega^2 - n^2\omega_0^2}, \tag{9.34}$$

has poles on the real axis, $\omega \equiv \omega_1 + \mathrm{i}\varepsilon$. Then,

$$\chi(\omega_1 + \mathrm{i}\varepsilon) = \frac{\pi}{\omega\omega_0}\left(1 + 2\mathrm{e}^{-\frac{2\pi\varepsilon}{\omega_0}}\mathrm{e}^{2\mathrm{i}\pi\frac{\omega_q}{\omega_0}}\right). \tag{9.35}$$

These poles blur and become a line dividing the upper and lower planes.

The Kramers-Krönig relations imply that

$$\chi_{AB}\left(\omega\right) = \chi'\left(\omega\right) + \mathrm{i}\chi''\left(\omega\right). \tag{9.36}$$

Let $\omega_0 \in \mathbb{R}$. Let's look on a half-circle contour Γ with $\mathrm{i}\varepsilon$ distance above the real axis. Its integral reads

$$\oint_{\Gamma} \frac{\chi\left(\omega\right)}{\omega - \omega_0} \mathrm{d}\omega = 0. \tag{9.37}$$

Let us define another contour Γ', which is half-circle around ω_0 with radius $\delta \gg \varepsilon$. Then, its integral reads

$$\oint_{\Gamma'} \frac{\chi\left(\omega\right)}{\omega - \omega_0} \mathrm{d}\omega = 0 = \int_{-\infty}^{\omega_0 - \delta} \cdots + \int_{\omega_0 + \delta}^{\infty} \cdots - \frac{1}{2} 2\mathrm{i}\pi\chi\left(\omega_0\right). \tag{9.38}$$

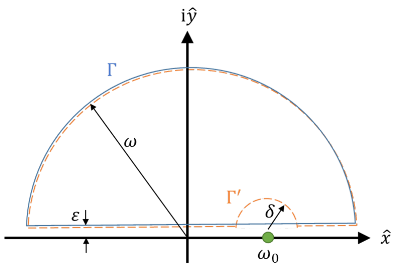


Figure 9.1: Integration contours of the Kramers-Krönig relations.

Let's look on the principal value,

$$\mathcal{P}\int_{-\infty}^{\infty} \frac{\chi\left(\omega\right)}{\omega - \omega_0} \mathrm{d}\omega = \int_{-\infty}^{\omega_0 - \delta} \cdots + \int_{\omega_0 + \delta}^{\infty}. \tag{9.39}$$

Hence,

$$\chi\left(\omega_0\right) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\chi\left(\omega\right)}{\omega - \omega_0} \mathrm{d}\omega. \tag{9.40}$$

Therefore we obtain the Kramers-Krönig relations,

$$\begin{cases} \chi'\left(\omega_0\right) = +\dfrac{1}{\pi}\mathcal{P}\displaystyle\int_{-\infty}^{\infty} \frac{\chi''\left(\omega\right)}{\omega - \omega_0} \mathrm{d}\omega, \\ \chi''\left(\omega_0\right) = -\dfrac{1}{\pi}\mathcal{P}\displaystyle\int_{-\infty}^{\infty} \frac{\chi'\left(\omega\right)}{\omega - \omega_0} \mathrm{d}\omega. \end{cases} \tag{9.41}$$

These Kramers-Krönig relations are a result of the causality.

Recall that we had

$$\chi_{AB} = \lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} \frac{\xi_{AB}\left(\omega'\right)}{\omega' - \omega - \mathrm{i}\varepsilon} \mathrm{d}\omega'. \tag{9.42}$$

10 Lesson 10

10.1 Quantum Statistical Mechanics

10.1.1 Back to KMS – QM at finite T

Let's recall the Boltzmann-Gibbs weight,

$$\hat{\rho} \propto \mathrm{e}^{-\beta \hat{H}}. \tag{10.1}$$

This has the same functional expression as the evolution operator,

$$U(t) = e^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}. \tag{10.2}$$

Therefore, the weight can be formally written as

$$\hat{\rho} = \frac{1}{Z}\mathrm{e}^{-\beta \hat{H}} = \frac{1}{Z}U(-\mathrm{i}\hbar\beta). \tag{10.3}$$

In other words, it is statistical mechanics as a kind of imaginary time QM.

