

Lesson 4- Canonical

Statement

So far, we have focused on the study of closed systems (N, V, E). Now we are going to learn to study parts of our system.

If we ignore most of our system—agreeing not to ask questions about certain degrees of freedom—the statistical mechanical predictions about the remaining parts of our system are embodied in a new statistical ensemble and its associated free energy.

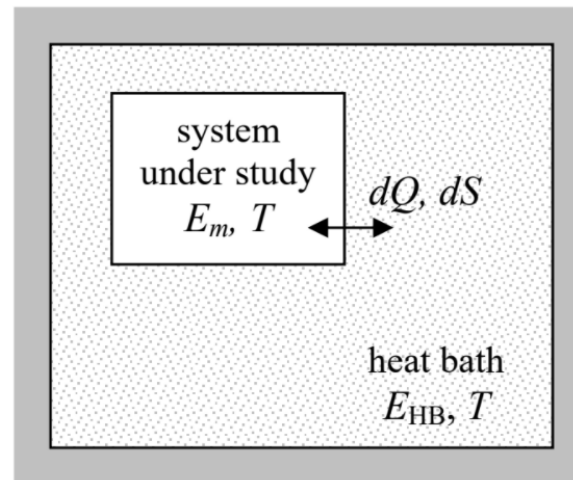
What do we ignore? We ignore the external world. If the coupling to the external world is weak, we can remove it from consideration.

Why? Most systems are typically not isolated (they can exchange energy, volume and particles with its environment)

- If the system exchanges energy with the ‘outside world’ (or heat bath at fixed temperature) then we have the **canonical ensemble** and the **Hemholtz free energy** to describe the system
- If the system exchanges energy and particles with the heat bath (with fixed temperature and chemical potential), then we have the **grand canonical ensemble** and the **grand free energy**.

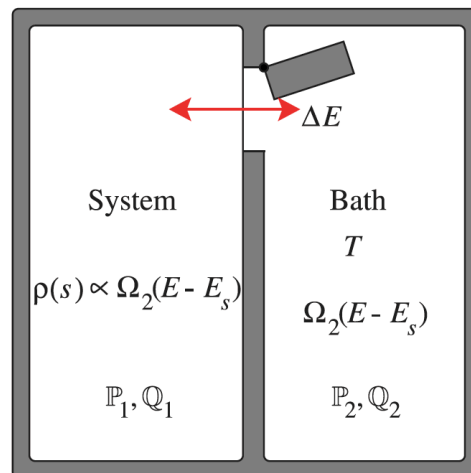
Canonical Ensemble

The canonical ensemble describes a system of N particles in a box of volume V **weakly coupled to and in thermal equilibrium with** an infinitely large heat reservoir at absolute temperature T . The number of particles in the system is fixed but heat is exchanged with the environment to maintain a temperature T .



Canonical Ensemble

It is intuitively evident that if the heat bath is sufficiently large, any **thermodynamic variables** characterizing the system under study **should not depend on the heat bath's environment**. In particular, we may assume that the heat bath is thermally insulated, so that the total energy of the composite system, consisting of the system of our interest plus the heat bath, does not change in time $E = E_s + E_b + E_{sb} \approx E_s + E_b = \text{constant}$. Because E_{sb} happens in the contact surface while E_s and E_b are proportional to volume.



Reminder microcanonical Ensemble

Let's assume we divide our system into two parts of volumes V_1, V_2 with N_1, N_2 particles:

These two subparts are in equilibrium.

$$\Omega(E) = \int dE_1 dE_2 \Omega(E_1) \Omega(E_2) \delta(E - (E_1 + E_2)) = \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1)$$

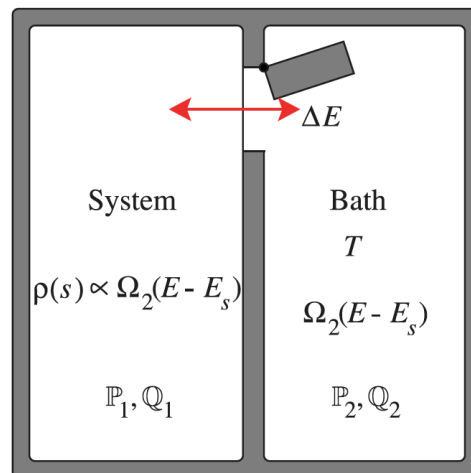
So that the density of states $\rho(E_1) = \frac{\Omega_1(E_1)\Omega_2(E - E_1)}{\Omega(E)}$

