HW 3 Solns

QP3

(a)[2 pts] $Z_1 = \sum \exp(-\epsilon_n/\tau) = 1 + e^{-\Delta/\tau} + e^{-2\Delta/\tau}$

(b)[1 pts] The atoms are distinguishable.

$$Z_N = Z_1^N = \left(1 + e^{-\Delta/\tau} + e^{-2\Delta/\tau}\right)^N$$

(c)[1 pts] Helmholtz free energy

$$F(\tau) = -\tau \log(Z_N) = -N\tau \log(1 + e^{-\Delta/\tau} + e^{-2\Delta/\tau})$$

(d)[2 pts] Entropy

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N \log\left(1 + e^{-\frac{\Delta}{\tau}} + e^{-\frac{2\Delta}{\tau}}\right) + N\left(\frac{\Delta}{\tau}\right)\frac{e^{-\frac{\Delta}{\tau}} + 2e^{-\frac{2\Delta}{\tau}}}{1 + e^{-\frac{\Delta}{\tau}} + e^{-\frac{2\Delta}{\tau}}}$$

(e)[2 pts] Energy

$$\langle \epsilon \rangle = F + \sigma\tau = N\Delta e^{-\frac{\Delta}{\tau}}\left(\frac{1 + 2e^{-\frac{\Delta}{\tau}}}{1 + e^{-\frac{\Delta}{\tau}} + e^{-\frac{2\Delta}{\tau}}}\right)$$

(f)[2 pts]

$$\lim_{\tau\to+0} \langle \epsilon \rangle = \lim_{\tau\to+0} N\Delta e^{-\frac{\Delta}{\tau}}\left(\frac{1 + 2e^{-\frac{\Delta}{\tau}}}{1 + e^{-\frac{\Delta}{\tau}} + e^{-\frac{2\Delta}{\tau}}}\right) = \lim_{\tau\to+0} N\Delta e^{-\frac{\Delta}{\tau}} = 0$$

All the atoms are in the ground state.

$$\lim_{\tau\to+\infty} \langle \epsilon \rangle = \lim_{\tau\to+\infty} N\Delta e^{-\frac{\Delta}{\tau}}\left(\frac{1 + 2e^{-\frac{\Delta}{\tau}}}{1 + e^{-\frac{\Delta}{\tau}} + e^{-\frac{2\Delta}{\tau}}}\right) = N\Delta\left(\frac{1 + 2\cdot 1}{1 + 1 + 1}\right) = N\Delta$$

All the states are equally likely.

$$\lim_{\tau\to-\infty} \langle \epsilon \rangle = \lim_{\tau\to-\infty} N\Delta e^{-\frac{\Delta}{\tau}}\left(\frac{1 + 2e^{-\frac{\Delta}{\tau}}}{1 + e^{-\frac{\Delta}{\tau}} + e^{-\frac{2\Delta}{\tau}}}\right) = N\Delta\left(\frac{1 + 2\cdot 1}{1 + 1 + 1}\right) = N\Delta$$

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2.5) ADDITIVITY OF ENTROPY FOR TWO SPIN SYSTEMS

(a) From (17), with $N_1 = N_2 = 10^{22}$, $\delta = 10^{11}$:

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$$g_1 g_2 = (g_1 g_2)_{max} \exp(-4\delta^2/N_1) = (g_1 g_2)_{max} \times \exp(-4),$$

$$(g_1 g_2)/(g_1 g_2)_{max} \cong 0.0183.$$

Compare this with 10^{-174} for $\delta = 10^{12}$.

(b) From (1.35):

$$g(N,s) = (2/\pi N)^{\frac{1}{2}} \times 2^N \times \exp(-2s^2/N).$$

This may be applied both to the two individual systems $(N = N_1 = N_2)$, and to the combined system $(N = N_1 + N_2)$. For the two individual systems in their most probable configuration we have from (14), $\hat{s}_1 = \hat{s}_2$. Hence

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$$(g_1 g_2)_{max} = [g(N_1, \hat{s}_1)]^2 = (2/\pi N_1) \times 2^{2N_1} \times \exp(-4\hat{s}_1^{\,2}/N_1) .$$

For the combined system, $s = 2\hat{s}_1$:

$$\sum_{s_1} g_1(N_1, s_1) g_2(N_x, s - s_1) = g(2N_1, 2\hat{s}1)$$

$$= (1/\pi N_1)^{\frac{1}{2}} \times 2^{2N_1} \times \exp(-4\hat{s}_1^{\,2}/N_1) \quad .$$

The two results differ by the factor

$$g(2N_1,2\hat{s}_1)/[g(N_1,\hat{s}_1)]^2 = (N_1/2\pi)^{\frac{1}{2}} \cong 4\times10^{10} \quad .$$

(c) The true entropy of the interacting combined system is

14

$$\sigma = \log g(2N_1,2\hat{s}_1) = 2N_1 \log 2 - 4\hat{s}_1{}^2/N_1 - \tfrac{1}{2}\log(\pi N_1)$$

$$\cong 1.3863\times10^{22} - 10^{18} - 25.9 \cong 1.3862\times10^{22} \quad .$$

The error made in the entropy by estimating the entropy as $\log(g_1g_2)_{max} = \sigma_1+\sigma_2$ is $\log(4\times10^{10}) \cong 24.4$. This is a fractional error of 1.76×10^{-21}.

