Statistical physics: Handin 1

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Task 1

Given a harmonic oscillator, with angular frequency ω_0; with the classical definition of H:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2.$$

a)

Calculate the Canonical partition function Z for the harmonic oscillator.

The partition function, in a continuous canonical ensemble, is given by:

$$\begin{aligned}
Z &= \frac{1}{h}\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \left[e^{-\beta H(q,p)}\right] \\
&= \frac{1}{h}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \left[\exp\left\{-\beta\left[\frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right]\right\}\right] \\
&= \frac{1}{h}\int_{-\infty}^{\infty} dx \exp\left[-\frac{\beta m\omega_0^2 x^2}{2}\right]\int_{-\infty}^{\infty} dp \exp\left[-\beta\left[\frac{p^2}{2m}\right]\right] \\
&= \frac{1}{h}\left(\frac{2\pi}{\beta\omega_0}\right).
\end{aligned}$$

b)

Calculate the average energy, $\langle E\rangle$ and the specific heat capacity.

The average energy is given by:

$$\begin{aligned}
\langle E\rangle &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\
&= -\frac{h\beta\omega_0}{2\pi}\cdot\left(-\frac{1}{h}\frac{2\pi}{\beta^2\omega_0}\right) \\
&= \frac{1}{\beta}.
\end{aligned}$$

The specific heat capacity C_v is computed accordingly:

$$\begin{aligned}
C_v &= \frac{\partial \langle E\rangle}{\partial T} \\
&= \frac{\partial}{\partial T}\left(k_b T\right) = k_b.
\end{aligned}$$

Task 2

The same oscillator as in the previous task, but with a quantum mechanical point of view leads to the eigenvalues:

$$E_n = \left(n + \frac{1}{2}\right) hf,$$

where f is the natural frequency of the oscillator.

a)

Evaluate the partition function Z, for a single harmonic oscillator.

The partition function is now discrete and thus is given by:

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta E_n} \\ &= \sum_{n=0}^{\infty} \exp\left[-\beta \left(n + \frac{1}{2}\right) hf\right] \\ &= \exp\left[-\frac{\beta hf}{2}\right] \sum_{n=0}^{\infty} \exp\left[-\beta n hf\right] \\ &= \exp\left[-\frac{\beta hf}{2}\right] \frac{1}{1 - \exp\left[-\beta hf\right]}. \end{aligned} \tag{1}$$

b)

From the partition function, find the average energy $\langle E\rangle$ at a temperature T. Also take the limit $T \to \infty$.

Using eq. (1) we can compute the average energy:

$$\begin{aligned}
\langle E\rangle &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\
&= -\left[\exp\left[-\frac{\beta h f}{2}\right]\frac{1}{1-\exp\left[-\beta h f\right]}\right]^{-1}\frac{\partial}{\partial \beta}\left(\exp\left[-\frac{\beta h f}{2}\right]\frac{1}{1-\exp\left[-\beta h f\right]}\right) \\
&= \left\{\frac{\partial}{\partial \beta}\left(\exp\left[-\frac{\beta h f}{2}\right]\right)\cdot\frac{1}{1-\exp\left[-\beta h f\right]}+\frac{\partial}{\partial \beta}\left(\frac{1}{1-\exp\left[-\beta h f\right]}\right)\cdot\exp\left[-\frac{\beta h f}{2}\right]\right\} \\
&\cdot(-1)\left[\frac{1-\exp\left[-\beta h f\right]}{\exp\left[-\frac{\beta h f}{2}\right]}\right] \\
&= \left\{-\frac{hf}{2\left(1-\exp\left[-\beta h f\right]\right)}\exp\left[-\frac{\beta h f}{2}\right]-\frac{hf\exp\left[\beta h f\right]}{\left(\exp\left[\beta h f\right]-1\right)^2}\cdot\exp\left[-\frac{\beta h f}{2}\right]\right\} \\
&\cdot(-1)\left[\frac{1-\exp\left[-\beta h f\right]}{\exp\left[-\frac{\beta h f}{2}\right]}\right] \\
&= \left\{\frac{hf}{2}+\frac{\left(1-\exp\left[-\beta h f\right]\right)\cdot hf\exp\left[\beta h f\right]}{\left(\exp\left[\beta h f\right]-1\right)^2}\right\} \\
&= \frac{hf}{2}+\frac{hf}{e^{\beta h f}-1} = \frac{hf}{2}\coth\left(\frac{\beta h f}{2}\right).
\end{aligned}$$

In the limit when $T \to \infty$ one has that $\beta \to 0$ which gives:

$$\langle E\rangle_\infty = \lim_{\beta\to 0} = \left\{\frac{hf}{2}\coth\left(\frac{\beta h f}{2}\right)\right\} = \infty$$

c)

Compute the specific heat capacity C_V for this system.