Note that $\rho(E_1) \propto \Omega_2(E - E_1)$

Canonical Ensemble

How does the probability that our system is in a state s depend upon its energy E_s ? Note that the full system is a microcanonical ensemble. Remember slides micro canonical definition of temperature (slides 15-16). the probability density that our system will be in the particular state s is proportional to the volume of the energy shell for our heat bath at bath energy $E_b = E - E_s$. Using the definition of entropy $\Omega(E_2) = e^{S_2(E_2)/K_B}$ we obtain

$$\rho(s) \propto \Omega_2(E - E_s) = e^{\frac{S_2(E - E_s)}{k_B}}$$



Canonical Ensemble

Let us compare the probability of two typical states A and B of our equilibrium system. We know that the energy fluctuations are small, and we assume that the heat bath is large. We can therefore assume that the inverse temperature $1/T_2 = \partial S_2 / \partial E_2$ of the heat bath is constant in the range $(E - E_A, E - E_B)$ hence

$$\begin{aligned} \frac{\rho(s_B)}{\rho(s_A)} &\propto \frac{\Omega_2(E - E_B)}{\Omega_2(E - E_A)} = e^{(S_2(E-E_B) - S_2(E-E_A))/k_B} \\ &= e^{(E_A - E_B)(\partial S_2 / \partial E)/k_B} = e^{(E_A - E_B)/k_B T_2} = \frac{e^{-E_B/k_B T}}{e^{-E_A/k_B T}} \end{aligned}$$

This is the general derivation of the **Boltzmann distribution**; the probability of a particular system state of energy E_s is:

$$\rho(s) \propto \exp(-E_s/k_B T)$$

Partition Function Canonical Ensemble

Given that the probability has to be normalized, for every state with energy E_s we have:

$$\begin{aligned}\rho(s) &= \frac{\exp(-E_s/k_B T)}{\int \frac{dQ_1 dP_1}{h^{3N_1}} e^{-\mathcal{H}(Q_1, P_1)/k_B T}} \\ &= \frac{\exp(-E_s/k_B T)}{\sum_n e^{\frac{-E_n}{K_B T}}} = \frac{\exp(-E_s/k_B T)}{Z}\end{aligned}$$

The partition function Z is just the normalization factor that keeps the total probability summing to one. It may surprise you to discover that this normalization factor plays a central role in the theory.

$$Z = \sum_n e^{-E_n/K_B T} = \int \frac{dP_1 dQ_1}{h^{3N_1}} \exp(-\mathcal{H}_1(P_1, Q_1)/K_B T)$$

Internal energy

$$\langle E \rangle = \sum_n E_n P_n = \frac{\sum_n E_n e^{-\beta E_n}}{Z} = - \frac{\partial Z / \partial \beta}{Z} = - \frac{\partial \log Z}{\partial \beta}$$

Specific heat

Let c_v be the specific heat per particle at constant volume.
(The specific heat is the energy needed to increase the temperature by one unit, $\partial \langle E \rangle / \partial T$)

$$Nc_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{d\beta}{dT} = \frac{1}{k_b T^2} \frac{\partial^2 \log Z}{\partial \beta^2}$$

Note that we could have derived this from the summation

Interpretation of specific heat

We could develop the summation as follows:

$$\begin{aligned} Nc_v &= \frac{\partial \langle E \rangle}{\partial T} = - \frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left(\frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \right) \\ &= - \frac{1}{k_B T^2} \left(\frac{-\sum_n E_n^2 e^{-\beta E_n} Z + (\sum_n E_n e^{-\beta E_n})^2}{Z^2} \right) \\ &= \frac{1}{k_B T} [\langle E^2 \rangle - \langle E \rangle^2] = \frac{\sigma_E^2}{k_B T^2} \end{aligned}$$

Remarkable; it is a relationship between a macroscopic susceptibility (c_v , the energy changes when the temperature is perturbed) and a microscopic fluctuation (σ_E , the energy fluctuation in thermal equilibrium).