We would identify

$$Z = \mathrm{Tr}\, U(-\mathrm{i}\hbar\beta), \tag{10.4}$$

and an expectation value of an operator

$$\left\langle \hat{A} \right\rangle = \frac{\mathrm{Tr}\left(U(-\mathrm{i}\hbar\beta)\,\hat{A}\right)}{\mathrm{Tr}\, U(-\mathrm{i}\hbar\beta)}. \tag{10.5}$$

Aficionados of Spacial Relativity and QED: this is called the "proper time method". It was developed by Schwinger, Feinman, Fock, and $\frac{1}{2}$Fock.

10.1.2 Generalizations

Let's look on an analytic continuation of time to the complex plane. Define a "time" τ through $\frac{\mathrm{i}t}{\hbar} \leftrightarrow \tau$. This τ has dimensions of [1/Energy]. Generalize $T = 0$ of QM:

$$\begin{cases} \text{Schroedinger eq.} \\ \text{Heisenberg eq.} \\ S\text{-matrix} \\ \text{Permutation theory} \end{cases}$$

Example.

- The Shroedinger representation:

$$H\left|\psi_s\right\rangle = \mathrm{i}\hbar\frac{\partial}{\partial t}\left|\psi_s\right\rangle \longleftrightarrow H\left|\psi_s\right\rangle = \frac{\partial}{\partial \tau}\left|\psi_s\right\rangle \tag{10.6a}$$

$$\left|\psi_s(\tau)\right\rangle = \mathrm{e}^{-Ht}\left|\psi_s(0)\right\rangle \tag{10.6b}$$

- The Heisenberg representation:

$$\left|\psi_H(\tau)\right\rangle = \left|\psi_s(0)\right\rangle \tag{10.7a}$$

$$A_H(\tau) = \mathrm{e}^{Ht}A_S\mathrm{e}^{-Ht} \tag{10.7b}$$

$$\frac{\partial A_H}{\partial \tau} = [H, A_H] \tag{10.7c}$$

Remark. The de Boglie wavelength:

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \frac{\partial}{\partial\tau}\psi. \tag{10.8}$$

- Ext. in space: $\nabla^2\psi \sim \frac{\psi}{\lambda^2}$;
- Ext. in time: $\frac{\partial\psi}{\partial\tau} \sim \frac{\psi}{\beta}$
- Hence, $\lambda^2 \sim \beta$, or $\lambda^{-1} = \sqrt{\frac{2mk_\mathrm{B}T}{\hbar^2}}$.

10.1.3 Free Particle Hamiltonian

Let's inspect

$$H = \sum_k \varepsilon_k c_k^\dagger c_k, \tag{10.9}$$

such that

$$\begin{cases} \frac{\partial c_k}{\partial\tau} = [H, c_k] = & -\varepsilon_k c_k, \\ \frac{\partial c_k^\dagger}{\partial\tau} = \left[H, c_k^\dagger\right] = & +\varepsilon_k c_k^\dagger. \end{cases} \tag{10.10}$$

Therefore

$$\begin{cases} c_k(\tau) = & \mathrm{e}^{-\varepsilon_k\tau} c_k(0) \\ c_k^\dagger(\tau) = & \mathrm{e}^{-\varepsilon_k\tau} c_k^\dagger(0). \end{cases} \tag{10.11}$$

The operators $c_k^\dagger$ and $c_k^\dagger$ are no longer Hermitian conjugates.

10.1.4 Interaction Representation

Here, $H = H_0 + V$, and we freeze the time evolution associated to H_0:

$$\begin{aligned} |\psi_I(\tau)\rangle &= \mathrm{e}^{H_0\tau}|\psi_S(\tau)\rangle \\ &= \mathrm{e}^{H_0\tau}\mathrm{e}^{-H\tau}|\psi_H\rangle \\ &\equiv U(\tau)|\psi_H\rangle. \end{aligned} \tag{10.12}$$

Here

$$\begin{aligned} |\psi_I(\tau_1)\rangle &= U(\tau_1)U^{-1}(\tau_2)|\psi_I(\tau_2)\rangle \\ &\equiv \underbrace{S(\tau_1,\tau_2)}_{S\text{-matrix}}|\psi_I(\tau_2)\rangle, \end{aligned} \tag{10.13}$$

and we have defined the S-matrix. Now,

$$\begin{aligned} -\frac{\partial}{\partial\tau}U(\tau) &= -\frac{\partial}{\partial\tau}\left(\mathrm{e}^{H_0\tau}\mathrm{e}^{-H\tau}\right) = \mathrm{e}^{H_0\tau}V\mathrm{e}^{-H\tau} \\ &= \mathrm{e}^{H_0\tau}V\mathrm{e}^{-H_0\tau}U(\tau) \equiv V_I(\tau)U(\tau). \end{aligned} \tag{10.14}$$