The specific heat capacity is given by:

$$\begin{aligned}
C_v &= \frac{\partial\langle E\rangle}{\partial T} \\
&= \frac{\partial}{\partial T}\left(\frac{hf}{2}\coth\left(\frac{hf}{2k_bT}\right)\right) \\
&= \frac{h^2f^2}{4k_bT^2}\frac{1}{\sinh^2\left(\frac{hf}{2k_bT}\right)}.
\end{aligned}$$

d)

Find an expression for the Helmholtz free energy for this system.

Helmholtz free energy is given by:

$$\begin{aligned}
\mathcal{F} &= -Tk_b \ln(Z) \\
&= -Tk_b \ln\left(\exp\left[-\frac{\beta hf}{2}\right]\frac{1}{1-\exp\left[-\beta hf\right]}\right) \\
&= -Tk_b\left[-\frac{\beta hf}{2} + \ln\left(\frac{1}{1-\exp\left[-\beta hf\right]}\right)\right] \\
&= \frac{hf}{2} + Tk_b \ln\big(1-\exp\left[-\beta hf\right]\big).
\end{aligned}$$

e)

Find an expression for the entropy of this system as a function of temperature.

The entropy of the system is given by:

$$\begin{aligned}
S &= -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_{V,N} \\
&= \frac{\partial}{\partial T}\left[\frac{hf}{2} + Tk_b \ln\left(1-e^{-\frac{hf}{k_bT}}\right)\right] \\
&= k_b \ln\left(1-e^{-\frac{hf}{k_bT}}\right) + \frac{hf}{k_bT}\frac{e^{-\frac{hf}{k_bT}}}{1-e^{-\frac{hf}{k_bT}}}.
\end{aligned}$$

Task 3

A specific system of N distinguishable particles has the Hamiltonian on the form:

$$H = -\mu B \sum_{i=1}^{N} S_i; \quad S_i \in \{-1, 0, 1\}.$$

a)

Write the canonical partition function for this system and hence find the free energy. (hint: First find the partition function for one particle!)

We consider that a single particle can have three different state $S_i \in \{-1, 0, 1\}$, and thus the partition function for a single particle is given by:

$$\begin{aligned}
Z_1 &= \sum_{S_i \in \{-1,0,1\}} e^{-\beta H} = e^{\beta\mu B} + 1 + e^{-\beta\mu B} \\
&= 2\cosh(\beta\mu B) + 1.
\end{aligned}$$

The partition function for N particles is then given by:

$$\begin{aligned}
Z &= \prod_{i=1}^{N} Z_1 \\
&= \prod_{i=1}^{N} \big(2\cosh(\beta\mu B) + 1\big) \\
&= \big(2\cosh(\beta\mu B) + 1\big)^N.
\end{aligned}$$

The free energy $\mathcal{F}$ is given:

$$
\begin{aligned}
\mathcal{F} &= -k_b T \ln(Z) \\
&= -N k_b T \ln\left(2\cosh(\beta\mu B) + 1\right).
\end{aligned}
$$

b)

Find the average energy U and entropy S and simplify these expressions in the limits $T \to 0$ and $T \to \infty$.