Entropy in the canonical ensemble

Recalling the definition of entropy (the one by Shannon):

$$\begin{aligned} S_{\text{shannon}} &= -k_B \sum_n P_n \log P_n = -k_B \sum_n \frac{\exp(-\beta E_n)}{Z} \log \left(\frac{\exp(-\beta E_n)}{Z} \right) \\ &= -k_B \sum_n \frac{\exp(-\beta E_n)}{Z} (-\beta E_n - \log Z) = k_B \beta \langle E \rangle + k_B \log Z \sum_n \frac{\exp(-\beta E_n)}{Z} \\ &= \frac{\langle E \rangle}{T} + k_B \log Z \end{aligned}$$

Then:

$$S_1 = \langle E \rangle / T + k_B \log Z \text{ or equivalently } -k_B T \log Z = \langle E \rangle - TS$$

remind us the definition of Helmholtz free energy: $F = U - TS$

The free energy of the canonical ensemble is $F = -k_B T \log Z$

Quantum parenthesis

So far we have referred to classical systems, for quantum systems statistical mechanics holds, but the statements have to be understood in terms of operators, with \hat{H} the Hamiltonian operator and the probability density is known as *density matrix* $\hat{\rho}$:

$$\hat{\rho} = \frac{1}{Z} e^{-\hat{H}/k_B T}$$

So, to apply the canonical formulation we must first diagonalize $\hat{H} |E_n\rangle = E_n |E_n\rangle$, i.e. solve the time-independent Schrödinger equation. In this basis, the density matrix is diagonal, then:

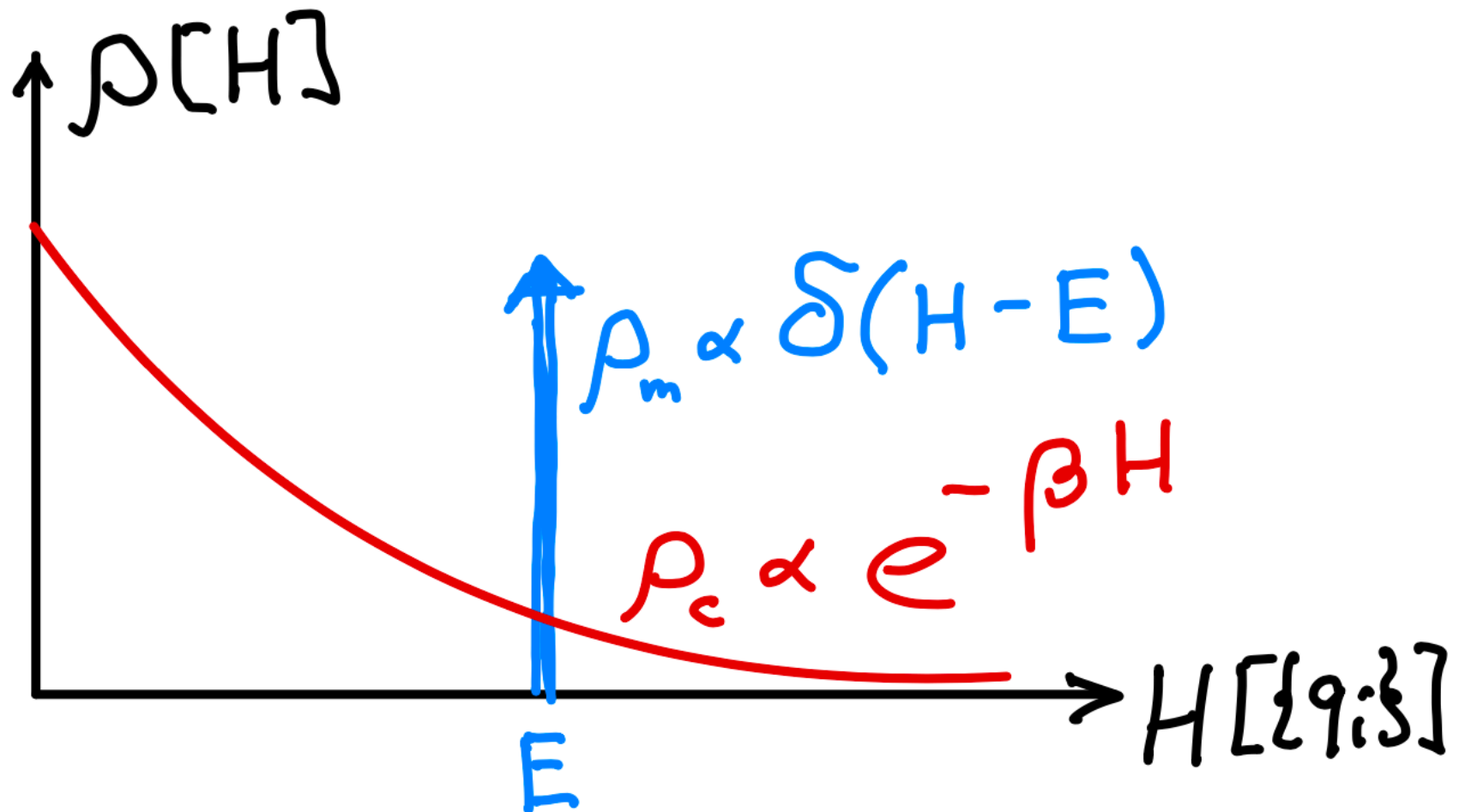
$$\rho_{nm} = \frac{1}{Z} e^{-E_n/k_B T} \delta_{nm}, \quad Z = \sum_n e^{-E_n/k_B T}, \quad \langle \hat{O} \rangle = \frac{1}{Z} \sum_n O_{nn} e^{-E_n/k_B T}$$

