Lecture 15: Ideal gas entropy; Ensemble equivalence.

Reading Assignment for Lectures 15--18: PKT Chapter 7
Midterm coming up Friday, Oct 29.

Comment: Entropy, number of states, and density of microstates in energy for a large system.
For a large system (like the ideal gas), the number of microstates is enormous and the density of microstates in energy is effectively a smooth function of E.
We calculated $W(E,V,N,\Delta E)$ by finding the number of microstates per unit energy $\Omega(E,V,N)$ and multiplying by ΔE: $W(E,V,N,\Delta E) = \Omega(E,V,N)\Delta E$.
When we took the log to construct the entropy,
$S \equiv k_B \ln W = k_B \ln(\Omega \Delta E) = k_B \ln \Omega + \text{small}$.
It follows that *for a large system*, we could just as well have defined the entropy as

$S \equiv k_B \ln \Omega$ or, equivalently, $\Omega(E,V,N) = e^{\frac{1}{k_B}S(E,V,N)}$.

Note that S is positive and extensive, so the density of states is a rapidly growing function of energy.

Continuation of Calculation from Tutorial 5 of the Entropy of the ICMG:
I showed you in tutorial yesterday that the number of microstates in the energy range $E < E_n < E + \Delta E$ can be written,

$$W(E,V,N,\Delta E) = \Omega(E,V,N)\Delta E = \frac{1}{N!}\left(\frac{V}{(2\pi\hbar)^3}\right)^N S_{3N}(R)\cdot \Delta R = \frac{1}{N!}\left(\frac{V}{(2\pi\hbar)^3}\right)^N S_{3N}(R)\cdot \frac{m\Delta E}{\sqrt{2mE}},$$

where $S_{3N}(R)$ is the surface area of a (hyper)sphere of radius $R = \sqrt{2mE}$ in 3N-dimensional space.
How to calculate $S_n(R)$? There's a trick:
Consider the n-dimensional volume integral:

$$K = \int_{-\infty}^{\infty} dx_1 dx_2 ... dx_n e^{-\left(x_1^2 + x_2^2 + ... + x_n^2\right)} = \left(\int_{-\infty}^{\infty} dx e^{-x^2}\right)^n = \pi^{n/2}.$$

But, now go to (hyper)spherical coordinates with $R^2 = x_1^2 + x_2^2 + ... + x_n^2$,

$$K = \int_0^{\infty} dR\, S_n(R) e^{-R^2} = S_n(1)\int_0^{\infty} dR\, R^{n-1} e^{-R^2}$$ *(note the dimensional scaling!)*

Now change variables according to $y = R^2; dy = 2RdR$, so

$$K = S_n(1)\int_0^{\infty} dR \frac{2R}{2R} R^{n-1} e^{-R^2} = \frac{S_n(1)}{2}\int_0^{\infty} dy\, y^{(n-2)/2} e^{-y} = \frac{S_n(1)}{2}\left(\frac{n}{2}-1\right)! = \frac{S_n(1)}{n}\left(\frac{n}{2}\right)!$$

Equating these expressions:

$$S_n(1) = \frac{n\pi^{n/2}}{\left(\frac{n}{2}\right)!} \quad \Rightarrow \quad \ln S_n(1) = \frac{n}{2}\ln \pi - \ln\left(\frac{n}{2}\right)! + \ln n$$

$$S = k_B \ln W = k_B\left[N\ln\left(\frac{V}{(2\pi\hbar)^3}\right) + \ln S_{3N}(1) + \frac{3N}{2}\ln(2mE) - \ln N!\right] + \text{small}$$

Thus, $$= k_B\left[N\ln(V) + \frac{3N}{2}\ln\left(\frac{2\pi mE}{2^2\pi^2\hbar^2}\right) - \ln N! - \ln\left(\frac{3N}{2}\right)!\right] + \text{small} \qquad \textbf{15.2}$$

$$= k_B\left[N\ln(V) + \frac{3N}{2}\ln\left(\frac{mE}{2\pi\hbar^2}\right) - N\ln N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{5N}{2}\right] + \text{small}$$

So, finally,

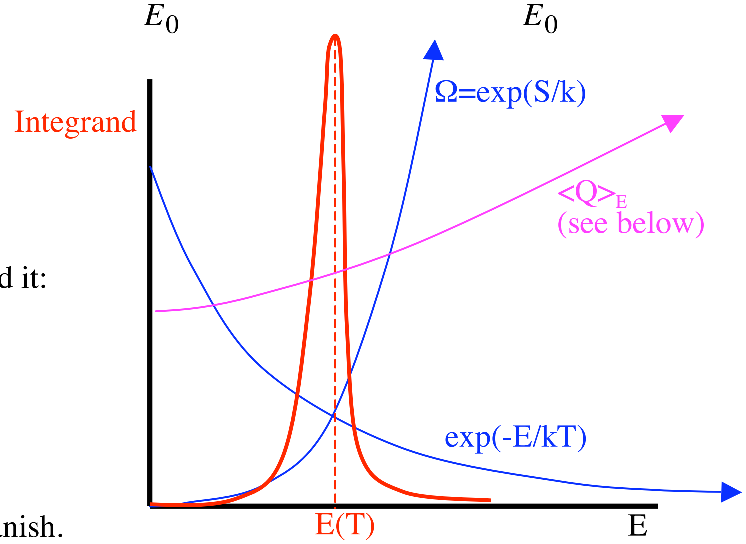
$$S((E,V,N) = Nk_B\left[\ln\left(\frac{E^{3/2}V}{N^{5/2}}\right) + \frac{3}{2}\ln\left(\frac{m}{3\pi\hbar^2}\right) + \frac{5}{2}\right],$$