We compute the average energy $U = \langle E \rangle$ by the following:

$$
\begin{aligned}
\langle E \rangle &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\
&= -\frac{N(2\sinh(\mu\beta B)\mu B)}{(1+\cosh(\mu\beta B))^N} \cdot (1+\cosh(\mu\beta B))^{N-1} \\
&= -N\mu B \frac{\sinh(\beta\mu B)}{\cosh(\beta\mu B)+1} \\
&= -N\mu B \tanh\left(\frac{\mu\beta B}{2}\right)
\end{aligned}
$$

The entropy S is computed accordingly:

$$
\begin{aligned}
S &= \frac{\langle E \rangle}{T} + k_b \ln(Z) \\
&= -BN\mu \frac{\tanh\left(\frac{\mu B}{2k_b T}\right)}{T} + k_b \ln\left(\left(2\cosh\left(\frac{\mu B}{k_b T}\right) + 1\right)^N\right) \\
&= -BN\mu \frac{\tanh\left(\frac{\mu B}{2k_b T}\right)}{T} + N k_b \ln\left(\left(2\cosh\left(\frac{\mu B}{k_b T}\right) + 1\right)\right).
\end{aligned}
$$

In the two limits one has the following:

$$
\begin{aligned}
S_\infty &= \lim_{T\to\infty}\left[-NB\mu \frac{\tanh\left(\frac{\mu B}{2k_b T}\right)}{T} + N k_b \ln\left(\left(2\cosh\left(\frac{\mu B}{k_b T}\right) + 1\right)\right)\right] \\
&= 0, \\
\langle E \rangle_\infty &= \lim_{T\to\infty}\left[-NB\mu \tanh\left(\frac{\mu B}{2k_b T}\right)\right] = 0, \\
S_0 &= \lim_{T\to 0}\left[-NB\mu \frac{\tanh\left(\frac{\mu B}{2k_b T}\right)}{T} + N k_b \ln\left(\left(2\cosh\left(\frac{\mu B}{k_b T}\right) + 1\right)\right)\right] \\
&= \infty, \\
\langle E \rangle_0 &= \lim_{T\to 0}\left[-BN\mu \tanh\left(\frac{\mu B}{2k_b T}\right)\right] = \mp NB\mu.
\end{aligned}
$$

The average energy is discontinuous at $T = 0$, and thus has a left and right limit. The entropy has a singularity at $T = 0$.

Task 4

Consider the canonical ensemble (and the canonical partition function).

a)

Show that the average energy $E = -\frac{\partial}{\partial\beta}\left(\ln(Z)\right)$. What would $E = -\frac{\partial}{\partial\beta}\left(\ln(Z_g)\right)$ be if Z_g is the grand Canonical partition function?

The average energy is given by:

$$\begin{aligned}
\langle E \rangle &= \sum_i E_i p_i = \frac{1}{z}\sum_i E_i e^{\beta E_i} \\
&= -\frac{1}{Z}\sum_i E_i \frac{\partial}{\partial\beta}\left(e^{-\beta E_i}\right) \\
&= -\frac{1}{Z}\frac{\partial}{\partial\beta}\left(\sum_i E_i e^{-\beta E_i}\right) \\
&= -\frac{\partial}{\partial\beta}\ln\left(\sum_i e^{-\beta E_i}\right) \\
&= -\frac{\partial}{\partial\beta}\ln(Z).
\end{aligned}$$

If one instead considers the grand canonical partition function Z_g, and evaluates the above, one obtains:

$$\begin{aligned}
-\frac{\partial}{\partial\beta}\ln(Z_g) &= -\frac{\partial}{\partial\beta}\ln\left(\sum_i e^{-\beta(E_i-\mu N_i)}\right) \\
&= \frac{\sum_i (E_i - N_i\mu)\exp\left[-\beta(E_i - N_i\mu)\right]}{\sum_i \exp\left[\beta(E_i - \mu N_i)\right]}
\end{aligned}$$

b)

Show that the fluctuations in the energy average energy:

$$\Delta E^2 = \bar{E}^2 - \left(\bar{E}\right)^2$$

is proportional to the specific heat capacity. Can specific heat capacity be negative?

