Ideal Gas Application PhL 10.15.16

How would my general analysis on Boltzmann be applied to the Maxwell distribution business.

I will first try to "roll my own" and see where I get, later I will look at Livesey.

1. Plan A

Box of simple point atoms (monatomic gas, no energy in rotation or vibration).

Energy of a particle is $(1/2)mv^2$ and we are 3D. Energy levels are $\varepsilon(\mathbf{v}_i) = (1/2)mv_i^2$. Box contains M atoms and has N energy, so $M = \Sigma_i N_i$ still applies. Imagine that the $\mathbf{v}_i$ are discrete somehow. N_i is the number of particles having energy near $\varepsilon(\mathbf{v}_i)$. How would you write this in math?

I think the first step is to make v-space be a lattice of tiny cubes each of volume V. Then consider a thin shell in v-space of thickness dv. The number of states in this volume is then

$$g_i = [4\pi v^2 dv]/V \equiv g(v)\,(dv/V) \qquad g(v) \equiv 4\pi v^2$$

where now g(v) is a state density function in v space. I want to think of dv as a small but finite quantity, and the same for V.

What about N_i ? This is the number of particles with v lying in the thin shell of volume $[4\pi v^2 dv]$. So you could invent a density function N(v) such that

$$N_i = N(v)\,[4\pi v^2 dv]$$

Note for later use that

$$g_i/N_i = g(v)\,(dv/V)/\ N(v)\,[4\pi v^2 dv] = \frac{g(v)}{N(v)4\pi v^2 V}$$

What then would you say about

$$\Omega(\mathbf{N}) = \frac{g_1^{N_1}}{N_1!}\frac{g_2^{N_2}}{N_2!}\cdots\frac{g_m^{N_m}}{N_m!} = \Pi_{i=1}^{m}\frac{g_i^{N_i}}{N_i!} \quad ?$$

This becomes somehow a product of an infinite number of factors. Each factor corresponds to a "shell" in v-space. I know a few infinite product formulas from GR7 page 14.

Now consider $\frac{g_1^{N_1}}{N_1!}$. The numerator is

$$g_1^{N_1} = [\ g(v)\,(dv/V)]^{N(v)\,[4\pi v^2 dv]}$$

$N_1! = (N(v)\,[4\pi v^2 dv])!$

Again, I am thinking of dv and V as finite, so these are finite numbers. The product for $\Omega(\mathbf{N})$ has a factor for v = 0, and v = dv and v = 2dv and so on. So write

$v = n(dv)$

Then the product is $\Pi_{n=1}^{\infty}$ where we ignore the n = 0 term perhaps. So we then have

$$\Omega(\mathbf{N}) = \Pi_{n=1}^{\infty} \{ [\, g(v)\,(dv/V)]^{N(v)\,[4\pi v2dv]} / (N(v)\,[4\pi v^2 dv])!$$

$$= \Pi_{n=1}^{\infty} \{ [\, g(ndv)\,(dv/V)]^{N(ndv)\,[4\pi (ndv)*ndv(dv)]} / (N(ndv)\,[4\pi (ndv)^2 dv])!$$

$$= \Pi_{n=1}^{\infty} \frac{[\, g(ndv)\,(dv/V)]^{N(ndv)\,[4\pi (ndv)*ndv(dv)]}}{(N(ndv)\,[4\pi (ndv)^2 dv])!}$$

Maybe I can just write it like so and they not use it, it is just some huge mess which hopefully converges because the N_i taper off at higher energies, which means in the higher factors.

Let's look at the form of one of these factors $\frac{g_1^{N_1}}{N_1!}$ where:

$g_1^{N_1} = [\, g(v)\,(dv/V)]^{N(v)\,[4\pi v2dv]}$

$N_1! = (N(v)\,[4\pi v^2 dv])!$

As $N(v) \to 0$ for large v, we see that $g_1^{N_1} \to [\, g(v)\,(dv/V)]^0 = 1$ if g(v) is reasonable.
And we see that $N_1! \to (0)! = 1$. Thus if you look at the far right end of the infinite product of factors, you see a product of numbers that each approach 1, so it is then at least conceivable that this limit approaches a finite number.

OK, what would I do next in following Lagrange doc? I assume N_i large which is at least valid for occupied energy levels. This would give

$f = \Sigma_i N_i\,[1 + \ln(g_i/N_i)]$

where now we have a sum instead of a product. Installing we get

$$f = \Sigma_v\ N(v)\,[4\pi v^2 dv]\,[1 + \ln(\frac{g(v)}{N(v)4\pi v^2 V})]$$

$$= \Sigma_{n=1}^{\infty}\ N(ndv)\,[4\pi (ndv)^2 dv]\,[1 + \ln(\frac{g(ndv)}{N(ndv)4\pi (ndv)^2 V})]$$

The limit here is not so obvious, but again just take this as what it is.