Or we can work in the independent basis formulation:

$$\rho_{nm} = \frac{1}{Z} e^{-\hat{H}/k_B T} \delta_{nm}, \quad Z = \text{Tr} \left[e^{-\hat{H}/k_B T} \right], \quad \langle \hat{O} \rangle = \text{Tr} \left[\hat{O} \hat{\rho} \right]$$

Canonical-microcanonical relations

Comparison between microcanonical ensemble (controlled by E), and canonical (controlled by $\beta = 1/k_B T$) ensemble probability densities



Canonical-microcanonical relations

Although the two ensembles appear to be drastically different, **in the thermodynamic limit both are equivalent.**

Correspondence between micro canonical and canonical ensembles

$$\begin{aligned}\Omega(E) &\longleftrightarrow Z(\beta) \\ S(E) = k_B \ln \Omega &\longleftrightarrow F(\beta) = -k_B T \ln Z \\ k_B \beta = \frac{\partial S}{\partial E} &\longleftrightarrow E = \frac{\partial(\beta F)}{\partial \beta}\end{aligned}$$

Canonical-microcanonical relations

Density of states: It is crucial to **distinguish** the summation **over microstates** $\{q_i, p_i\}$ or **over energies** E , often a point of confusion in canonical ensemble. The connection, of course, is the degeneracy $g(E)dE$ at E counting a number of microstates $\{q_i, p_i\}$ between energy E and $E + dE$.

To make this explicit, we consider the partition function Z , as an integration over energies:

$$Z = \sum_{\{q_i, p_i\}} e^{-\beta H(p_i, q_i)} = \int dE \sum_{\{q_i, p_i\}} \delta(E - H(p_i, q_i)) e^{-\beta E} = \int g(E) e^{-\beta E} dE$$

where $g(E) = \sum_{\{q_i, p_i\}} \delta(E - H(p_i, q_i))$ is the density of states, related

to multiplicity of the microcanonical ensemble, $\Omega(E) = g(E)$.

