1. Show that in the canonical ensemble we have

$$C_V = T^{-2}\langle(E - \langle E\rangle)^2\rangle \qquad (1)$$

which shows that the heat capacity is related to the magnitude of fluctuations of the energy of a system about its mean value

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$$\langle(E-\langle E\rangle)^2\rangle = \langle E^2 - 2E\langle E\rangle + \langle E\rangle^2\rangle = \langle E^2\rangle - 2\langle E\rangle^2 + \langle E\rangle^2$$
$$= \langle E^2\rangle - \langle E\rangle^2$$

From last week's homework (or many other sources) we have learned:

$$\langle E\rangle = \frac{\sum E_n \exp(-\beta E_n)}{\sum \exp(-\beta E_n)} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

And also: $$\langle E^2\rangle = \frac{\sum E_n^2 \exp(-\beta E_n)}{Z} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

(In the case of continues energy levels the sums turn into integrals, but the expression as derivatives remain unchanged)

And additionally: $$C_V = \frac{\partial\langle E\rangle}{\partial T} = -\frac{1}{T^2}\frac{\partial}{\partial\beta}\langle E\rangle$$

So, plugging everything in:

$$\langle(E-\langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) = -\frac{\partial}{\partial\beta}\langle E\rangle = T^2 C_V$$

$$\Leftrightarrow \quad \boxed{C_V = T^{-2}\langle(E-\langle E\rangle)^2\rangle}$$

2. Consider a one-dimensional classical gas of distinguishable particles moving in a single-particle potential $U_i = \kappa x_i^2$, so that the energy of the system is $E = \sum_i^N (p_i^2/2m + \frac{1}{2}m\omega^2 x_i^2)$ with $\omega = \sqrt{2\kappa/m}$. Assume that the system can move anywhere in the $2N$-dimensional phase space.

(a) Calculate the volume of phase space with energy below some energy E, and use this to calculate the number of states with energy at or below E, $\Sigma(E)$, assuming the fiducial phase space volume is h for this one-dimensional system. You may need the result

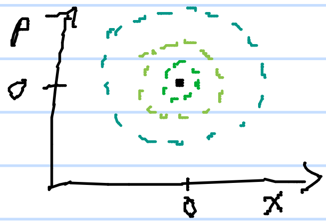
$$\int_{-\infty}^{\infty} dx_1 \ldots \int_{-\infty}^{\infty} dx_M \Theta(R^2 - \sum_{i=1}^{M} x_i^2) = \frac{\pi^{M/2}}{\Gamma(M/2+1)} R^M, \qquad (2)$$

which is just the M-dimensional volume of an M-sphere of radius R. Here

$$\Theta(x) = \begin{cases} 1 & \text{for } x \geq 0 \\ 0 & \text{for } x < 0 \end{cases} \qquad (3)$$

is the Heaviside step function.

For one particle:



Harmonic oscillator, so lines with constant energy in phase space are circles with $E = p^2/2m + u^2$
$= p^2/2m \big|_{x=0}$
$= u^2 \big|_{p=0}$

Those will be spheres in the phase space of the entire ensemble, because the particles don't interact.

So: $$\Omega(E) = \int_{-\infty}^{\infty}\!\!\cdots\!\int \prod_i^N [dx_i \, dp_i] \underbrace{\int_0^E d\varepsilon \, \delta\Big(\varepsilon - \Big(\sum_i^N \overbrace{\frac{p_i^2}{2m}}^{=: v_i^2} + \overbrace{\frac{m}{2}\omega^2 x_i^2}^{=: u_i^2}\Big)\Big)}_{= \Theta\left(E - \left(\sum_i \frac{p_i^2}{2m} + \frac{m}{2}\omega^2 x_i^2\right)\right)}$$

We need to transform to a space with same dimensionality along both axes by changing variables: (energy)

$$\left.\begin{aligned} v_i &:= \frac{p_i}{\sqrt{2m}} \Rightarrow dp_i = \sqrt{2m}\, dv_i \\ u_i &:= \sqrt{\tfrac{m}{2}}\,\omega x_i \Rightarrow dx_i = \sqrt{\tfrac{2}{\omega^2 m}}\, du_i \end{aligned}\right\} dp_i \, dx_i = 2\omega^{-1} dv_i \, du_i$$

So we get: $$V(E) = \int_{-\infty}^{\infty}\!\!\cdots\!\int \prod_i^N \Big[\frac{2}{\omega} dv_i \, du_i\Big] \Theta\Big(E - \sum_i (v_i^2 + u_i^2)\Big)$$
$$= \Big(\frac{2}{\omega}\Big)^N \int_{-\infty}^{\infty}\!\!\cdots\!\int \prod_i^{2N} d\tilde{x}_i \, \Theta\Big(E - \sum_i^{2N} \tilde{x}_i^2\Big)$$
$$\overset{(2)}{=} \Big(\frac{2}{\omega}\Big)^N \frac{\pi^N}{N!} E^N = \Big(\frac{2\pi}{\omega}\Big)^N \frac{E^N}{N!}$$

