Physics 12c: Problem Set 2

Due: Thursday, April 18, 2019

1. **Partition function identities**

   Consider a system $\mathcal{S}$ with partition function $Z_{\mathcal{S}}(\beta) = \sum_s e^{-\beta E_s}$, where the sum runs over states of $\mathcal{S}$, and $\beta = 1/\tau$ is the inverse temperature.

   (a) Show that $U = \langle E \rangle = -\frac{\partial}{\partial \beta} \log Z_{\mathcal{S}}(\beta)$.

   (b) Show that $\Delta E^2 = \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2}{\partial \beta^2} \log Z_{\mathcal{S}}(\beta)$.

   (c) The heat capacity is $C = \frac{\partial U}{\partial \tau}$. How is C related to ΔE^2?

   (d) Consider N non-interacting copies of $\mathcal{S}$. Compute the partition function and use the above identities to show that that the fractional fluctuation $\Delta E / \langle E \rangle$ for the combined system scales like $1/\sqrt{N}$.

2. **Model of a large reservoir**

   (a) Consider a system $\mathcal{S}$ divided into two subsystems $\mathcal{S}_1$ and $\mathcal{S}_2$ in thermal contact, sharing total energy E. If $\mathcal{S}_1$ has energy E_1 and $\mathcal{S}_2$ has energy $E_2 = E - E_1$, the total entropy of $\mathcal{S}$ is

   $$\sigma_{\text{total}} = \sigma_1(E_1) + \sigma_2(E_2), \tag{1}$$

   where σ_1 is the entropy of $\mathcal{S}_1$ and σ_2 is the entropy of $\mathcal{S}_2$. Show that if E_1 is chosen to maximize σ_{total} ("the most probable configuration") with the total energy E fixed, then the two subsystems have the same temperature: $\tau_1 = \tau_2$. (To verify that this configuration is really a maximum rather than a minimum, check the sign of the second derivative of σ_{total} with respect to E_1, assuming the heat capacity $C_i = dE_i/d\tau_i$ is positive for both subsystems.)

   (b) Now suppose $\mathcal{S}$ is divided into N subsystems $\mathcal{S}_1, \mathcal{S}_2, \ldots, \mathcal{S}_N$ in thermal contact, with total entropy

   $$\sigma_{\text{total}} = \sum_{i=1}^{N} \sigma_i(E_i), \tag{2}$$

   where σ_i, E_i are the entropy and energy of $\mathcal{S}_i$. Using mathematical induction and part (2a), show that if the total energy $E = E_1 + E_2 + \cdots + E_N$ is fixed, then the total entropy σ_{total} is maximized when all N systems have the same temperature.

(c) Now consider a large reservoir consisting of N identical subsystems, all in thermal contact with one another and each with the same entropy function $\sigma(E)$. It follows from part (2b) that in the most probable configuration all subsystems have the same temperature and all therefore have the same energy as well; hence the total entropy is

$$\sigma_{\text{total}}(E) = N\sigma(E/N), \tag{3}$$

where E is the total energy.

Suppose that the total energy decreases from E to $E - E_s$. Find the corresponding change $\Delta\sigma_{\text{total}}$ in the total entropy, expanded in a power series to quadratic order in E_s. Express your answer in terms of the reservoir's temperature τ and the heat capacity C of an individual *subsystem.* Argue that it is reasonable to neglect the term of order E_s^2 when the number of subsystems is $N \gg 1$.

* *Optional* What is the form of higher-order terms in the power-series expansion of $\sigma_{\text{total}}(E - E_s)$ in E_s? Assuming the function $\sigma(E)$ has finite derivatives, argue that in the limit $N \to \infty$ with τ fixed, all the higher-order terms can be neglected as well.

3. **Anisotropic well**

The Hamiltonian for a particle of mass m in an anisotropic potential well is

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{m}{2}(\omega_1^2 x^2 + \omega_2^2 y^2 + w_3^2 z^2). \tag{4}$$

Since H is the sum of three one-dimensional harmonic oscillator Hamiltonians with circular frequencies $\omega_1, \omega_2, \omega_3$, the energy eigenvalues are

$$E(n_1, n_2, n_3) = \hbar\omega_1 n_1 + \hbar\omega_2 n_2 + \hbar\omega_3 n_3 \tag{5}$$

(ignoring the zero-point energy), where n_1, n_2, n_3 are nonnegative integers.