Canonical-microcanonical relations

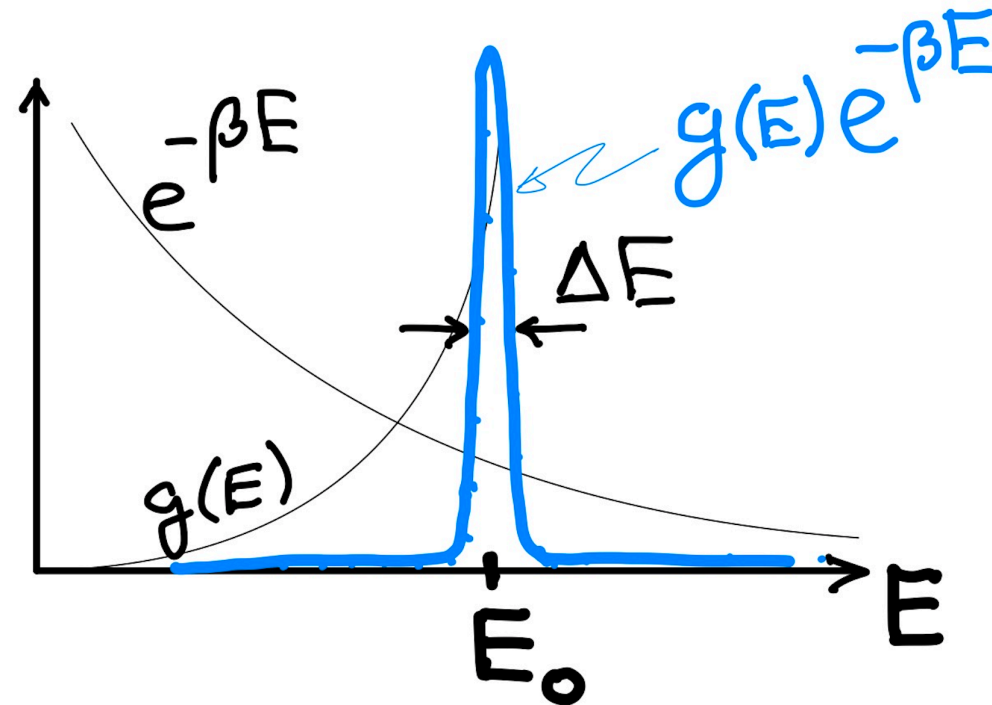
Let us examine in detail

$$Z = \int g(E) e^{-\beta E} dE \quad \text{where } g(E) = \sum_{\{q_i, p_i\}} \delta(E - H(p_i, q_i))$$

We note that $g(E)$ extremely strongly increasing function of E , in fact growing exponentially with system size (e.g., in an ideal gas ($\Omega(E) \sim E^{3N/2}$), exponent of order Avogadro number).

On the other hand, $e^{-\beta E}$ is a strongly decreasing function of E , with the rate of increase set by β . Thus, the integrand $g(E)e^{-\beta E}$ is an extremely strongly peaked function (becoming a δ function of E in the thermodynamic limit), with the location of the peak at $E_0 = E_0(\beta)$.

Canonical-microcanonical relations



An illustration of the peak form of the canonical ensemble $g(E)e^{-\beta E}$, with peak located at energy $E_0 = E(\beta)$ and a width vanishingly small in the thermodynamic limit. This thereby demonstrates the equivalence to the microcanonical ensemble, with $Z(\beta) = \Omega(E(\beta))e^{-\beta E(\beta)}$

Summary

Thus, with **partition function** $Z(T)$ and the **corresponding Helmholtz free energy** $F(T) = -k_B T \ln Z$ in hand, we can compute any thermodynamic property (at least in principle, though it may be difficult). The problem thus reduces to a computation of the partition function $Z(T)$.

In the following we gonna see some useful math tricks.

Gaussian integral calculus

You can easily prove that

$$Z_0(a) = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}}$$

$$Z_1(a) = \int_{-\infty}^{\infty} dx x^2 e^{-\frac{1}{2}ax^2} = -2 \frac{\partial}{\partial a} Z_0(a) = \frac{1}{a} \sqrt{\frac{2\pi}{a}} = \frac{1}{a} Z_0$$

$$Z_n(a) = \int_{-\infty}^{\infty} dx x^{2n} e^{-\frac{1}{2}ax^2} = \frac{(2n-1)!!}{a^n} Z_0$$

where the double factorial is the product of all the positive integers up to n that have the same parity (odd or even) as the argument.