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3.3) FREE ENERGY OF AN HARMONIC OSCILLATOR

The partition function is a geometric series:

$$Z = \sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau) = 1/[1-\exp(-\hbar\omega/\tau)].$$

(a) Inserted into (55):

16 $$F = -\tau \log Z = \tau \log[1-\exp(-\hbar\omega/\tau)] \quad . \tag{87}$$

At high temperatures, $\hbar\omega/\tau \ll 1$, so that $1-\exp(-\hbar\omega/\tau) \cong \hbar\omega/\tau$. Hence from (S1):

$$F \cong \tau \log(\hbar\omega/\tau) \quad . \tag{S2}$$

14 (b) The expression (88) follows directly by inserting (87) into (49), $\sigma = -(\partial F/\partial\tau)$.

<u>Comment</u>. The low-temperature ($\tau \ll \hbar\omega$) behavior of the harmonic oscillator is the same as for the two state system with $\varepsilon = \hbar\omega$, as is apparent from comparing Figs. 3.13 and 3.14 with Figs. 3.11 and 3.4: Only the two lowest states matter. The high-temperature behavior ($\tau \gg \hbar\omega$) is quite different, because the number of accessible states is not limited to 2. In this limit, from (S2):

$$\sigma = -(\partial F/\partial\tau) \rightarrow 1 + \log(\tau/\hbar\omega).$$

If this is inserted into (17a):

$$C_V = \tau(\partial\sigma/\partial\tau) \rightarrow 1,$$

in fundamental units.

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3.7) ZIPPER PROBLEM

(a) A state in which s links are open can be realized in only one way. Thus the partition function is

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$$Z = 1 + \exp(-\varepsilon/\tau) + \exp(-2\varepsilon/\tau) + \ldots + \exp(-N\varepsilon/\tau) \quad .$$

$$= \sum_{s=0}^{N} x^s = \frac{1-x^{N+1}}{1-x} \quad , \text{ where } x = \exp(-\varepsilon/\tau) \quad . \qquad (93)$$

(b) The average number of open links is

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$$\langle s \rangle = \frac{1}{Z} \sum_{s=0}^{N} s x^s = x \frac{d}{dx} \log Z \quad . \qquad (S1)$$

If $\varepsilon \gg \tau$, then $x \ll 1$, and we may neglect the term x^{N+1} in (93) to obtain

$$\langle s \rangle = - x \frac{d}{dx} \log(1-x) = \frac{x}{1-x} = 1/[\exp(\varepsilon/\tau) - 1] \quad .$$

This is of the form of the Planck distribution.

Extension. Our assumption that each link has only one open state is an unrealistic assumption, which neglects that the two halves of an open link may have many different orientations relative to each other. It is instructive to generalize the problem by assuming that each open link has G open states with the energy ε. The change has far-reaching consequences. A state of the zipper with s open links is then G^s-fold degenerate, and the partition function now becomes

$$Z = 1 + G\exp(-\varepsilon/\tau) + G^2\exp(-2\varepsilon/\tau) + \ldots$$

$$\ldots + G^N\exp(-N\varepsilon/\tau) = \sum_{s=0}^{N} x^s = \frac{1-x^{N+1}}{1-x} \quad ,$$

where

$$x = G\exp(-\varepsilon/\tau) \quad ,$$

which differs from the earlier form only by the factor $G > 1$ in the definition of x. Because of this factor, values $x > 1$ are now possible. This has drastic consequences if the total number of links is very large, $N \gg 1$. In this case the opening of the zipper approaches the behavior of an abrupt phase transition at the sharp transition temperature

$$\tau_0 = \varepsilon/\log G \quad ,$$

which is the temperature for which $x = 1$. For temperatures very little below τ_0, only a very small fraction of the links are open, for temperatures very little above τ_0 almost all links are open. The larger N, the narrower the temperature interval over which the opening takes place. We give here only the key points in the derivation of this result.

It is not difficult to show that the expression (S1) for $\langle s\rangle$ can be written as

$$\langle s \rangle \cong (N+1)\left[\frac{1}{1-\exp(-y)} - \frac{1}{y}\right] \tag{S2}$$

where

$$y = -(N+1) \times \varepsilon \times \Delta(1/\tau) \cong +(N+1)(\log G)^2(\Delta\tau/\tau_0) \tag{S3}$$

and where in the 1/y-term in (S2) we assumed $|y| << N+1$. If N is very large, this does not exclude values $|y| >> 1$. If $|y| >> 1$ the square bracket in (S2) is easily seen to have the limits

$$[\ldots] \cong \begin{cases} 1/|y| & \text{for} \quad -y >> 1 \ , \\ 1 - 1/y & \text{for} \quad +y >> 1 \ . \end{cases}$$

For example, for $y = \mp 100$, we have $\langle s \rangle/(N+1) \cong 0.01$ and 0.99, corresponding to 1% or 99% open links. But if N is much larger than $|y|$, these values of y correspond to a very small temperature deviation from τ_0. Suppose $N+1 = 1000$ and $\log G = 10$. Then, from (S3), $y = \mp 100$ corresponds to $\Delta\tau/\tau_0 = \mp 10^{-5}$, a very narrow transition interval indeed.

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