Physics 6311: Stat. Mech. - Solutions of Homework 5

Problem 1: Comparison of the microcanonical and canonical ensembles: system of two-level atoms

a) Microcanonical ensemble

$N_0 + N_1 = N$, $n_0 = N_0/N$, $n_1 = N_1/N$, $n_0 + n_1 = 1$
$E = N_0E_0 + N_1E_1 = N_1\epsilon$

(i) $\Omega = N!/(N_0!N_1!)$
$S = k_B \ln \Omega = k_B[\ln(N!) - \ln(N_0!) - \ln(N_1!)]$
minimum S: $S = 0$ for $N_0 = 0, N_1 = N$ or $N_0 = N, N_1 = 0$
(just a single microstate, i.e maximum order)
maximum S: $S = k_B[\ln(N!) - 2\ln(N/2!)]$
(maximum disorder)
$S/N = (k_B/N)[N \ln N - N - N_0 \ln N_0 + N_0 - N_1 \ln N_1 + N_1]$
$S/N = k_B[-(N_0/N) \ln N_0 - (N_1/N) \ln N_1 + \ln N]$
$S/N = k_B[-(N_0/N) \ln(N_0/N) - (N_1/N) \ln(N_1/N)]$
$S/N = k_B[-n_0 \ln n_0 - n_1 \ln n_1]$

(ii) $1/T = (\partial S/\partial E)$, $E = N_1\epsilon$
$1/T = (1/\epsilon)(\partial S/\partial N_1) = (1/\epsilon)(\partial(S/N)/\partial(N_1/N))$
$1/T = (k_B/\epsilon)(\partial/\partial n_1)[-(1 - n_1) \ln(1 - n_1) - n_1 \ln n_1]$
$1/T = (k_B/\epsilon)[\ln(1 - n_1) + 1 - ln n_1 - 1]$
$1/T = (k_B/\epsilon) \ln(n_0/n_1)$
$k_BT = \epsilon/ \ln(n_0/n_1)$
$T > 0$ if $n_0 > n_1$, usual case – occupation probability decreases with increasing energy
$T < 0$ if $n_0 < n_1$, inversion, important i.e in lasers, in *equilibrium* only possible with bounded energy spectrum
with increasing energy the temperature goes $T = 0+ \rightarrow +\infty \rightarrow -\infty \rightarrow 0-$

(iii) $C = (\partial E/\partial T) = \epsilon(\partial N_1/\partial T)$
$1/C = (1/\epsilon)(\partial T/\partial N_1) = 1/(Nk_B)(\partial/\partial n_1)[1/ \ln((1 - n_1)/n_1)]$
$1/C = -1/(Nk_B)1/ \ln^2(n_0/n_1)(-1/n_0 - 1/n_1)$
$C = Nk_Bn_0n_1 \ln^2(n_0/n_1)$
$C > 0$ for all temperatures!

b) Canonical ensemble

(i)

$$Z_1(\beta) = 1 + e^{-\beta\epsilon}, \quad p_0 = 1/(1 + e^{-\beta\epsilon}), \quad p_1 = e^{-\beta\epsilon}/(1 + e^{-\beta\epsilon})$$
$$A = -Nk_BT \ln Z_1(\beta) = -Nk_BT \ln(1 + e^{-\beta\epsilon})$$

(ii)

$$U = -N(\partial \ln Z_1/\partial\beta) = N\epsilon e^{-\beta\epsilon}/(1 + e^{-\beta\epsilon}) = N\epsilon p_1$$

$$TS = (U - A) = N\epsilon e^{-\beta\epsilon}/(1 + e^{-\beta\epsilon}) + Nk_BT\ln(1 + e^{-\beta\epsilon})$$
$$C = (\partial U/\partial T) = \frac{N\epsilon^2}{k_BT^2}\frac{e^{\epsilon/k_BT}}{(1 + e^{\epsilon/k_BT})^2}$$

(iii)

$$k_BT = \epsilon/\ln(p_0/p_1)$$
$$U = N\epsilon p_1$$
$$C = Nk_B\ln^2(p_0/p_1)p_0p_1$$
$$S = -k_B(p_0\ln p_0 + p_1\ln p_1)$$

Results are identical to those obtained from the microcanonical approach above.