Hence,

$$-\frac{\partial}{\partial\tau_1}S(\tau_1,\tau_2) = V_I(\tau_1)S(\tau_1,\tau_2). \tag{10.15}$$

We would therefore write U and S in a time-ordered manner:

$$U(\tau) = \mathcal{T}\exp\left[-\int_0^\tau \mathrm{d}\tau'\,V_I(\tau')\right], \tag{10.16}$$

$$S(\tau_1,\tau_2) = \mathcal{T}\exp\left[-\int_{\tau_1}^{\tau_2} \mathrm{d}\tau'\,V_I(\tau')\right]. \tag{10.17}$$

10.1.5 A Straightforward Consequence: Peierls Perturbation Th.

Let's inspect the partition function

$$\begin{aligned} Z = \mathrm{Tr}\left(\mathrm{e}^{-\beta H}\right) &= \mathrm{Tr}\left(\mathrm{e}^{-\beta H_0} U(\beta)\right) \\ &= \underbrace{\mathrm{Tr}\left(\mathrm{e}^{-\beta H_0}\right)}_{Z_0} \underbrace{\frac{\mathrm{Tr}\left(\mathrm{e}^{-\beta H_0} U(\beta)\right)}{\mathrm{Tr}\left(\mathrm{e}^{-\beta H_0}\right)}}_{\langle U(\beta)\rangle_0} . \end{aligned} \tag{10.18}$$

Therefore we define this partition as a time ordering on the interaction

$$\frac{Z}{Z_0} = \mathrm{e}^{-\beta\Delta F} = \left\langle \mathcal{T} \exp\left[-\int_0^\beta \mathrm{d}\tau'\, V_I(\tau')\right]\right\rangle_0 . \tag{10.19}$$

This is an exact relation. It can be solved using a perturbation approach.

10.1.6 Imaginary Time Green's Function

Let's inspect the quantum fields $\hat{\psi}_\lambda(\tau)$ with quantum number λ. Let us define

$$G_{\lambda\lambda'}(\tau,\tau') \equiv -\left\langle \mathcal{T}\hat{\psi}_\lambda(\tau)\,\hat{\psi}^\dagger_{\lambda'}(\tau')\right\rangle = \mathrm{Tr}\left(\mathrm{e}^{-\beta(H-F)}\hat{\psi}_\lambda(\tau)\,\hat{\psi}^\dagger_{\lambda'}(\tau')\right), \tag{10.20}$$

where the average $\langle\cdot\rangle$ is wrt. H, $\mathcal{T}$ is the time ordering operator, and $F \equiv -T\ln Z$.

Remark. Provided that H is time independent, we have $G_{\lambda\lambda'}(\tau-\tau')$. In most cases, the quantum number λ is conserved:

$$G_{\lambda\lambda'}(\tau-\tau') = \delta_{\lambda\lambda'} G_\lambda(\tau-\tau') . \tag{10.21}$$

10.1.7 Non-interacting Systems

In non-interacting system with Hamiltonian

$$H = \sum_\lambda \varepsilon_\lambda \hat{\psi}^\dagger_\lambda \hat{\psi}_\lambda, \quad \varepsilon_\lambda = \underbrace{E_\lambda}_{\text{single particle energies}} - \mu. \tag{10.22}$$

Let us seek the expectation value of

$$\left\langle \hat{\psi}^\dagger_\lambda \hat{\psi}_{\lambda'}\right\rangle = \delta_{\lambda\lambda'} \times \begin{cases} n(\varepsilon_\lambda) & \text{bosons} \\ f(\varepsilon_k) & \text{fermions} \end{cases} . \tag{10.23}$$

where we have defined the occupation probabilities by

$$n(\varepsilon_\lambda) = \frac{1}{\mathrm{e}^{\beta\varepsilon_\lambda}-1}, \quad f(\varepsilon_\lambda) = \frac{1}{\mathrm{e}^{\beta\varepsilon_\lambda}+1}. \tag{10.24}$$

In a similar matter,

$$\left\langle \hat{\psi}_\lambda \hat{\psi}^\dagger_{\lambda'}\right\rangle = \delta_{\lambda\lambda'} \pm \left\langle \hat{\psi}^\dagger_\lambda \hat{\psi}_{\lambda'}\right\rangle = \delta_{\lambda\lambda'} \times \begin{cases} 1+n(\varepsilon_\lambda) & \text{bosons} \\ 1-f(\varepsilon_k) & \text{fermions} \end{cases} . \tag{10.25}$$

