2.2 Thermodynamics

Outline: We now apply the path integral formalism to statistical physics, computing the partition function, $Z \equiv \mathrm{Tr}\, e^{-\beta\hat{H}}$, where $\beta \equiv \frac{1}{k_B T}$, k_B = Boltzmann constant.

Imaginary time: Let us evaluate the trace in the eigenbasis of $\hat{\phi}$:

$$Z = \int_{-\infty}^{\infty} d\phi \, \langle \phi | e^{-\beta\hat{H}} | \phi \rangle .$$

Compare this with (cf. p. 33)

$$K(\phi_2, t; \phi_1, 0) = \langle \phi_2 | e^{-\frac{i\hat{H}t}{\hbar}} | \phi_1 \rangle = \int_{\phi(0)=\phi_1}^{\phi(t)=\phi_2} \mathcal{D}\phi(t') \exp\left\{ \frac{i}{\hbar} \int_0^t dt' \left[\frac{m}{2}\dot{\phi}^2 - V(\phi) \right] \right\}$$

$$\Rightarrow \quad Z = \int_{-\infty}^{\infty} d\phi \; K(\phi, -i\beta\hbar; \phi, 0) .$$

We now substitute

$$t' = -i\tau \quad \Leftrightarrow \quad \tau = it' , \qquad \text{"imaginary time"}$$

$$i\,dt' = d\tau ,$$

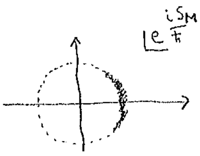
$$\dot{\phi}^2 = \left(\frac{d\phi}{dt'}\right)^2 = -\left(\frac{d\phi}{d\tau}\right)^2 .$$

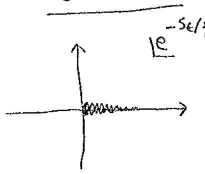
We also define a "Euclidean Lagrangian" as

$$\mathcal{L}_E \equiv -\mathcal{L}_M(t' = -i\tau) = \frac{m}{2}\left(\frac{d\phi}{d\tau}\right)^2 + V(\phi) .$$

$$\Rightarrow \boxed{ Z = \int_{\phi(\beta\hbar)=\phi(0)} \mathcal{D}\phi(\tau) \exp\left\{ -\frac{1}{\hbar} S_E \right\} , \quad S_E \equiv \int_0^{\beta\hbar} d\tau \, \mathcal{L}_E . }$$

Remarks:





* The "Euclidean action", S_E, is real and positive

$\Rightarrow 0 < e^{-S_E/\hbar} < 1 \quad \Rightarrow$ no destructive interference (cancellations)

$\Rightarrow$ the path integral can even be carried out numerically.

* Large gradients ($\left|\frac{d\phi}{d\tau}\right|$ large) and field values with large potential energy ($V(\phi)$ large) appear to give an exponentially suppressed contribution.

* Nevertheless, the typical paths are not smooth:

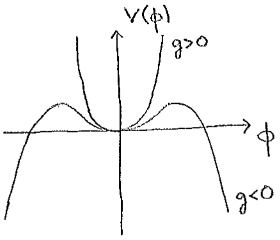
$$d\tau \equiv \varepsilon , \quad \frac{d\phi}{d\tau} \approx \frac{\phi(\tau+\varepsilon) - \phi(\tau)}{\varepsilon}$$

$$\Rightarrow \exp\left(-\frac{S_E}{\hbar}\right) \supset \exp\left(-\frac{m}{2\hbar} \frac{[\phi(\tau+\varepsilon) - \phi(\tau)]^2}{\varepsilon} \right) \sim 1$$

$$\Rightarrow |\phi(\tau+\varepsilon) - \phi(\tau)| \sim \sqrt{\frac{2\hbar\varepsilon}{m}}$$

$$\Rightarrow \frac{|\phi(\tau+\varepsilon) - \phi(\tau)|}{\varepsilon} \sim \sqrt{\frac{2\hbar}{m\varepsilon}} \xrightarrow{\varepsilon \to 0} \infty$$

$\Rightarrow$ not differentiable!



Example: We illustrate the formalism with an <u>anharmonic oscillator</u>:

$$\hat{H} \equiv \frac{\hat{\pi}^2}{2m} + \frac{1}{2} m\omega^2 \hat{\phi}^2 + g\,\frac{m^2\omega^3}{4\hbar}\,\hat{\phi}^4 .$$

The goal is to compute Z up to $O(g)$.