And $$\boxed{\Sigma(E) = \frac{V(E)}{h^N} = \Big(\frac{2\pi}{h\omega}\Big)^N \frac{E^N}{N!} = (\hbar\omega)^{-N} \frac{E^N}{N!}}$$

✓

(b) Calculate the entropy of the gas in the large N limit working in the microcanonical ensemble.

Since we calculated $\Sigma(E)$ as all states with $\varepsilon \le E$, we have:

$$\Omega(E) = \frac{d\Sigma(E)}{dE}\,\delta E = \,\sim$$

$$\Rightarrow \quad S = \ln \Omega(E) = \ln \frac{d\Sigma(E)}{dE}\,\delta(E) = \ln\left[\frac{N}{N!}(\hbar\omega)^{-N} E^{N-1}\,\delta E\right]$$

$$= \ln\left(\frac{N}{N!}\left(\frac{E}{\hbar\omega}\right)^{N}\frac{\delta E}{E}\right) \approx \underbrace{N\ln\frac{E}{\hbar\omega} + \ln N - N\ln N}_{\text{leading order}} + \underbrace{N}_{\text{2nd order}} + \ln\frac{\delta E}{E}$$

$$\ln N! = N\ln N - N + O(\ln N)$$

$$\Rightarrow \ln\frac{N}{N!} = \ln N - \ln N! \approx \ln N - N\ln N + N$$

So for large N: $S \approx N\left(\ln\frac{E}{\hbar\omega} - \ln N\right) = N \ln\frac{E}{N\hbar\omega}$

Or, if we also take the next order:

$$S \approx N\left(\ln\frac{E}{N\hbar\omega} + 1\right)$$

(c) Write down the energy of the gas in terms of the temperature using your result from part (b).

$$\left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{T} \overset{\text{here}}{=} \frac{N}{E} \Rightarrow E = (k_B)\,NT \quad (\text{ideal gas eqn of state})$$

(d) Calculate the Helmholtz free energy, entropy and energy of the gas using the canonical ensemble. These should be the same as the results you found in the microcanonical ensemble.

$Z_N = \prod_i^N Z_1$, because no interactions.

$$Z_1 = \frac{1}{h}\iint_{-\infty}^{\infty} dx\,dp\,\exp(-\beta\varepsilon), \quad \varepsilon = \frac{p^2}{2m} + \frac{m}{2}\omega^2 x^2)$$

$$= \frac{1}{h}\int_{-\infty}^{\infty} dp\,\exp\left(-\beta\frac{p^2}{2m}\right)\int_{-\infty}^{\infty} dx\,\exp\left(-\frac{\beta m}{2}\omega^2 x^2\right)$$

Using $\int_{-\infty}^{\infty} dx\,\exp(-|\alpha|x^2) = \sqrt{\frac{\pi}{|\alpha|}}$

$$= \frac{1}{h}\sqrt{\frac{2m\pi}{\beta}}\sqrt{\frac{2\pi}{\beta m\omega^2}} = \frac{2\pi T}{h\omega} = \frac{T}{\hbar\omega}\cdot k_B$$

$$F = -T\ln Z_N = -NT\ln\frac{T}{\hbar\omega} = -NT\left[\ln T - \ln\hbar\omega\right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = N\left(\ln\frac{T}{\hbar\omega} + \frac{T}{T}\right) = N\left(\ln\frac{T}{\hbar\omega} + 1\right)$$

Legendre trafo to get E: $F = E - TS$

$$\Rightarrow E = F + TS = -\cancel{NT\ln\frac{T}{\hbar\omega}} + NT\left(\cancel{\ln\frac{T}{\hbar\omega}} + 1\right) = NT$$

Everything the same as before! ✓

(e) Calculate the Helmholtz free energy from the canonical partition function for a system of N one-dimensional quantum harmonic oscillators with single-particle energies $\epsilon_i = \frac{1}{2}\omega(2n_i + \frac{1}{2})$ (with $n_i \in \{0, 1, 2, \ldots, \infty\}$) and verify that you arrive at the same result as for the classical expression in the ~~low density~~ high T limit aside from a zero-point energy offset.