In order to show that the fluctuations in the ΔE^2 is proportional to the specific heat capacity, we first compute the fluctuations:

$$\begin{aligned}
\Delta E^2 &= \langle E^2 \rangle - \langle E \rangle^2 \\
&= \frac{\sum_i E_i^2 \exp\left(E_i\beta\right)}{\sum_i \exp\left(E_i\beta\right)} - \left(\frac{\sum_i E_i \exp\left[E_i\beta\right]}{\sum_i \exp\left[E_i\beta\right]}\right)^2 \\
&= \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 \\
&= \frac{\partial^2}{\partial\beta^2}\left[\ln(Z)\right]
\end{aligned}$$

The heat capacity is given by:

$$\begin{aligned} C_v &= \frac{\partial \langle E \rangle}{\partial T} \\ &= \frac{\partial}{\partial T}\frac{\partial}{\partial \beta}\left[\ln(Z)\right] \\ &= \frac{1}{k_b T^2}\frac{\partial^2}{\partial \beta^2}\left[\ln(Z)\right]. \end{aligned}$$

By this, one has that $\Delta E^2 = k_b T^2 C_v$, i.e. $C_v \propto \Delta E^2$. Moreover, the specific heat capacity can be negative. This often occurs in stellar system with the phenomena called 'negative heat capacity', as well as in ions. In terms of the expression for the specific heat, the following can be debated:

$$C_v = \underbrace{\frac{1}{k_b T^2}}_{>=0}\underbrace{\Delta E^2}_{?}.$$

The first term is always zero or positive, however zero temperature have never been observed, however the second term could potentially be negative. This would then in turn lead to a negative heat capacity.

Task 5

Consider the following definition of entropy,

$$S = -k_b \sum_s P(s)\ln(P(s)), \tag{2}$$

where s is a microstate of the system and $P(s)$ is the probability of the system being in the microstate s.

a)

Show that this definition of entropy is equivalent to our usual definitions, for a system in thermal equilibrium with a reservoir at temperature T.

Let $P(s)$ be the probability of the system being in a microstate s, then:

$$P(s) = \frac{e^{-\beta E_s}}{Z}; \quad Z = \sum_s e^{-\beta E_s}.$$

Substituting the expression for $P(s)$ into eq (2) yields:

$$\begin{aligned}
S &= -k_b \sum_s \left[\frac{e^{-\beta E_s}}{Z} \cdot \ln\left(\frac{e^{-\beta E_s}}{Z} \right) \right] \\
&= -k_b \sum_s \left[\frac{e^{-\beta E_s}}{Z} \cdot \left(\ln\left(e^{-\beta E_s}\right) - \ln(Z) \right) \right] \\
&= -k_b \sum_s \left[\frac{e^{-\beta E_s}}{Z} \cdot \left(-\beta E_s - \ln(Z) \right) \right] \\
&= k_b \sum_s \left[\frac{e^{-\beta E_s}}{Z} \cdot (\beta E_s) \right] + k_b \ln(Z) \underbrace{\sum_s \left[\frac{e^{-\beta E_s}}{Z} \right]}_{=1} \\
&= \frac{\langle E \rangle}{T} + k_b \ln(Z) .
\end{aligned}$$

Thus, as shown above, the definition of entropy in eq. (2) is equivalent to the usual definition of entropy which is used in previous tasks.

b)

Show that this definition is consistent even for a system in contact with a reservoir at fixed temperature T and fixed chemical potential μ. (Hint: remember $kT\ln(Z_g) = PV$ where Z_g is the grand partition function!).

In order to show that the solution is consistent, we first say that the probability of a microstate s is given by:

$$P(s) = \frac{e^{-\beta(E_s - \mu N_s)}}{Z_g}; \quad Z_g = \sum_s e^{-\beta(E_s - \mu N_s)}.$$

We use this result in the definition of entropy in eq. (2):

$$\begin{aligned}
S &= -k_b \sum_s \left[\frac{e^{-\beta(E_s - \mu N_s)}}{Z_g} \ln\left(\frac{e^{-\beta(E_s - \mu N_s)}}{Z_g} \right) \right] \\
&= -k_b \sum_s \left[\frac{e^{-\beta(E_s - \mu N_s)}}{Z_g} \left(-\beta(E_s - \mu N_s) - \ln(Z_g) \right) \right] \\
&= k_b \sum_s \frac{e^{-\beta(E_s - \mu N_s)} \beta(E_s - \mu N_s)}{Z_g} + k_b \ln(Z_g) \underbrace{\sum_s \frac{e^{-\beta(E_s - \mu N_s)}}{Z_g}}_{=1} \\
&= \frac{\langle E \rangle}{T} + k_b \ln(Z_g) \frac{T}{T} \\
&= \frac{\langle E \rangle}{T} + \frac{PV}{T} .
\end{aligned}$$