Order $O(g^0)$: Exercise 9.3: $\displaystyle\int_{-\infty}^{\infty} d\phi\, K(\phi,t;\phi,0) = \frac{1}{2i\sin\left(\frac{\omega t}{2}\right)} = \frac{1}{e^{i\omega t/2} - e^{-i\omega t/2}}$.

With $t = -i\beta\hbar$: $\displaystyle Z_0 \equiv Z(g=0) = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}}$.

Check: $\displaystyle\sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}}$ OK!

Order $O(g^1)$: We write down the path integral and expand it in g:

$$Z = \int_{\phi(\beta\hbar)=\phi(0)} \mathcal{D}\phi(\tau)\, \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left[\underbrace{\frac{m}{2}\left(\frac{d\phi}{d\tau}\right)^2 + \frac{m\omega^2\phi^2}{2}}_{\equiv S_0} + \underbrace{\frac{g m^2\omega^3\phi^4}{4\hbar}}_{\equiv L_I} \right]\right\}$$

"boundary conditions", i.e. $\phi(\beta\hbar)=\phi(0)$

$$= \int_{\text{b.c.}} \mathcal{D}\phi(\tau)\, e^{-\frac{S_0}{\hbar}} \left\{ 1 - \frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, L_I + O(g^2) \right\}$$

$$= Z_0 \left\{ 1 - \frac{g m^2\omega^3}{4\hbar^2}\int_0^{\beta\hbar} d\tau \left[\frac{\int_{\text{b.c.}} \mathcal{D}\phi\, \phi^4(\tau)\, e^{-S_0/\hbar}}{\int_{\text{b.c.}} \mathcal{D}\phi\, e^{-S_0/\hbar}} \right] + O(g^2) \right\}.$$

Given that S_0 is quadratic in $\phi(\tau)$, the path integrals here are <u>Gaussian integrals</u>, and can be handled with <u>Wick's theorem</u>.

Wick's theorem: General Gaussian integral (with Einstein convention):

$$\int_{-\infty}^{\infty} \prod_i dx_i\, \exp\left(-\frac{1}{2}x_i A_{ij} x_j + b_i x_i\right) = \frac{(2\pi)^{N/2}}{\sqrt{\det A}}\, \exp\left(\frac{1}{2} b_i (A^{-1})_{ij} b_j\right).$$

$$\Rightarrow \int_{-\infty}^{\infty} \prod_i dx_i\; x_k x_l x_m x_n\, \exp\left(\text{—}\,''\,\text{—}\right) = \frac{d}{db_k}\frac{d}{db_l}\frac{d}{db_m}\frac{d}{db_n} \int_{-\infty}^{\infty}\prod_i dx_i\, \exp\left(-\frac{1}{2}x_i A_{ij}x_j + b_i x_i\right)$$

$$\Rightarrow \frac{\int_{-\infty}^{\infty}\prod_i dx_i\; x_k x_l x_m x_n \exp\left(-\frac{1}{2}x_i A_{ij} x_j\right)}{\int_{-\infty}^{\infty}\prod_i dx_i\, \exp\left(-\frac{1}{2}x_i A_{ij} x_j\right)} = \frac{d}{db_k}\frac{d}{db_l}\frac{d}{db_m}\frac{d}{db_n} \exp\left(\frac{1}{2}b_i (A^{-1})_{ij} b_j\right)\Big|_{\vec{b}=\vec{0}}$$

A^{-1} is symmetric

$$= \frac{d}{db_k}\frac{d}{db_l}\frac{d}{db_m}\; b_i (A^{-1})_{in}\, \exp\left(\frac{1}{2}b_i (A^{-1})_{ij} b_j\right)\Big|_{\vec{b}=\vec{0}}$$

$$= \frac{d}{db_k}\frac{d}{db_l}\left\{ (A^{-1})_{mn} + b_i (A^{-1})_{in}\, b_j (A^{-1})_{jm} \right\} \exp\left(\frac{1}{2}b_i (A^{-1})_{ij} b_j\right)\Big|_{\vec{b}=\vec{0}}$$

$$= \frac{d}{db_k}\left\{ (A^{-1})_{mn}\, b_i (A^{-1})_{il} + (A^{-1})_{ln}\, b_j (A^{-1})_{jm} + b_i (A^{-1})_{in} (A^{-1})_{lm} \right\}$$

$$= \underbrace{(A^{-1})_{mn}(A^{-1})_{kl}}_{x_k x_l x_m x_n} + \underbrace{(A^{-1})_{ln}(A^{-1})_{km}}_{x_k x_l x_m x_n} + \underbrace{(A^{-1})_{kn}(A^{-1})_{lm}}_{x_k x_l x_m x_n}$$