Using the time evolution of the operators

$$\begin{cases} \hat{\psi}_\lambda(\tau) = & \mathrm{e}^{-\varepsilon_\lambda\tau}\hat{\psi}_\lambda(0) \\ \hat{\psi}^\dagger_\lambda(\tau) = & \mathrm{e}^{-\varepsilon_\lambda\tau}\hat{\psi}^\dagger_\lambda(0) \end{cases} , \tag{10.26}$$

we will obtain the Green's function

$$G_{\lambda\lambda'}(\tau-\tau') = -\left[\Theta(\tau-\tau')\left\langle\hat{\psi}_\lambda\hat{\psi}^\dagger_{\lambda'}\right\rangle + \varphi\Theta(\tau'-\tau)\left\langle\hat{\psi}^\dagger_{\lambda'}\hat{\psi}_\lambda\right\rangle\right]\mathrm{e}^{-\varepsilon_\lambda(\tau-\tau')}, \quad (10.27)$$

where $\Theta(\tau-\tau')$ is the time ordering operator and

$$\varphi = \begin{cases} +1 & \text{bosons} \\ -1 & \text{fermions.} \end{cases} \quad (10.28)$$

Therefore,

$$G_{\lambda\lambda'}(\tau-\tau') = -\left[\Theta(\tau-\tau')\left\langle\hat{\psi}_\lambda(\tau)\hat{\psi}^\dagger_{\lambda'}(\tau')\right\rangle \pm \Theta(\tau'-\tau)\left\langle\hat{\psi}^\dagger_{\lambda'}(\tau')\hat{\psi}_\lambda(\tau)\right\rangle\right]. \quad (10.29)$$

Consider

$$\begin{aligned} G_{\lambda\lambda'}(\tau) &= -\varphi\left\langle\hat{\psi}^\dagger_{\lambda'}(0)\hat{\psi}_\lambda(\tau)\right\rangle \\ &= -\varphi\,\mathrm{Tr}\left(\mathrm{e}^{-\beta(H-F)}\hat{\psi}^\dagger_{\lambda'}\mathrm{e}^{\tau H}\hat{\psi}_\lambda\mathrm{e}^{-\tau H}\right) \\ &= -\varphi\,\mathrm{Tr}\left(\mathrm{e}^{\tau H}\hat{\psi}_\lambda\mathrm{e}^{-\tau H}\mathrm{e}^{-\beta(H-F)}\hat{\psi}^\dagger_{\lambda'}\right) \\ &= -\varphi\,\mathrm{Tr}\left(\mathrm{e}^{\beta F}\mathrm{e}^{\tau H}\hat{\psi}_\lambda\mathrm{e}^{-(\tau+\beta)H}\hat{\psi}^\dagger_{\lambda'}\right) \\ &= -\varphi\,\mathrm{Tr}\left(\mathrm{e}^{-\beta(H-F)}\mathrm{e}^{(\tau+\beta)H}\hat{\psi}_\lambda\mathrm{e}^{-(\tau+\beta)H}\hat{\psi}^\dagger_{\lambda'}\right), \end{aligned} \quad (10.30)$$

where from the 3rd to the 4th line we demanded $\tau+\beta>0$ so that the operator is trace class. Hence

$$G_{\lambda\lambda'}(\tau) = -\varphi\left\langle\hat{\psi}_\lambda(\tau+\beta)\hat{\psi}^\dagger_{\lambda'}(0)\right\rangle = \varphi G_{\lambda\lambda'}(\tau+\beta), \quad (10.31)$$

or

$$\boxed{G_{\lambda\lambda'}(\tau) = \varphi G_{\lambda\lambda'}(\tau+\beta)}, \quad -\beta<\tau<0. \quad (10.32)$$

Corollary. *The imaginary time Green's function is either periodic (bosons) or anti-periodic (fermions) wrt. τ.*

10.1.8 Fourier Series Expansion – Matsubara Frequencies

Let us define

$$\begin{cases} \nu_n = \frac{2\pi n}{\beta} & \text{bosons} \\ \omega_n = \frac{\pi(2n+1)}{\beta} & \text{fermions,} \end{cases} \quad (10.33)$$

so that

$$\begin{cases} \mathrm{e}^{\mathrm{i}\nu_n(\tau+\beta)} = \mathrm{e}^{\mathrm{i}\nu_n\tau} & \text{bosons} \\ \mathrm{e}^{\mathrm{i}\omega_n(\tau+\beta)} = \mathrm{e}^{\mathrm{i}\omega_n\tau}\mathrm{e}^{\mathrm{i}\pi(2n+1)} = -\mathrm{e}^{\mathrm{i}\omega_n\tau} & \text{fermions.} \end{cases} \quad (10.34)$$

