Lecture 4 – Energy & Entropy from Equations of State

02/11/16

continuing from Lecture 3...

ex: Non-relativistic, classical, ideal, monoatomic gas
(we don't even let it rotate! The ground-state is in an s-wave)

the # of microstates

$$S = k_B \ln(\Gamma)$$

a 6N-dimensional integral

$$= k_B \int \prod_{i=1}^{N} d^3\vec{r}_i\, d^3\vec{p}_i\, \underbrace{\delta\left(E - \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}\right)}$$

the microcanonical distribution function ρ constraining our calculation to locations in phase space with the same energy

This integral is the computation of the surface area of a 3N-dimensional sphere.

Γ not dependent on position, $d^3\vec{r} \rightarrow$ volume

$$= k_B \ln\left[V^N\, 2m \underbrace{\frac{2\pi^{3N/2}}{\Gamma(3N/2)}}\, (2mE)^{3N-1/2}\right] \quad (\mathrm{I})$$

Γ-function, not # of microstates here

radius of the sphere $= \sqrt{2mE}$

then for very large systems

can neglect this (very small w.r.t. N)

$$\lim_{N\to\infty} = k_B\left[N\ln(V) + \frac{3N-1}{2}\ln(E) - \underbrace{\ln\left\{\Gamma\left(\tfrac{3N}{2}\right)\right\}}_{\simeq \ln\left(\frac{3N}{2}!\right)} + N\ldots + \ldots\right] \quad (\mathrm{II})$$

use Stirling's appx: for N → ∞

$$\simeq \frac{3N}{2}\underbrace{\ln\left(3N/2\right)}_{= \ln(N) + \cancel{\ln(3/2)}} + \ldots$$

small

constants we don't care about (includes m-term)

→ recombine large terms

$$S \simeq k_B N \ln\left(\frac{VE^{3/2}}{N^{3/2}}\right)$$, the entropy of an ideal gas

Check: Relevant properties

① S is a function of an independent set of extensive variables

- If you double everything, you pick up a factor of $k_B N \ln(2)$

It should double, and it does not!

③ Entropy is always going to grow with energy

✓ this works

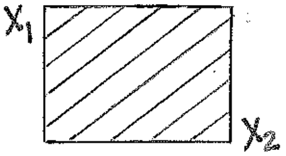
⑤ $S = 0$ for $(\partial E/\partial S|_{V,N}) = T = 0$

- This does not work, but it is also not really a concern

This is a <u>classical</u> approximation, so we don't expect it to work at supercooled conditions

⟹ We must fix the extensivity problem

This is actually a quantum statistical effect that survives even in Macroscopic conditions.



When we integrated over all space, we accidentally double-counted all our particles

- Divide by all possibilities

$$d^3\vec{r}_i\, d^3\vec{p}_i \longrightarrow \frac{d^3\vec{r}_i\, d^3\vec{p}_i}{N!}$$

Equation (I) now becomes:

$$S = k_B \ln\left[V^N 2m \frac{2\pi^{3N/2}}{\boxed{N!}\,\Gamma(3N/2)}(2mE)^{3N-1/2}\right]$$

yielding an extra term in Equation (II):

$$\lim_{N\to\infty} = k_B\left[N\ln(V) + \frac{3N-1}{2}\ln(E)\underbrace{-\ln(N!)}_{\simeq -N\ln(N)} - \ln\left[\Gamma\left(\frac{3N}{2}\right)\right] + N\ldots + \ldots\right]$$

Our "statistical fudge factor" now yields an entropy equation that satisfies extensivity

$$\Rightarrow S \simeq k_B N \ln\left(\frac{VE^{3/2}}{N^{5/2}}\right)$$

- doubling values of all variables now doubles S

→

Equations of State of a Free Gas:

- We want to inspect our E.O.S.'s now that we know the entropy equation

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N} = \frac{3}{2}\frac{k_B N}{E} \implies E = \boxed{\frac{3}{2}} N k_B T$$

we now have a better intuition about this 3/2 factor rather than just attributing it to equipartition of energy like in undergrad.

$$\frac{P}{T} = \frac{\partial S}{\partial V}\bigg|_{E,N} = \frac{k_B N}{V} \implies PV = \underbrace{N k_B T}$$

"We don't use moles in this class! Who came up with that anyway? What a silly name!"

$$\frac{-\mu}{T} = \frac{\partial S}{\partial N}\bigg|_{E,V} = k_B \ln\left(\frac{V E^{3/2}}{N^{5/2}}\right) - \frac{5}{2}k_B$$

→ These are very intuitive observables! When we don't obtain the entropy directly from first principles, we can use these to calculate it. (because S is not an easy thing to measure)

Euler Relation

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$$

└ by extensivity of variables

now take $\frac{d}{d\lambda} S(\lambda E, \lambda V, \lambda N)\big|_{\lambda=1}$

$$\underbrace{E\frac{\partial S}{\partial E}\bigg|_{V,N}}_{1/T} + \underbrace{V\frac{\partial S}{\partial V}\bigg|_{E,N}}_{P/T} + \underbrace{N\frac{\partial S}{\partial N}\bigg|_{E,V}}_{-\mu/T} = S(E,V,N)$$

$$\implies \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T} = S$$

or $E = TS - PV + \mu N$

→ These variables are not independent! Every system will satisfy this no matter the entropy.