Problem 2: Two interacting magnetic moments (10 points)

a) In the ground state, the two moments will be parallel.

b)

$$Q = \int d\phi d\theta \ \sin\theta \ \exp(\beta J \cos\theta) = 2\pi \int_{-1}^{1} dx \ \exp(\beta J x) = \frac{4\pi}{\beta J} \sinh(\beta J)$$

$$A = -k_B T \ln\left[\frac{4\pi}{\beta J} \sinh(\beta J)\right]$$

c)

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = -J \coth(\beta J) + 1/\beta$$

$$C = \frac{\partial \langle E \rangle}{\partial T} = k_B \left[1 + \frac{J^2}{k_B^2 T^2}(1 - \coth^2(\beta J))\right]$$

d) At low temperatures, the angle θ will be small. Thus we can expand $\sin\theta \approx \theta$ and $\cos\theta \approx 1 - \theta^2/2$.

$$\langle \theta \rangle = \frac{\int_0^\infty \theta d\theta \ \theta \exp(-\beta J \theta^2/2)}{\int_0^\infty \theta d\theta \ \exp(-\beta J \theta^2/2)} = \sqrt{\pi/(2\beta J)}$$

$$\langle \theta^2 \rangle = \frac{\int_0^\infty \theta d\theta \ \theta^2 \exp(-\beta J \theta^2/2)}{\int_0^\infty \theta d\theta \ \exp(-\beta J \theta^2/2)} = 2/(\beta J)$$

$$\langle \theta^2 \rangle - \langle \theta \rangle^2 = \frac{k_B T}{J}(2 - \pi/2)$$

One could argue that $\langle \theta \rangle = 0$ because of symmetry. This depends on how exactly you define θ. I count both answers as correct.

Problem 3: Specific heat of an anharmonic oscillator

At low temperatures, the particle is close to the minimum of the potential at $x = 0$! We can therefore expand the potential in a power series about $x = 0$. The kinetic energy is quadratic in the momentum, it thus contributes $k_B/2$ to the specific heat, and we can focus on the positional part of Q.

$$Q_{pot} = \int_{-\infty}^{\infty} dx \exp[-\beta V_0 \cosh(x/x_0)] = \int_{-\infty}^{\infty} dx \exp[-\beta V_0(1+x^2/(2x_0^2)+x^4/(4!\, x_0^4)+x^6/(6!\, x_0^6)+O(x^8))]$$

The quadratic term restricts the x values to $|x| \lesssim x_{max} = \sqrt{x_0^2/\beta}$. Therefore, the higher order terms in the expansion are of order T or smaller for small T, and we can expand the exponentials of these terms.

$$Q_{pot} \sim \int_{-\infty}^{\infty} dx \exp[-\beta V_0 x^2/(2x_0^2)] \left\{1 - \beta V_0 x^4/(4!\, x_0^4) - \beta V_0 x^6/(6!\, x_0^6) + (\beta V_0 x^4/(4!\, x_0^4))^2/2 + O(\beta x^8)\right\} =$$

$$= \sqrt{2\pi x_0^2/\beta V_0} \left[1 - 3/(4!\beta V_0) - 15/(6!\beta^2 V_0^2) + 105/[2 * 4!^2 \beta^2 V_0^2]\right]$$

$$\ln Q_{pot} = -\frac{1}{2} \ln \beta + \ln \left[1 - 1/(8\beta V_0) + 9/(128\beta^2 V_0^2)\right]$$

For small T, the log can be expanded $\ln(1+x) = 1 + x - x^2/2 + ...$

$$\ln Q_{pot} = -\frac{1}{2} \ln \beta - 1/(8\beta V_0) + 1/(16\beta^2 V_0^2)$$

$$\langle E_{pot} \rangle = -\frac{\partial \ln Q_{pot}}{\partial \beta} = 1/(2\beta) - 1/(8\beta^2 V_0) + 1/(8\beta^3 V_0^2)$$

$$C = \frac{\partial \langle E \rangle}{\partial T} = \frac{k_B}{2} + \frac{k_B}{2} - \frac{k_B^2 T}{4V_0} + \frac{3k_B^3 T^2}{8V_0^2}$$