Now just jump to our major result which is

$$N_i = A\ g_i\ e^{-\beta\varepsilon_i}$$

which we can translate to read

$$N(v)\ [4\pi v^2 dv] = A\ [4\pi v^2 dv]/V\ \exp(-\beta m v^2/2)$$

or

$$N(v) = (A/V)\exp(-\beta m v^2/2)$$

Remember that my N(v) is a shell radial density, and thus differs from N(**v**). Now integrate to get

$$M = \int_0^\infty N(v)\ [4\pi v^2 dv] = (A/V)\ 4\pi \int_0^\infty \exp(-\beta m v^2/2) v^2 dv$$

Evaluate the integral with $\alpha = \beta m/2$ $\alpha = \beta m/2$

$$\int_0^\infty \exp(-\beta m v^2/2) v^2 dv = \int_0^\infty \exp(-\alpha v^2) v^2 dv$$

According to Schaum page 98 item 15.76 the integral is

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assume(alpha>0);
Int(x^2*exp(-alpha*x^2),x=0..infinity);
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$$\int_0^\infty x^2\, e^{(-\alpha x^2)}\, dx$$

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value(%);
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$$\frac{1}{4}\,\frac{\sqrt{\pi}}{\left(\frac{3}{2}\right)}\,\alpha$$

$$M = (A/V)\ 4\pi\ *(\sqrt{\pi}/4)\ [\beta m/2]^{-3/2} = (A/V)\ \pi^{3/2}\ [2/(\beta m)]^{3/2} = (A/V)\ [2\pi/(\beta m)]^{3/2}$$

This lets you solve for A to be

$$A = MV\ [2\pi/(\beta m)]^{-3/2} = MV\ [\beta m/(2\pi)]^{3/2}$$

and then we seem to have our solution

$$N(v) = (A/V)\exp(-\beta m v^2/2) = M\ [\beta m/(2\pi)]^{3/2} \exp(-\beta m v^2/2)$$

and the V's have cancelled! Livesey does not state his final result. Remember that

$N_i = N(v)\,[4\pi v^2 dv]$ = number of particles in a thin shell at v with thickness dv

so we are finding that

$$N_i = [4\pi v^2 dv]\, M\, [\beta m/(2\pi)]^{3/2} \exp(-\beta m v^2/2)$$

$$= 4\pi M\, [\beta m/(2\pi)]^{3/2}\ v^2\ \exp(-\beta m v^2/2)\, dv$$

$$= 4\pi M\, [\beta m/(2)]^{3/2}\, \pi^{-3/2}\, v^2\ \exp(-\beta m v^2/2)\, dv$$

$$= 4M\, \pi^{-1/2}\, [\beta m/(2)]^{3/2}\ \ v^2\ \exp(-\beta m v^2/2)\, dv$$

and this then is the traditional Maxwell velocity curve which has a smooth peak.

2. Let's look now at various in-house authors

Livesey page 16 gets results similar to me, but he does not quite state the final result with the constant evaluated. He uses symbol f(v) I think in the sense that I use N_i/dv above, and he gets $f(v) = C\, v^2 \exp(-\beta m v^2/2)$.

Zemansky does his derivation starting page 147 and ends up with his final result on page 159 which is this, changing w→v and β = 1/(kT) :

$$dN_v/dv\ = (\ 4M/\sqrt{\pi}\ )(m\beta/2)^{3/2}\ v^2 \exp(-\beta m v^2/2)$$

This agrees exactly with my Plan A result, hurray!

Big Reif: Page 267 gives this speed distribution

$$F(v) = 4\pi n\, (m\beta/2\pi)^{3/2}\, v^2 \exp(-\beta m v^2/2)$$

where I think his n is the particle density in volume space. Now $\pi\ \ (1/\pi)^{3/2}\ = \pi\ \pi^{-3/2}\ = \pi^{-1/2}$ so he agrees with Zemansky apart from the definition of F(v).

3. Where is the super strong peak I keep talking about in Lagrange doc?

A box of gas has the Maxwell speed distribution which is a smooth peak. Based on the above discussion, you can regard it as a plot of N_i which solves the gas problem. This set of many N_i makes the vector **N** I talk about.

Now take an ensemble of 1 billion boxes of gas, and each has a solution vector **N** which means each one has a speed curve.

Fact: The speed curve and its peak are NOT the curve I am talking about with my billion systems comment. Each of the billion boxes of bas has a curve which is its **N**, and the curves of all the systems are very close. The speed curve IS the stationary point solution vector **N**.

Now you can look at a particular component N_i of this vector and ask about its probability distribution. If this is a value My existing curvature formula does now work very well.

Maybe I can back up to my results above which reads,

$$f = \Sigma_v \; N(v)\,[4\pi v^2 dv]\,[1 + \ln(\frac{g(v)}{N(v)4\pi v^2 V})] \qquad \text{// which is } \ln\Omega$$

$$= \int_0^\infty dv \; N(v)\,[4\pi v^2]\,[1 + \ln(\frac{g(v)}{N(v)4\pi v^2 V})]$$

But I know that,

$$g(v) \equiv 4\pi v^2$$

$$N(v) = M\,[\beta m/(2\pi)]^{3/2} \exp(-\beta m v^2/2) = C \exp(-\beta m v^2/2) \qquad C = M\,[\beta m/(2\pi)]^{3/2}$$

$$\frac{g(v)}{N(v)4\pi v^2 V} = \frac{4\pi v^2}{C \exp(-\beta m v^2/2) 4\pi v^2 V} = \frac{1}{C \exp(-\beta m v^2/2) V}$$

Then

$$f = \int_0^\infty dv\,[4\pi v^2]\; C \exp(-\beta m v^2/2)\,[\,1 - \ln[\,CV \exp(-\beta m v^2/2)\,]$$

which is just some number. So how do you talk about a derivative like $\frac{\partial F}{\partial N_i}$? Something is wrong here.