(a) Find the partition function Z_1 for a single particle in the potential well at temperature τ.

(b) Now suppose that N distinguishable non-interacting particles are in the potential well. Express the partition function Z_N in terms of the single-particle partition function Z_1.

(c) Compute the average energy $U(\tau, N)$.

(d) Find the heat capacity $C = \left(\frac{\partial U}{\partial \tau}\right)_N$ in the high-temperature limit, $\tau \gg \hbar\omega_1, \hbar\omega_2, \hbar\omega_3$. (The subscript N on the partial derivative means that N is held fixed during differentiation.)

4. **Particle on a circle**

Consider a single quantum mechanical particle confined to a circle with length L. The Hamiltonian is

$$H = \frac{p^2}{2m}, \tag{6}$$

where p is the momentum, which is quantized so that the wavefunction is periodic around the circle. Let the temperature be τ.

(a) Show that the partition function is

$$Z = \sum_{n=-\infty}^{\infty} e^{-yn^2} \tag{7}$$

for some y (that you should determine).

(b) Compute the partition function in the large-τ limit.

(c) The partition function for the particle on a circle possesses a surprising high/low temperature "duality". Specifically, the function (7) satisfies the identity

$$Z(y) = \sqrt{\frac{\pi}{y}} Z\left(\frac{\pi^2}{y}\right). \tag{8}$$

Use this identity to re-derive your answer to part (4b).

5. **Imaginary time**

Let us prove the duality (8) from problem (4c). In class, we derived a general expression for the partition function of a quantum mechanical system:

$$Z = \mathrm{Tr}(e^{-\beta H}), \tag{9}$$

where $\beta = 1/\tau$. The trace of a matrix can be computed using any basis. The key to deriving (8) is to evaluate the trace using the position basis instead of the momentum basis (that you used in problem 4). In position space, we have

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \tag{10}$$

The trace is

$$\mathrm{Tr}(e^{-\beta H}) = \int_0^L dx \langle x|e^{-\beta H}|x\rangle = \int_0^L dx f(x,x,\beta), \tag{11}$$

where we have defined

$$f(x,x',\beta) \equiv \langle x'|e^{-\beta H}|x\rangle. \tag{12}$$

Here, we used the fact that $|x\rangle$ for $x \in [0,L)$ is a complete orthonormal basis of states for the particle on a circle, so that $\int_0^L dx|x\rangle\langle x|$ is a resolution of the identity.

(a) Show that $f(x, x', \beta)$ satisfies the differential equation

$$-\frac{\partial}{\partial \beta} f(x, x', \beta) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(x, x', \beta). \tag{13}$$

(b) What is the initial condition for $f(x, x', \beta)$ at $\beta = 0$?

(c) Show that if $\psi(x, t)$ is any solution to the Schrodinger equation

$$i \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t), \tag{14}$$

then $f(x, x', \beta) = \psi(x, -i\beta)$ is a solution to (13).

Thus (13) is called the "imaginary-time" Schrodinger equation. As we will discuss later in the course, it is also an example of a diffusion equation.

(d) Show that a solution to (13) is

$$\frac{A}{\sqrt{\beta}} e^{-\frac{m}{2\hbar^2} \frac{(x-x')^2}{\beta}}, \tag{15}$$

where A is a constant. You might recognize this as the wavefunction for a free particle that starts in a position eigenstate, and then undergoes Schrodinger evolution, after replacing $t = -i\beta$.

(e) The above solution is not periodic under $x \to x + L$. Obtain a periodic solution by summing over shifts

$$f(x, x', \beta) = \frac{A}{\sqrt{\beta}} \sum_{n=-\infty}^{\infty} e^{-\frac{m}{2\hbar^2} \frac{(x-x'-nL)^2}{\beta}}. \tag{16}$$

Verify that the above solution is periodic under $x \to x + L$. Compute the value of A such that $f(x, x', \beta)$ has the correct initial conditions as $\beta \to 0$. Recover (8) by evaluating (11).

Note: This computation to derive formula (8) is a special case of *Poisson resummation*. It also has a beautiful interpretation in terms of the path integral formulation of quantum mechanics, which you may encounter later in your physics studies. The function $Z(y)$ is famous in the mathematics literature. It is a type of "θ-function" and is perhaps the simplest example of a *modular form*.