Inverse:
$$\frac{S_0}{\hbar} = \frac{1}{2}\frac{m}{\hbar}\int_0^{\beta\hbar} d\tau \left[\left(\frac{d\phi}{d\tau}\right)^2 + \omega^2\phi^2\right] = \frac{1}{2}\cdot\frac{m}{\hbar}\int_0^{\beta\hbar} d\tau\, \phi(\tau)\left[-\frac{d^2}{d\tau^2}+\omega^2\right]\phi(\tau).$$

partial integration with periodicity

$$\Rightarrow \text{"}A(\tau,\tau')\text{"} = \frac{m}{\hbar}\,\delta_p(\tau-\tau')\left[-\frac{d^2}{d\tau^2}+\omega^2\right], \quad \delta_p = \text{periodic mod } \beta\hbar$$

$$\Rightarrow \text{"}AA^{-1}=\mathbb{1}\text{" corresponds to } \frac{m}{\hbar}\left[-\frac{d^2}{d\tau^2}+\omega^2\right]A^{-1}(\tau,\tau') = \delta(\tau-\tau' \text{ mod } \beta\hbar).$$

Fourier representation: $A^{-1}(\tau,\tau') = \sum_n c_n\, e^{\frac{i2\pi n(\tau-\tau')}{\beta\hbar}}$.

Insert this above and integrate $\int_0^{\beta\hbar} d\tau\, e^{-\frac{i2\pi n(\tau-\tau')}{\beta\hbar}}$ on both sides

$$\Rightarrow \frac{m}{\hbar}\left[\left(\frac{2\pi n}{\beta\hbar}\right)^2+\omega^2\right]c_n\cdot\beta\hbar = 1$$

$$\Rightarrow A^{-1}(\tau,\tau') = \frac{1}{m\beta}\sum_{n=-\infty}^{\infty}\frac{e^{\frac{i2\pi n(\tau-\tau')}{\beta\hbar}}}{\left(\frac{2\pi n}{\beta\hbar}\right)^2+\omega^2}.$$

Insert in Wick's theorem:

$$Z = Z_0\left\{1 - \frac{gm^2\omega^3}{4\hbar^2}\int_0^{\beta\hbar} d\tau\, 3A^{-1}(\tau,\tau)A^{-1}(\tau,\tau) + O(g^2)\right\}$$

$$= Z_0\left\{1 - \frac{3g\omega^3}{4\beta\hbar}\left[\sum_{n=-\infty}^{\infty}\frac{1}{\left(\frac{2\pi n}{\beta\hbar}\right)^2+\omega^2}\right]^2 + O(g^2)\right\}.$$

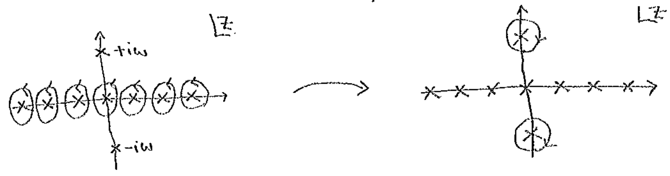
Sums: We may note that $\frac{1}{e^{i\beta\hbar z}-1}$ has poles at $z = \frac{2\pi n}{\beta\hbar}$.

Residues: $$\frac{1}{e^{i\beta\hbar\left(\frac{2\pi n}{\beta\hbar}+\delta z\right)}-1} = \frac{1}{e^{i\beta\hbar\,\delta z}-1} \approx \frac{1}{i\beta\hbar\,\delta z}.$$

Residue theorem: $$I \equiv \sum_{n=-\infty}^{\infty}\frac{1}{\left(\frac{2\pi n}{\beta\hbar}\right)^2+\omega^2} = i\beta\hbar\sum_{n=-\infty}^{\infty}\frac{1}{i\beta\hbar}\,\frac{1}{\left(\frac{2\pi n}{\beta\hbar}\right)^2+\omega^2}$$

$$= i\beta\hbar\int_\Gamma \frac{dz}{2\pi i}\,\frac{1}{e^{i\beta\hbar z}-1}\cdot\frac{1}{z^2+\omega^2},$$

where the contour Γ can subsequently be deformed:

