Midterm 1 for Thermal and Statistical Physics I

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• Binary model

(A) The thermal entropy is logarithm of the multiplicity function,

$$\sigma(N, U) = \log g = \log g_0 - \frac{U^2}{2Nm^2B^2},$$
(1)

where we have use the relation $U = -2smB$. **(B)** Treating U as a continuous variable, one can derive the relation between the average energy U and the temperature τ,

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N \quad \Rightarrow \quad U = -N\frac{m^2B^2}{\tau}.$$
(2)

Note that $\tau \to 0^{\pm}$ limits correspond to completely different thermal distributions for the binary spins.

• Quantum oscillators

(A) For a single oscillator, it is rather trivial that the multiplicity is always unity,

$$g(1, n) = 1.$$
(3)

The generation function for $N = 1$ is just a simple geometric series,

$$\begin{aligned} G(1, z) &= \sum_n g(1, n)z^n \\ &= 1 + z + z^2 + \cdots = \frac{1}{1-z} \end{aligned}$$
(4)

(B) Because the system consists of N independent and identical oscillators, the generating function $G(N, z)$ can be expressed as product of $G(1, z)$,

$$G(N, z) = [G(1, z)]^N = \frac{1}{(1-z)^N}.$$
(5)

The multiplicity function can be extracted from the generating function by taking derivatives,

$$g(N, n) = \frac{1}{n!} G^{(n)}(N, 0) = \frac{N!}{n!(N-1)!}. \tag{6}$$

• Overhauser effect

(A) Because of the external setup, the energy is no longer conserved. The change of the reservoir energy $\Delta \epsilon_{\mathcal{R}}$ and that of the system $\Delta \epsilon$ are related,

$$\Delta \epsilon_{\mathcal{R}} = -(1+\gamma)\Delta \epsilon. \tag{7}$$

For $\gamma = 0$, the energy conservation is restored. Following the standard derivations in the textbook, the modified relation for energy conservation leads to the abnormal Boltzmann distribution,

$$P(\gamma, \epsilon) = \frac{1}{Z_\gamma} \exp\left[-\frac{(1+\gamma)\epsilon}{\tau}\right]. \tag{8}$$

(B) For $\gamma = -1$, the abnormal Boltzmann distribution becomes constant,

$$P(-1, \epsilon) = \frac{1}{Z_{\bar{1}}} = \text{constant}. \tag{9}$$

It means that all states with *different energies* share the same probability. This seems to be in direct conflict with the fundamental assumption of statistical physics: states with *the same energy* share the same probability. The paradox is resolved when the total multiplicity is considered. For $\gamma = -1$, the energy of the reservoir remains constant and thus has the same multiplicity. Therefore, the abnormal Boltzmann distribution reduces to a constant.

• Zipper model for DNA

(A) In thermal equilibrium, the probability ratio of the open and closed states for the first link is determined by the energy difference ϵ,

$$p = e^{-\epsilon/\tau} \tag{10}$$

The partition function form a geometric series of N terms,

$$Z_N = 1 + p + p^2 + \cdots + p^N = \frac{1 - p^{N+1}}{1 - p}. \tag{11}$$

(B) In the thermodynamic limit ($N \to \infty$), the partition function simplifies,

$$Z_\infty = \frac{1}{1-p}. \tag{12}$$

The average number of the open links can be evaluated from the partition function,

$$\langle s \rangle = \frac{1}{Z_\infty} \sum_{s=0}^{\infty} s\, p^s = p \frac{\partial}{\partial p} \log Z_\infty \tag{13}$$

Because $\log Z_\infty = -\log(1-p)$, the average number of the open links is

$$\langle s \rangle = \frac{p}{1-p} = \frac{1}{\exp(\epsilon/\tau) - 1}. \tag{14}$$

You may realize that the above is nothing but the famous Planck distribution.