Hence

$$G_{\lambda\lambda'}(\tau) = \begin{cases} \sum_{-\infty}^{\infty} G_{\lambda\lambda'}(\nu_n)\,\mathrm{e}^{-\mathrm{i}\nu_n\tau} & \text{bosons} \\ \sum_{-\infty}^{\infty} G_{\lambda\lambda'}(\omega_n)\,\mathrm{e}^{-\mathrm{i}\omega_n\tau} & \text{fermions.} \end{cases} \quad (10.35)$$

10.1.9 Simple Examples

Free fermions or bosons:

$$G_{\lambda\lambda'}(\tau) = -\mathrm{e}^{-\mathrm{i}\varepsilon_\lambda\tau}\times\begin{cases} (1+n(\varepsilon_\lambda))\,\Theta(\tau) + n(\varepsilon_\lambda)\,\Theta(-\tau) & \text{bosons} \\ (1-f(\varepsilon_k))\,\Theta(\tau) - f(\varepsilon_\lambda)\,\Theta(-\tau) & \text{fermions.} \end{cases} \quad (10.36)$$

For fermions we have

$$\begin{aligned} G_\lambda(\omega_n) &= -\int_0^\beta \mathrm{d}\tau\, \mathrm{e}^{(\mathrm{i}\omega_n - \varepsilon_\lambda)\tau}\,(1 - f(\varepsilon_k)) \\ &= -\frac{1}{\mathrm{i}\omega_n - \varepsilon_\lambda}\frac{\mathrm{e}^{(\mathrm{i}\omega_n - \varepsilon_\lambda)\beta} - 1}{1 + \mathrm{e}^{-\beta\varepsilon_\lambda}} = -\frac{1}{\mathrm{i}\omega_n - \varepsilon_\lambda}(-1)\frac{\mathrm{e}^{-\varepsilon_\lambda\beta} + 1}{1 + \mathrm{e}^{-\beta\varepsilon_\lambda}}, \end{aligned} \tag{10.37}$$

Or

$$G_\lambda(\omega_n) = \frac{1}{\mathrm{i}\omega_n - \varepsilon_\lambda}, \quad \text{fermions.} \tag{10.38a}$$

Similarly, for bosons,

$$G_\lambda(\nu_n) = \frac{1}{\mathrm{i}\nu_n - \varepsilon_\lambda}, \quad \text{bosons.} \tag{10.38b}$$

11 Lesson 11

11.1 Quantum Statistical Mechanics

11.1.1 A few additional words on Matsubara Frequencies

A flavor on how it works. We will use the contour integral method.

For example, let's inspect free Fermions,

$$f(z) = \frac{1}{e^{\beta z} + 1}. \tag{11.1}$$

This function has poles at each $z = i\omega_n$ with strength $-k_B T$. We see it immediately from

$$f(z = i\omega + \delta) = \frac{1}{e^{\beta(i\omega+\delta)} + 1} \simeq -\frac{1}{\beta\delta} = -\frac{k_B T}{\delta}. \tag{11.2}$$

Now, suppose we have a general function $F(i\omega_n)$. Then

$$k_B T \sum_n F(i\omega_n) = \int_C \frac{dz}{2\pi i} F(z) f(z), \tag{11.3}$$

and C represents some contour, and we applied Jordan's lemma.

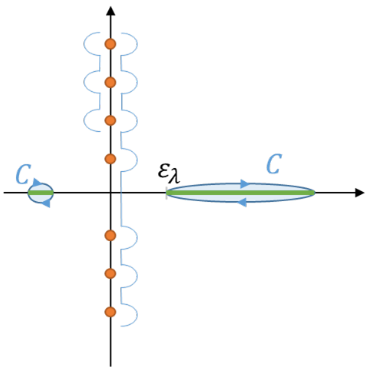


Figure 11.1: The contour on Matsubara Frequencies.