Gaussian integral calculus

You can easily prove that (moment generating function!)

$$\begin{aligned} Z(a, h) &= \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}ax^2 + hx} = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}a(x-h/2)^2} e^{\frac{h^2}{2a}} = e^{\frac{h^2}{2a}} Z_0(a) \\ &= \sum_{n=0}^{\infty} \frac{(h^2/2a)^n}{(n)!} Z_0(a) = \sum_{n=0}^{\infty} \frac{h^{2n}}{(2n)!} Z_n(a) \end{aligned}$$

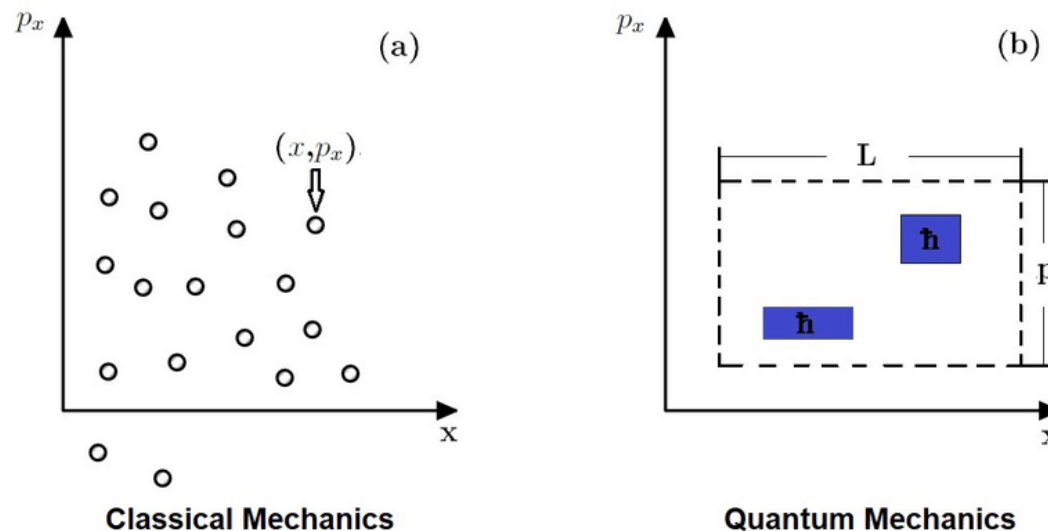
Quite clearly, odd powers of x vanish by symmetry, and even powers give the $2n$ -point correlation function

$$C_{2n} \equiv \frac{Z_n(a)}{Z_0(a)} = \langle x^{2n} \rangle = \frac{1}{Z_0(a)} \frac{\partial^{2n}}{\partial h^{2n}} Z(a, h) \big|_{h=0} = (2n-1)!! (C_2)^n$$

Connection Classical-Quantum in the Canonical Ensemble

Classical and Quantum Physics differ in the notion of a "**state**". Classically, a state is a **point in phase space** (= all positions and momenta). Quantum Mechanically, it's a **vector in Hilbert space** (e.g., all permissible wave functions).

Either way, we're scanning across all "states" and "sum up" Boltzmann factors. Classically, that's just an integral; in Quantum Mechanics, it's the so-called "trace": the sum over a set of basis vectors in Hilbert space.



Connection Classical-Quantum in the Canonical Ensemble

In terms of the partition function of a single particle:

The diagram illustrates the connection between classical and quantum partition functions. It features two equations, one for the classical partition function $Z_{\text{classical}}$ and one for the quantum partition function Z_{quantum} . Blue arrows point from descriptive labels to specific parts of the equations.

Classical Partition Function:

$$Z_{\text{classical}} = \int \frac{dp \, dq}{2\pi\hbar} e^{-\beta[p^2/2m + V(q)]}$$

Labels for the classical equation:

- momentum (points to dp)
- position (points to dq)
- $\beta = 1/k_B T$ (points to β)
- mass (points to m)
- potential energy (points to $V(q)$)

Quantum Partition Function:

$$Z_{\text{quantum}} = \text{Tr} \left\{ e^{-\beta[P^2/2m + V(Q)]} \right\}$$

Labels for the quantum equation:

- "trace" (points to Tr)
- momentum *operator* (points to P^2)
- position *operator* (points to Q)

Connection Classical-Quantum in the Canonical Ensemble

The negative logarithm of the partition function, multiplied by the thermal energy kT , gives the free energy—in either case. And thus we get our thermodynamics. And with it, the bizarre quantum differences. WHERE ON EARTH DO THEY COME FROM?

Connection Classical-Quantum in the Canonical Ensemble

The negative logarithm of the partition function, multiplied by the thermal energy kT , gives the free energy—in either case. And thus we get our thermodynamics. And with it, the bizarre quantum differences. Where do these differences comes from?