$$Z_1 = \mathrm{tr}\left(e^{-\beta H}\right) = \sum_{i=0}^{\infty} \exp(-\beta\epsilon_i) = \exp\left(-\beta\frac{\hbar}{2}\omega\right)\sum_{i=0}^{\infty}\exp(-\beta\hbar\omega i)$$

$$\sum_{i=0}^{N}\exp(-\beta\hbar\omega i) = \sum_{i=0}^{\infty}\alpha^i, \quad \alpha = \exp(-\beta\hbar\omega)$$

$$= \frac{1}{1-\alpha}, \quad |\alpha| < 1$$

$$= \exp\left(-\beta\frac{\hbar\omega}{2}\right)\left(1 - \exp(-\beta\hbar\omega)\right)^{-1}$$

Again: $Z_N = Z_1^N$ (No interaction)

$$F = -T\ln Z_N = -NT\left(\ln\left[\frac{1}{1-\exp(-\beta\hbar\omega)}\right] - \beta\frac{\hbar\omega}{2}\right)$$

High T limit: $\exp(-\beta\hbar\omega) \approx 1 - \beta\hbar\omega = 1 - \frac{\hbar\omega}{T}$

$$e^{-x} \overset{x \ll 1}{\approx} 1 - x + \frac{1}{2}x^2 - \ldots$$

So in high T limit:

$$F \approx -NT\left[\ln\left(\frac{1}{1-1+\beta\hbar\omega}\right) - \beta\frac{\hbar\omega}{2}\right]$$

$$= \underbrace{-NT\ln\left(\frac{T}{\hbar\omega}\right)}_{\text{same as in classical case!}} + \underbrace{N\frac{\hbar\omega}{2}}_{\text{zero offset}}$$

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3. If the "free volume" $\bar{V}$ of a classical gas is defined by the equation

$$\bar{V}^N = \int d^3r_1 \ldots d^3r_N \exp[\beta(\langle U\rangle - U(\vec{q}))]$$

where $\langle U\rangle$ is the average potential energy of the system and $U(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{i<j} u(\vec{r}_i - \vec{r}_j)$ is the total potential energy for a particular position of the particle in configuration space, then show that

$$S = k_B N \ln\left[\frac{\bar{V}}{N}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right] + \frac{5}{2}k_B N$$

In what sense is it justified to refer to the quantity $\bar{V}$ as the free volume? Substantiate your answer by considering a gas of hard spheres (*i.e.* particles with a two-body potential given by

$$u(r_{ij}) = \begin{cases} 0 & \text{for } r_{ij} > a \\ \infty & \text{for } r_{ij} < a \end{cases}$$

where a is the radius of the spheres and r_{ij} is the distance between particles i and j.)

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4. Consider a low-density, relativistic gas of particles moving in one-dimension (i.e. $\epsilon = \sqrt{p^2+m^2}$). Show that

$$\langle \frac{p^2}{\epsilon} \rangle = T$$

both by the equipartition theorem and by integration over the phase-space density in the canonical ensemble.

$$H = \sum_{i=1}^{N} \varepsilon_i \quad , \quad \varepsilon_i = \sqrt{p_i^2 + m_i^2}$$

Equipartition theorem:

$$T = \langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \frac{1}{2} \frac{2 p_i}{\sqrt{p_i^2 + m^2}} \rangle = \langle \frac{p_i^2}{\varepsilon_i} \rangle = \langle \frac{p^2}{\varepsilon} \rangle$$

Phase space integration:

$$\langle \frac{p_i^2}{\varepsilon_i} \rangle = \frac{\cancel{\int_L d^N x} \int_{-\infty}^{\infty} d^N p \, \frac{p_i^2}{\varepsilon_i} \exp(-\beta H)}{\cancel{\int_L d^N x} \int_{-\infty}^{+\infty} d^N p \, \exp(-\beta H)}$$

$$= \frac{\int_{-\infty}^{\infty} d^N p \, \frac{p_i^2}{\varepsilon_i} \exp(-\beta \sqrt{p^2+m^2})}{\int_{-\infty}^{+\infty} d^N p \, \exp(-\beta \sqrt{p^2+m^2})}$$

$$\int_{-\infty}^{\infty} d^N p \, \frac{p_i^2}{\varepsilon_i} \exp(-\beta \sqrt{p^2+m^2}) = \quad \text{I think:} \quad T \int_{-\infty}^{+\infty} d^N p \, \exp(-\beta \sqrt{p^2+m^2})$$

but don't have any more time...

$$\Rightarrow \langle \frac{p_i^2}{\varepsilon_i} \rangle = \frac{T \cancel{\int_{-\infty}^{+\infty} d^N p \, \exp(-\beta \sqrt{p^2+m^2})}}{\cancel{\int_{-\infty}^{+\infty} d^N p \, \exp(-\beta \sqrt{p^2+m^2})}} = T$$

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