11.1.2 Free energy of a gas of free Fermions

Let's recall the Free energy of a gas of Fermions,

$$H = \sum_\lambda \varepsilon_\lambda c_\lambda^\dagger c_\lambda, \qquad \varepsilon_\lambda = E = \lambda - \mu. \tag{11.4}$$

The number of particles $N(\mu)$ is given by the Green's function

$$N_\lambda = \left\langle c_\lambda^\dagger c_\lambda \right\rangle = G_\lambda\left(0^-\right), \tag{11.5}$$

where

$$G_\lambda(\tau) = T \sum_{i\omega_n} G_\lambda(\omega_n) e^{-i\omega_n \tau}. \tag{11.6}$$

Therefore,

$$N(\mu) = \sum_\lambda N_\lambda = T \sum_{\lambda,\omega_n} G_\lambda(i\omega_n) e^{i\omega_n 0^+}. \tag{11.7}$$

Hence,

$$N(\mu) = -\frac{\partial F}{\partial \mu} \quad \Rightarrow \quad F = -\int^{\mu} \mathrm{d}\mu' \, N(\mu') \,. \tag{11.8}$$

Explicitly,

$$F = -T \sum_{\lambda,\omega_n} \int^{\mu} \mathrm{d}\mu \frac{\mathrm{e}^{\mathrm{i}\omega_n 0^+}}{\mathrm{i}\omega_n - E_\lambda - \mu} = -T \sum_{\lambda,\omega_n} \mathrm{e}^{\mathrm{i}\omega_n 0^+} \ln(\varepsilon_\lambda - \mathrm{i}\omega_n) \,, \tag{11.9}$$

and we have

$$F = \sum_{\lambda} \oint \frac{\mathrm{d}z}{2\pi \mathrm{i}} f(z) \ln(\varepsilon_\lambda - z) \, \mathrm{e}^{z 0^+} . \tag{11.10}$$

Notice that $F(z) \equiv \ln(\varepsilon_\lambda - z)$ has a branch cut running from $\varepsilon_\lambda \to +\infty$. Hence

$$F = \sum_{\lambda} \int_{\varepsilon_\lambda}^{\infty} \frac{\mathrm{d}\omega}{\pi} f(\omega) = -T \ln\left(1 + \mathrm{e}^{-\beta \varepsilon_\lambda}\right) . \tag{11.11}$$

Similarly for free Bosons we'd have the same expression, but with a $-$ sign and another set of ε_λ.

11.1.3 Another approach

Let's look on free Bosons (photon gas). Their partition function reads

$$\ln Z(T,V) = \sum_{\text{modes}} \left(-\ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right)\right) . \tag{11.12}$$

But,

$$\begin{aligned} -\ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) &= \sum_{n=1}^{\infty} \frac{1}{n} \mathrm{e}^{-n\beta\hbar\omega} \\ &= \sum_{n=1}^{\infty} \frac{1}{n} \int_0^{\infty} \frac{\mathrm{d}\tau}{\tau} \cdot \frac{\mathrm{e}^{-\omega^2\tau}}{\sqrt{\tau}} \cdot \mathrm{e}^{-n^2 \frac{(\hbar\beta)^2}{4\tau}} \cdot \frac{\hbar\beta n}{4\pi} \\ &= \frac{\hbar\beta}{4\pi} \int_0^{\infty} \frac{\mathrm{d}\tau}{\tau} \frac{1}{\sqrt{\tau}} \mathrm{e}^{-\omega^2\tau} \left(\sum_{n=1}^{\infty} \mathrm{e}^{-n^2 \frac{(\hbar\beta)^2}{4\tau}} \right) . \end{aligned} \tag{11.13}$$

We shall now use the Poisson formula

$$\sum_{n=-\infty}^{\infty} \mathrm{e}^{-n^2 t} = \sqrt{\frac{\pi}{t}} \sum_{n=-\infty}^{\infty} \mathrm{e}^{-\frac{\pi^2 n^2}{t}} . \tag{11.14}$$

We also have to account for the zero point energy $\frac{\hbar\omega}{2}$ (since we are dealing with harmonic oscillators). Therefore, the partition function goes to

$$\ln Z(T,V) = \sum_{\text{modes}} \left(-\frac{\beta\hbar\omega}{2} - \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) \right) , \tag{11.15}$$

and after some calculation we have

$$\ln Z(T,V) = \frac{1}{2} \sum_{\text{modes}} \int_0^{\infty} \frac{\mathrm{d}\tau}{\tau} \mathrm{e}^{-\omega^2\tau} \sum_{n=-\infty}^{\infty} \mathrm{e}^{-n^2 \left(\frac{2\pi}{\hbar\omega}\right)^2 \tau} . \tag{11.16}$$

Note that τ has units of $\left[\text{time}^2\right]$.

