1. Show that in the canonical ensemble we have

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

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

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

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 derrivatives 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:

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

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

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 $E = \sum_i^N (p_i^2/2m + \frac{m}{2}\omega^2 x_i^2)$ 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

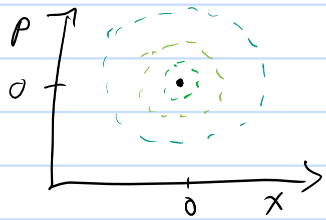
$$\int_{-\infty}^{\infty} dx_1 ... \int_{-\infty}^{\infty} dx_M \Theta(R^2 - \sum_{i=1}^{M} x_i^2) = \frac{\pi^{M/2}}{\Gamma(M/2+1)} R^M, \qquad (2)$$

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 $E = p^2/2m + u^2$
$= p^2/2m|_{x=0}$
$= u^2|_{p=0}$

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

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

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

$$\left.\begin{array}{l} v_i := \dfrac{p_i}{\sqrt{2m}} \Rightarrow dp_i = \sqrt{2m}\, dv_i \\[2ex] u_i := \sqrt{\dfrac{m}{2}}\,\omega x_i \Rightarrow dx_i = \sqrt{\dfrac{2}{\omega^2 m}}\, du_i \end{array}\right\} dp_i\, dx_i = 2\omega^{-1}\, dv_i\, du_i$$

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

$$= \Big(\frac{2}{\omega}\Big)^N \int_{-\infty}^{\infty}\cdots\int \prod_i^{2N} d\tilde{x}_i\, \Theta\Big(E - \sum_i^{2N} \tilde{x}_i^2\Big)$$

$$\overset{(2)}{=} \Big(\frac{2}{\omega}\Big)^N \frac{\pi^N}{N!} E^N = \Big(\frac{2\pi}{\omega}\Big)^N \frac{E^N}{N!}$$

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 $\varepsilon \leq E$, we have:

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

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

$$= \ln\left(\frac{N}{N!}\left(\frac{E}{\hbar\omega}\right)^{N}\frac{\delta E}{E}\right) \approx N\ln\frac{E}{\hbar\omega} + \ln N - N\ln N + N + \ln\frac{\delta E}{E}$$

leading order     2nd order

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

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

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.

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

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

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

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

$$F = -T\ln Z_N = -NT\ln\frac{T}{\hbar\omega} = -NT(\ln T - \ln\hbar\omega)$$

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

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 $\epsilon_i = \frac{\hbar}{2}\omega(2n_i + \frac{1}{2})$ (with $n_i \in$ {0, 1, 2, ..., ∞}) 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.

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

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

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

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

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

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

So in high T limit:

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

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

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

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

where $\langle U\rangle$ is the average potential energy of the system and $U(\vec{r}_1, ..., \vec{r}_N) = \sum_{i<j} u(\vec{r}_i - \vec{r}_j)$ 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 $j$.)

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:

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

Phase Space Integration:

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

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

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

but don't have any more time...

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