It turns out, everything hinges on the fact that in the quantum case we're taking the exponential of something that involves both the momentum and the position operator, and these two operators do not commute: QP is not the same as PQ .

$$[QP] := QP - PQ = i\hbar$$

Connection Classical-Quantum in the Canonical Ensemble

If A and B are operators that do not commute, then in general:

$$e^{A+B} \neq e^A e^B$$

assuming that these exponentials exists.

Proof as an exercise.

Connection Classical-Quantum in the Canonical Ensemble

If A and B are operators that do not commute, then in general:

$$e^{A+B} \neq e^A e^B$$

assuming that these exponentials exists.

Proof: To show explicitly that $e^{A+B} \neq e^A e^B$ when $[A, B] \neq 0$, consider expanding both sides in a Taylor series:

$$e^{A+B} = I + (A + B) + \frac{1}{2!}(A + B)^2 + \frac{1}{3!}(A + B)^3 + \dots$$

$$e^A e^B = \left(I + A + \frac{1}{2!}A^2 + \frac{1}{3!}A^3 + \dots \right) \left(I + B + \frac{1}{2!}B^2 + \frac{1}{3!}B^3 + \dots \right)$$

Upon expanding $(A + B)^2$, $(A + B)^3$ etc., and comparing with the corresponding terms in $e^A e^B$, you'll find that the series differ if $[A, B] \neq 0$.

Connection Classical-Quantum in the Canonical Ensemble

It turns out, no longer being able to factorize the position and momentum part of the Boltzmann factor makes the evaluation of the quantum trace more difficult. So what would happen if we just boldly **ignored** that and brute force factorize anyways? What would we get?

Connection Classical-Quantum in the Canonical Ensemble

It turns out, no longer being able to factorize the position and momentum part of the Boltzmann factor makes the evaluation of the quantum trace more difficult. So what would happen if we just boldly **ignored** that and brute force factorize anyways? What would we get? **The classical partition function!**

But there is more ... There is a truly amazing inequality for the trace of the exponential functional relation, the Golden-Thompson inequality:

$$\mathrm{Tr}(e^{A+B}) \leq \mathrm{Tr}(e^A)\mathrm{Tr}(e^B)$$

Look what this implies in our case: the trace with the "usual" Boltzmann factor is the quantum partition function, while the trace with the "factored Boltzmann factor" is the classical partition function. The latter is bigger, and so its negative logarithm is smaller:

Connection Classical-Quantum in the Canonical Ensemble

then

$$\mathrm{Tr} \left[e^{-\beta \left(\frac{p^2}{2m} + V(Q) \right)} \right] \leq \mathrm{Tr} \left[e^{-\beta \frac{p^2}{2m}} e^{-\beta V(Q)} \right]$$

$$Z_{\text{quantum}} \leq Z_{\text{classical}}$$

$$-k_B T \log(Z_{\text{quantum}}) \geq -k_B T \log(Z_{\text{classical}})$$

$$F_{\text{quantum}} \geq F_{\text{classical}}$$

In other words: the quantum free energy is always bigger than the classical one. Or, phrased differently: quantum fluctuations will only ever increase the free energy! But how much?

Connection Classical-Quantum in the Canonical Ensemble

The quick answer says that for $T \rightarrow \infty$, or $\beta \rightarrow 0$, all exponents become small and the non-commutation troubles vanish. Hence, for large temperatures quantum effects vanish and we get the classical answer! But we can do better, expanding Taylor and collapsing terms:

$$e^{t(A+B)} = e^{tA} e^{tB} \prod_{n=2}^{\infty} e^{-t^n C_n / n!}$$

The first few C_n are given by:

$$C_2 = [A, B]$$

$$C_3 = [A, [B, A]] + 2[A, [B, B]]$$

$$C_4 = [[A, B], A, A] + 3[[A, B], B, B]$$

$$C_5 = \dots$$

Connection Classical-Quantum in the Canonical Ensemble

Wigner's leading quantum (1932) correction to the classical free energy:

$$F_{\text{quantum}} = F_{\text{classical}} + \frac{\hbar^2}{24m(k_B T)^2} \left\langle \left(\frac{\partial U}{\partial q} \right)^2 \right\rangle$$

Quadratic in \hbar
and inversely
quadratic in T

Classical average

Classical force