11.1.4 Matsubara modes

Let's define $\partial_0^2 \equiv \frac{\partial^2}{\partial t^2}$ + PBCs (periodic boundary conditions). Hence

$$\partial_0^2 \varphi(t) = \lambda^2 \varphi(t), \qquad \varphi(t + \hbar\beta) = \varphi(t). \tag{11.17}$$

Also,

$$\mathrm{Tr}_M \left(\mathrm{e}^{-\tau \partial_0^2}\right) = \sum_{n=-\infty}^{\infty} \mathrm{e}^{-n^2 \left(\frac{2\pi}{\hbar\omega}\right)^2 \tau}. \tag{11.18}$$

We now can write

$$\ln Z(T, V) = \frac{1}{2} \sum_{\text{modes}} \int_0^\infty \frac{\mathrm{d}\tau}{\tau} \mathrm{e}^{-\omega^2 \tau}\, \mathrm{Tr}_M \left(\mathrm{e}^{-\tau \partial_0^2}\right). \tag{11.19}$$

Here M represents the Matsubara frequencies. Next, let $\omega = c\,|\boldsymbol{k}|$ and $\omega^2 = c^2 k^2$ so that $\mathrm{e}^{-\omega^2 \tau} = \mathrm{e}^{-c^2 k^2 \tau}$. Therefore

$$\sum_{\text{modes}} \mathrm{e}^{-\omega^2 \tau} = \mathrm{Tr}_{\mathbb{M}} \left(\mathrm{e}^{-\tau c^2 \Delta}\right), \tag{11.20}$$

where Δ is the Laplacian and $\mathbb{M}$ is some manifold, on which we integrate.

Hence we write

$$\begin{aligned} \ln Z(T, V) &= \frac{1}{2} \int_0^\infty \frac{\mathrm{d}\tau}{\tau} \mathrm{Tr}_{\mathbb{M}} \left(\mathrm{e}^{-\tau c^2 \Delta}\right) \mathrm{Tr}_M \left(\mathrm{e}^{-\tau \partial_0^2}\right) \\ &= \frac{1}{2} \int_0^\infty \frac{\mathrm{d}\tau}{\tau} \mathrm{Tr}_{\mathbb{M} \times M} \left(\mathrm{e}^{-\tau \left(\partial_0^2 + c^2 \Delta\right)}\right) \\ &= -\frac{1}{2} \mathrm{Tr}_{\mathbb{M} \times M} \ln \left(\partial_0^2 + c^2 \Delta\right). \end{aligned} \tag{11.21}$$

Here we used $-\int_0^\infty \frac{\mathrm{d}\tau}{\tau} \exp\left(-\hat{O}\tau\right) = \ln \hat{O}$. We now use the identity $\mathrm{Tr} \ln \hat{A} = \ln \det \hat{A}$, and obtain

$$\boxed{\ln Z(T, V) = -\frac{1}{2} \ln \det_{\mathbb{M} \times M} \left(\partial_0^2 + c^2 \Delta\right).} \tag{11.22}$$

Note that though it looks like the wave equation, it is not. First, we used a special time derivative ∂_0^2. Second, the wave equation has a minus sign; we have a plus because we have an imaginary time.

11.1.5 Some Calculations

We shall now see how the equation (11.22) is useful. Let the volume of the system be $V = L^d$. Therefore

$$\begin{aligned} \ln Z(T, V) &= \int_0^\infty \frac{\mathrm{d}\tau}{\tau} \left(\sum_{n=-\infty}^{\infty} \mathrm{e}^{-n^2 \left(\frac{2\pi}{\hbar\omega}\right)^2 \tau}\right) \sum_{\text{modes}} \mathrm{e}^{-\omega^2 \tau} \\ &= \int_0^\infty \frac{\mathrm{d}u}{u} f(u) \sum_{\text{modes}} \mathrm{e}^{-(\hbar\beta)^2 \omega^2 u} \qquad\qquad u \equiv \frac{\tau}{(\hbar\beta)^2} \\ &= \int_0^\infty \frac{\mathrm{d}u}{u} f(u) \sum_{n} \mathrm{e}^{-\left(\hbar\beta c V^{-1/d}\right)^2 u \boldsymbol{n}^2}. \qquad\qquad \omega = c\,|\boldsymbol{k}| = c\frac{2\pi \boldsymbol{n}}{V^{1/d}} \text{(in a box)} \end{aligned} \tag{11.23}$$

Hence

$$\ln Z(T, V) = g\left(\hbar\beta c V^{-1/d}\right) = g\left(L_\beta / L\right), \tag{11.24}$$

and $L_\beta = \hbar\beta c$ is the deBroglie wavelength and L is the geometrical wavelength.