• Sackur-Tetrode equation

Starting from a single gas molecule in a box first, the partition function $Z_1 = n_Q V$. It is important to emphasize that the expression contains the Planck constant and is thus quantum in nature. Generalize the calculation to N independent and identical particles. The N-th power comes from the independence and the $N!$ arises from the identical,

$$Z_N = \frac{(Z_1)^N}{N!}. \tag{15}$$

Taking logarithm of the partition function and making use of Stirling formula, the free energy is

$$F = -\tau \log Z_N = -\tau N \log(n_Q/n) - \tau N. \tag{16}$$

It is important to appreciate the inclusion of the $N!$ factor. The free energy is now extensive and the corresponding free energy density $f \equiv F/N = -\tau \log(n_Q/n) - \tau$ is well defined in thermodynamic limit ($N \to \infty$). Finally, according to the thermodynamic identity, the entropy is

$$\sigma = -\left(\frac{\partial F}{\partial \tau} \right)_{N,V} = N \left[\log(n_Q/n) + \frac{5}{2} \right]. \tag{17}$$

It is not surprising that the entropy is also extensive as well.

• Criterion for thermal equilibrium

Because a single binary spin only has two states, the temperature is ill-defined. However, one can still compute the multiplicity for the total system in thermal equilibrium,

$$
\begin{aligned}
g(U_0) &= g_{\text{spin}}(-\epsilon)g_{\mathcal{R}}(U_0 + \epsilon), +g_{\text{spin}}(\epsilon)g_{\mathcal{R}}(U_0 - \epsilon) \\
&= g_{\mathcal{R}}(U_0 + \epsilon) + g_{\mathcal{R}}(U_0 - \epsilon),
\end{aligned} \tag{18}
$$

where U_0 is the total energy of the total system. According to the fundamental assumption of statistical mechanics, in thermal equilibrium, all states of the total system appears with the same probability $1/g(U_0)$. This can be used as the criterion for thermal equilibrium.

Or, one can evaluate the probability ratio for the spin up/down states,

$$
\frac{P(\epsilon)}{P(-\epsilon)} = \frac{g_{\mathcal{R}}(U_0 - \epsilon)}{g_{\mathcal{R}}(U_0 + \epsilon)} = \exp[\sigma(U_0 - \epsilon) - \sigma(U_0 + \epsilon)]. \tag{19}
$$

Following the same steps in the textbook, it is straightforward to find the probability ratio in thermal equilibrium,

$$
\frac{P(\epsilon)}{P(-\epsilon)} = e^{-2\epsilon/\tau_{\mathcal{R}}}. \tag{20}
$$

Note that the temperature of the reservoir is well defined and the above relation can be used as the criterion for thermal equilibrium as well.

The following derivations are for curious cats only. When dealing with the reservoir, we often keep the first-order term of the Taylor expansion. Is it reasonable to drop the higher-order terms? Well, write down the first-order and the second-order terms for comparison,

$$
\text{the 1}^{\text{st}}\text{-order term} = \frac{\partial \sigma}{\partial U}\Delta U, \tag{21}
$$

$$
\text{the 2}^{\text{nd}}\text{-order term} = \frac{1}{2}\frac{\partial^2 \sigma}{\partial U^2}(\Delta U)^2. \tag{22}
$$

In order to drop the second-order term, the following ratio must be much less than unity,

$$
\left|\frac{(\partial^2 \sigma/\partial U^2)\Delta U}{2(\partial \sigma/\partial U)}\right| \ll 1 \quad \rightarrow \quad \epsilon/U_0 \ll 1 \tag{23}
$$

For the binary spin in thermal contact of the reservoir considered here, as long as $\epsilon/U_0 \ll 1$, it is legitimate to ignore the higher-order terms.

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(1) Please do not flip the sheet until instructed.
(2) Please try to be as neat as possible so that I can understand your answers without ambiguity.
(3) While it is certainly your rights to make wild guesses or memorize irrelevant details, I would truly appreciate if you try to make your answers logical.
(4) Good luck for all hard-working students!