$\Gamma =$ 

Then we can pick up the poles:

$$I = i\beta\hbar\left[-\underbrace{\frac{1}{e^{-\beta\hbar\omega}-1}\cdot\frac{1}{2i\omega}}_{z=+i\omega} - \underbrace{\frac{1}{e^{\beta\hbar\omega}-1}\cdot\frac{1}{-2i\omega}}_{z=-i\omega}\right]$$

$$= \frac{\beta\hbar}{2\omega}\left[\frac{1}{1-e^{-\beta\hbar\omega}} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right]$$

$$= \frac{\beta\hbar}{2\omega}\cdot\frac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}.$$

Energy spectrum: Combining p. 37 $\left(Z_0 = \dfrac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right)$ and p. 39 we find

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \left\{ \frac{1}{1-e^{-\beta\hbar\omega}} - \frac{3g}{16}\cdot\beta\hbar\omega\,\frac{(1+e^{-\beta\hbar\omega})^2}{(1-e^{-\beta\hbar\omega})^3} + \mathcal{O}(g^2) \right\}.$$

This needs to be matched onto

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\left[E_n^{(0)} + E_n^{(1)} + \mathcal{O}(g^2)\right]}$$

$$= \sum_{n=0}^{\infty} e^{-\beta E_n^{(0)}} \left\{ 1 - \beta E_n^{(1)} + \mathcal{O}(g^2) \right\}, \quad E_n^{(0)} = \hbar\omega\left(n+\tfrac{1}{2}\right).$$

In order to identify $E_n^{(1)}$, we need to re-expand the result as a series in $e^{-\beta\hbar\omega n}$!

$$\frac{1}{1-e^{-\beta\hbar\omega}} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \qquad \Big| \ \frac{d}{d\omega} \text{ on both sides}$$

$$\frac{(-\beta\hbar)\,e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2} = (-\beta\hbar)\sum_{n=1}^{\infty} n\,e^{-\beta\hbar\omega n} \qquad \Big| \ \frac{d}{d\omega} \text{ on both sides}$$

$$(-\beta\hbar)^2\left[\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2} + \frac{2\,(e^{-\beta\hbar\omega})^2}{(1-e^{-\beta\hbar\omega})^3}\right] = (-\beta\hbar)^2\sum_{n=1}^{\infty} n^2\,e^{-\beta\hbar\omega n}.$$

Subtracting the last two [after division by $(-\beta\hbar)$ or $(-\beta\hbar)^2$] gives

$$\frac{2\,(e^{-\beta\hbar\omega})^2}{(1-e^{-\beta\hbar\omega})^3} = \sum_{n=1 \to 2}^{\infty} (n^2-n)\,e^{-\beta\hbar\omega n}.$$

Then

$$\frac{(1+e^{-\beta\hbar\omega})^2}{(1-e^{-\beta\hbar\omega})^3} = \frac{\left[(e^{\beta\hbar\omega})^2 + 2e^{\beta\hbar\omega} + 1\right](e^{-\beta\hbar\omega})^2}{(1-e^{-\beta\hbar\omega})^3}$$

$$= \frac{1}{2}\left\{ \underbrace{\sum_{n=2}^{\infty}(n^2-n)\,e^{-\beta\hbar\omega(n-2)}}_{n=2+n'} + 2\underbrace{\sum_{n=2}^{\infty}(n^2-n)\,e^{-\beta\hbar\omega(n-1)}}_{n=1+n'} + \underbrace{\sum_{n=2}^{\infty}(n^2-n)\,e^{-\beta\hbar\omega n}}_{n=n'} \right\}$$

$$= \frac{1}{2}\sum_{n'=0}^{\infty} e^{-\beta\hbar\omega n'}\left\{ 4 + \cancel{4n'} + n'^2 - \cancel{2} - \cancel{n'} + \cancel{2} + 4n' + 2n'^2 - 2 - \cancel{2n'} + n'^2 - \cancel{n'} \right\}$$

$$= \sum_{n'=0}^{\infty} e^{-\beta\hbar\omega n'}\left\{ 1 + 2n' + 2n'^2 \right\}.$$

Inserting above, we find $E_n^{(1)} = \frac{3g}{16}\cdot\hbar\omega\cdot(1+2n+2n^2)$.

This agrees with the result found in the lecture QT II (time-independent perturbation theory).

Summary: It is possible to deduce the quantum-mechanical energy spectrum without solving eigenvalue problems — from convergent and real ("Euclidean") sums!

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