Since we know the partition function, we can calculate several thermodynamic properties:

$$F(T,V) = -\frac{1}{\beta}\ln Z, \tag{11.25a}$$

$$U = -\frac{\partial}{\partial\beta}\ln Z \tag{11.25b}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{11.25c}$$

and

$$PV = \frac{1}{d}U. \tag{11.26}$$

11.1.6 Another approach: One-loop Quantum Corrections

Now, in the previous section we cheated a bit. We obtained an equation of the form

$$\ln Z(T,V) = -\frac{1}{2}\ln \det_{\mathbb{M}\times M}\left(\hat{A}\right). \tag{11.27}$$

Now, for example, the manifold as a line $\mathbb{M} = [0, L]$ and $\hat{A} = -\frac{\mathrm{d}^2}{\mathrm{d}x^2}$. The spectrum now is $\lambda_n = \frac{\pi^2}{L^2}n^2$, $n \in \mathbb{Z}^*$. Hence $\det \hat{A} = \prod_{n=-\infty}^{\infty} n^2$. In other words, we got a beautiful result (11.22), but never stopped to ask whether this $g\left(\hbar\beta c V^{-1/d}\right)$ exists at all.

11.1.7 A useful representation: ζ-functions

Let's use a regularization to solve this problem. Let an operator $\hat{A}$ with spectrum $\{\lambda_n\}$. Let us define

$$\zeta_A(s) = \sum_n{}' \frac{1}{\lambda_n^s}, \qquad s \in \mathbb{C}. \tag{11.28}$$

Also

$$\ln\det\hat{A} = \operatorname{Tr}\ln\hat{A} = \sum_n \ln\lambda_n. \tag{11.29}$$

Formally, we write

$$\frac{\mathrm{d}}{\mathrm{d}s}\zeta_A(s) = \frac{\mathrm{d}}{\mathrm{d}s}\sum_n{}' \mathrm{e}^{-s\ln\lambda_n} = -\sum_n \ln\lambda_n \mathrm{e}^{-s\ln\lambda_n}, \tag{11.30}$$

hence

$$\left.\frac{\mathrm{d}}{\mathrm{d}s}\zeta_A(s)\right|_{s=0} = -\sum_n \ln\lambda_n = -\ln\det\hat{A}. \tag{11.31}$$

Herr Riemann (1859) defined the ζ-function as

$$\zeta(s) = \sum_{n=1}^{\infty}\frac{1}{n^s}, \qquad s \in \mathbb{C} \text{ (except for } s = 1). \tag{11.32}$$

It has some useful relations

$$\left.\begin{aligned} \zeta(s) &= \zeta(1-s)\,\chi(s) \\ \chi(s) &\equiv 2^s\pi^{s-1}\sin\left(\tfrac{\pi s}{2}\right)\Gamma(1-s) \end{aligned}\right\} \Rightarrow \ldots \Rightarrow \Gamma\left(\tfrac{s}{2}\right)\zeta(s) = \pi^{s-\frac{1}{2}}\Gamma\left(\tfrac{1-s}{2}\right)\zeta(1-s). \tag{11.33}$$

So that if it is defined somewhere, it is defined everywhere. For example, we have

$$\zeta(0) = 1 + 1 + \ldots = -\frac{1}{2}. \tag{11.34}$$

Let's return to our sheep.

$$\begin{aligned} \ln Z(T,V) &= -\frac{1}{2}\operatorname{Tr}\ln \overbrace{\hat{A}}^{\partial_0^2 + c^2\Delta} \\ &= -\frac{1}{2} 2 \sum_{n=1}^{\infty} V \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \ln\left[\left(\frac{2\pi n}{\hbar\beta}\right)^2 + c^2 k^2\right]. \end{aligned} \tag{11.35}$$

Now, use the relation

$$\int \frac{\mathrm{d}^3 k}{(2\pi)^3} \ln\left(\alpha^2 + k^2\right) = -\frac{\Gamma\left(-\frac{d}{2}\right)}{(4\pi)^{\frac{d}{2}}} \alpha^d, \tag{11.36}$$

and have

$$\ln Z(T,V) = V \underbrace{\sum_{n=1}^{\infty} \frac{\Gamma\left(-\frac{3}{2}\right)}{(4\pi)^{\frac{3}{2}}} \left(\frac{2\pi n}{\hbar\beta}\right)^3}_{\zeta(-3) \propto \zeta(4) = \frac{\pi^4}{90}} \tag{11.37}$$

hence

$$\boxed{\ln Z(T,V) = \frac{\pi^2}{90}\left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^3 V.} \tag{11.38}$$

Note that all of this is for equilibrium statistical mechanics.