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1. Binary model (20%) Consider the binary model of N spins in magnetic field. The energies of a single spin with up and down orientations are $\epsilon_\uparrow = -mB$ and $\epsilon_\downarrow = mB$ respectively. In the large N limit, the multiplicity function is well approximated by a Gaussian function,

$$g(N, s) = g_0\, e^{-2s^2/N},$$

where the spin excess $s = (N_\uparrow - N_\downarrow)/2$ and $g_0 = \sqrt{2/\pi N}\, 2^N$. **(A)** Compute the entropy $\sigma = \sigma(U)$ and plot your result versus the average energy U. **(B)** Suppose the binary spin system is in thermal equilibrium with a reservoir of temperature τ. Compute the average energy $U = U(\tau)$ and plot your result versus the temperature τ.

2. Quantum oscillators (20%) Consider N independent and identical quantum oscillators with natural frequency ω. The energy of system $U = n\hbar\omega$ is quantized in units of $\hbar\omega$. The multiplicity function $g(N, n)$ can be extracted from the generating function,

$$G(N, z) = \sum_n g(N, n) z^n.$$

(A) For the simplest $N = 1$ case, find $G(1, z)$ and the corresponding multiplicity function $g(1, n)$. **(B)** Because the oscillators are independent and identical, $G(N, z)$ can be computed from $G(1, z)$ easily. Find $G(N, z)$ and the corresponding multiplicity function $g(N, n)$.

3. Overhauser effect (20%) By appropriate external setup, extra energy $\gamma\Delta\epsilon$ is extracted from the reservoir of temperature τ whenever the reservoir passes energy $\Delta\epsilon$ to the system. **(A)** Explain how the energy conservation law is modified and derive the abnormal Boltzmann distribution $P(\gamma, \epsilon)$ for the system. **(B)** For $\gamma = -1$, compute the corresponding abnormal Boltzmann distribution $P(-1, \epsilon)$. If computed correctly, your result would seem to violate the fundamental assumption of statistical physics. Explain your reasoning in details.

4. Zipper model for DNA (20%) A two-stranded DNA can be modeled by a zipper with N links: each link has a closed state with energy 0 and an open state with energy $\epsilon > 0$. The zipper can only unzip from the left end , i.e. the link number s can only open if all links to the left $(1, 2, ..., s - 1)$ are already open. At temperature τ, the probability ratio of the open and the closed states for the first link is $0 < p < 1$. **(A)** Find the partition function $Z = Z(N, p)$ in terms of the probability ratio p. **(B)** In the thermodynamic limit $N \to \infty$, the expression for the partition function simplifies. Find the average number of open links $\langle s \rangle$.

5. Sackur-Tetrode equation (20%) Entropy plays a central role in thermal and statistical physics. For ideal gas in three dimensions, Tetrode and Sackur derived the semiclassical expression for the entropy,

$$\sigma = N \left[\log\left(\frac{n_Q}{n}\right) + \frac{5}{2} \right],$$

where n is the particle density of the gas and $n_Q = (m\tau/2\pi\hbar^2)^{\frac{3}{2}}$ is the so-called quantum concentration. Starting from the partition function for a single gas molecule $Z_1 = n_Q V$, explain how one can derive the partition function Z_N for the N identical particles. Make use of appropriate thermal identities to reach the Sackur-Tetrode expression for the entropy. Do not just write down mathematical equations – explain your reasoning, logic and thoughts clearly.

6. Criterion for thermal equilibrium (Bonus 20%) A binary spin with energy $\mp\epsilon$ is in thermal equilibrium of a reservoir. The multiplicity for the binary spin is unity $g_{\rm spin} = 1$ while that for the reservoir is $g_\mathcal{R}(U) = AU^{3N/2}$, where N is a large number. It is reasonable to suspect that the criterion for thermal equilibrium is no longer $\tau_{\rm spin} = \tau_\mathcal{R}$ because $\tau_{\rm spin}$ cannot be obtained from its multiplicity function and, therefore, is ill-defined. What is the criterion for thermal equilibrium in this case then?