which is called the Sakur-Tetrode formula.
See Lecture 13.4. The constant term was undetermined before, now has a specific value.
Left to the reader to show that this is consistent with the formula for F=E-TS.
(Logic: Stop ideal gas here and go back to general case.)

Close relation between canonical and microcanonical (equal-a-priori) ensembles for large systems.
Start with the partition function:

$$Z(T,V,N) \equiv \sum_n e^{-\frac{E_n}{k_BT}} \to \int_{E_0}^{\infty} dE\,\Omega(E,V,N)e^{-\frac{E}{k_BT}} = \int_{E_0}^{\infty} dE\, e^{\frac{1}{k_B}\left(S(E,V,N)-\frac{E}{T}\right)} = \int_{E_0}^{\infty} dE\, e^{F_{T,V,N}(E)}$$

The integrand is a product of two factors.
One Ω is rapidly increasing.
The other exp(-E/kT) is rapidly decreasing.
The overall effect is an integrand which, for a large system, is sharply peaked.



Let's look for the maximum and expand around it:
This is a theme of this part of the course!

$$\frac{\partial F}{\partial E} = \frac{1}{k_B}\left(\frac{\partial S}{\partial E} - \frac{1}{T}\right)$$

Note that T is just a parameter here.
This vanishes when E is chosen to have the particular value E(T) that makes the bracket vanish.
We now expand around the maximum:

$$\frac{\partial^2 F}{\partial E^2} = \frac{1}{k_B}\frac{\partial^2 S}{\partial E^2} \underset{E=E(T)}{\to} \frac{1}{k_B}\frac{\partial}{\partial E}\left(\frac{1}{T(E)}\right) = -\frac{1}{k_BT^2}\left.\frac{\partial T}{\partial E}\right|_{V,N} = -\frac{1}{k_BT^2}\cdot\frac{1}{\left.\frac{\partial E}{\partial T}\right|_{V,N}} = -\frac{1}{k_BT^2C_{V,N}}$$

Note the negative sign showing that the stationary point is a maximum.
Now, E is extensive and T is intensive, so the derivative in the denominator (which is the heat capacity, see Lect. 13.1) is extensive. It follows that $|E - E(T)| \sim \sqrt{N}$. In the region of the maximum, all the higher order terms in the Taylor expansion give small corrections (as for the coin-toss!), and we can do the integral,

$$Z(T,V,N) = \int_{E_0}^{\infty} dE\, e^{\frac{1}{k_B}\left(S(E,V,N) - \frac{E}{T}\right)}$$

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$$\to e^{\frac{1}{k_B}\left(S(E(T),V,N) - \frac{E(T)}{T}\right)} \int_{-\infty}^{\infty} dE\, e^{-\frac{(E-E(T))^2}{2k_B T^2 C_{V,N}}} = \sqrt{2\pi k_B T^2 C_{V,N}}\, e^{\frac{1}{k_B}\left(S(E(T),V,N) - \frac{E(T)}{T}\right)},$$

which has the consequence that

$$F(T,V,N) \equiv -k_B T \ln Z = -k_B T\left[\frac{1}{k_B}\left(S(E(T),V,N) - \frac{E(T)}{T}\right) + \frac{1}{2}\ln\left(2\pi k_B T^2 C_{V,N}\right)\right].$$

The second term is small $O(\ln N)$, so the final result is $F = E - TS$, as expected.
This same sharp peaking is a feature of (almost) any canonical average you might take:

$$\langle Q\rangle_c = \frac{1}{Z}\sum_n Q_n e^{-\frac{E_n}{k_B T}} \to \frac{1}{Z}\int_{E_0}^{\infty} dE\,\Omega(E) e^{-\frac{E}{k_B T}} \frac{\left(\sum\limits_{\substack{n \\ E<E_n<E+dE}} Q_n\right)}{\left(\begin{matrix}\#\, states \\ E < E_n < E + dE\end{matrix}\right)} = \frac{1}{Z}\int_{E_0}^{\infty} dE\,\Omega(E) e^{-\frac{E}{k_B T}} \langle Q\rangle_E$$

,
where $\langle Q\rangle_E$ is the microcanonical average of Q over microstate with energy between E and E+dE.
The first two factors in the integrand are the same as before. Unless $\langle Q\rangle_E$ varies significantly on the scale of $\sqrt{N} \sim \sqrt{E}$, we find $\langle Q\rangle_c = \langle Q\rangle_{E(T)}$ (see Figure above).

The only important exceptions are quantities like the energy fluctuations, which are by definition quite different in the two ensembles.