→

We want to be able to recover S from the E.O.S.'s:

- In the case where we know <u>all three</u> E.O.S.'s

$T(E,V,N),\ P(E,V,N),\ \mu(E,V,N)$ known

$$S(E,V,N) = \frac{E}{T(E,V,N)} + \frac{P(E,V,N)}{T(E,V,N)}V - \frac{\mu(E,V,N)}{T(E,V,N)}N$$

The entropy may be expressed as a function of other state variables, such as T&P, but you only know all of the information about your system by having $S(E,V,N)$

equivalently...

$T(S,V,N),\ P(S,V,N),\ \mu(S,V,N)$ known

$$\underbrace{E(S,V,N)} = T(S,V,N)S - P(S,V,N)V + \mu(S,V,N)N$$

it's this combination of variables that yields the most information; it does not matter how you write it!

- In the case where we only know <u>two</u> E.O.S.'s

$T(S,V,N),\ P(S,V,N)$ known

* Can we construct $S(E,V,N)/E(S,V,N)$ without knowing μ?

↳ Yes, up to a constant

$$\underbrace{E(S,V,N)} = N\cdot E\left(S/N,\ V/N,\ 1\right)$$

Secretly a function of only two variables because of extensivity

$$T = \frac{\partial E}{\partial S}\bigg|_{V,N} = \boxed{T}(S,V,N) = T\left(S/N,\ V/N,\ 1\right)$$

intensive variables → values* don't change

$$-P = \frac{\partial E}{\partial V}\bigg|_{S,N} = \boxed{-P}(S,V,N) = -P\left(S/N,\ V/N,\ 1\right)$$

*values assumed given by experiment

$$E\left(\frac{S}{N},\frac{V}{N},1\right) = \int_0^{S/N} d(S'/N)\,T\left(\frac{S'}{N},\frac{V}{N},1\right) + \underbrace{E\left(0,\frac{V}{N},1\right)}$$

needed because E(0) may not depend just on T

$$= \int_0^{S/N} d(S'/N)\,T\left(\frac{S'}{N},\frac{V}{N},1\right) - \int_0^{V/N} d(V'/N)\,P\left(0,\frac{V'}{N},1\right) + \underbrace{E(0,0,1)}_{\text{constant}}$$

only change one variable at a time

- In the case where we know only one E.O.S.
There is nothing you can do to find the Entropy this way

A simple example

Recover the entropy from the equations of state for the ideal gas

* Find $E(S,V,N)$

$$S = k_B N \ln\left(\frac{VE^{3/2}}{N^{5/2}}\right) \longrightarrow E = \frac{N^{5/3}}{V^{2/3}} \exp\left[\frac{2S}{3k_BN}\right]$$

- assume the experimentor did not provide μ

$$T = \left.\frac{\partial E}{\partial S}\right|_{V,N} = \frac{2}{3k_BN}\frac{N^{5/3}}{V^{2/3}} e^{2S/3k_BN}$$

$$-P = \left.\frac{\partial E}{\partial V}\right|_{S,N} = -\frac{2}{3}\frac{N^{5/3}}{V^{5/3}} e^{2S/3k_BN}$$

→ NOW, forget where these came from and try to recover $E(S,V,N)$

$$E(S/N, V/N, 1) = \int_0^{S/N} d(S'/N)\frac{2}{3k_B}\left(\frac{N}{V}\right)^{2/3} e^{2S'/3k_BN}$$

$$- \int_0^{V/N} d(V'/N)\frac{2}{3}\left(\frac{N}{V}\right)^{5/3} \bigcirc$$ - remember, $S=0$ for this integrand

$$+ E(0,0,1)$$

$$= \frac{2}{3k_B}\left(\frac{N}{V}\right)^{2/3}\frac{3k_BN}{2}\left[e^{2S/3k_BN} \cancel{-1}\right] - \cancel{\frac{2}{3}}\left(\cancel{\frac{-3}{2}}\right)\left(\frac{N}{V}\right)^{2/3}_{\wedge} + E(0,0,1)$$

The evaluation at $(V/N)=0$ does go to ∞, but we can change this bottom bound to anything, as long as we also change $E(0,{}^{\searrow}a^{\swarrow},1)$, but since it's just a fixed constant, we can say the ∞ from integrating $(-P)$ is absorbed by the corresponding value in $E(0,0,1)$.