Fri. 3/ 16	**C 10.8.0-10.8.7, S. B.1** Gaussian, **6.3-.5** Equipartion, Maxwell	**HW17 S.** 31,36, 41 **B.** 1,2,3	
Mon. 3/19 Wed. 3/21 Fri. 3/23	**S 6.5-7** Partition Function **S A.5** Q.M. Background: Bose and Fermi **S 7.1 -2** Q. Stats, Bos- and Fermions	**HW 18 S.** 44, 48, 49, 52 **HW19 S.** 21, 22 **HW20 S.** 3, 8, 9 , 10, 11, 13ac, 18	HW15,16, 17

It's a Gas

Last time we considered a few specific systems – dipole, Einstein solid, and rotating molecule. Of course, our other favorite system is an ideal gas. So now we'll apply our new found tool to that.

In point of fact, to *completely* specify a gas molecule's micro-state, you'd need to specify *every* freedom it has: what kind of molecule it is, the nuclear state, the electronic state, the rotational state, the vibrational state, the translational state, and, oh yeah, its position, and other stuff too. Each of these could have energy ramifications, and thus effect the probability.

$$P(s) = \frac{e^{-E(s)b}}{Z} = \frac{e^{-(Etrans+Evib+Erot+Eposition+Eelectron+Enuclear)b}}{Z}$$

But, remember the old mantra that probabilities of indedependent freedoms multiply. So, we can separate out the different freedoms and speak just of the probability of being in a particular rotational state, translational state, or whatever.

$$Z = \sum_{all.states} e^{-(Etrans+Evib+Erot+Eposition+Eelectronic+Enuclear)b} = \sum_{trans} e^{-(Etran)b} \sum_{vib} e^{-(Evib)b} \sum_{pos} e^{-(Epos)b} \sum_{ele} e^{-(Eele)b} \sum_{nuc} e^{-(Enuc)b}$$

$$Z = Z_{trans} Z_{vib} Z_{pos} Z_{ele} Z_{nuc}$$

$$P(s) = \frac{e^{-E(s)b}}{Z} = \frac{e^{-(Etrans)b} e^{-(Evib)b} e^{-(Eposition)b} \ldots}{Z_{trans} Z_{vib} Z_{pos} \ldots} = \frac{e^{-(Etrans)b}}{Z_{trans}} \frac{e^{-(Evib)b}}{Z_{vib}} \frac{e^{-(Eposition)b}}{Z_{pos}} \ldots = P(s_{trans}) P(s_{rot}) P(s_{p\ldots}$$

So, when we were considering the statistics of rotational states last time, and completely ignoring any other freedoms, that was perfectly valid. Similarly, we can now consider just the freedoms of translation and position independently. In fact, we'll start with position since it's darn simple and we get a familiar result.

The exponential Atmosphere, revisited

- $P(s_z) = \frac{e^{-E(z)b}}{Z}$
- In the Earth's gravitational, E(z) = mgz, so $P(s_z) = \frac{e^{-mgzb}}{Z} = \frac{e^{-mgz/kT}}{Z}$.
- Now, the relative densities of particles at two elevations should scale with their probabilities, so $\frac{D(Z_{high})}{D(Z_{low})} = \frac{e^{-mgz_{high}/kT}}{e^{-mgz_{low}/kT}} = e^{-mg(\Delta z/kT}$.
- Does that look familiar?
- So we quite simply find that the density of air decreases exponentially with elevation.

- Now we'll move on to the velocity dependence. Okay, maybe not *quite* yet. First we'll look at a fairly general result which happens to apply to the velocity dependence, as well as many others. In fact, we've invoked this a few times in the past.
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6.2 The Equipartition Theorem

- **What's so special?** If you recall, for gasses in particular, except for specific ranges of temperature, the equipartition theorem holds. It's a powerful rule of thumb. We've run into it over and over again for different specific systems. Using the Boltzmann statistics we can show were it's generality comes form, and we can explain why it doesn't apply for all temperatures.
- Now that we have the Boltzmann factor, it's quite easy to prove this is true for any quadratic energy term, that is, any term of the form $E(q) = cq^2$ where c is a constant and q is a freedom such as x, p_x, L_x,…
    - Note, cq^2 here is a stand-in for ½ mv_x^2 or ½ L^2/I or… they all have the same basic form.
    - **Student Question:** The author says we'll treat one degree of freedom as our 'system', what does he mean?
        - Say you've got a particle that's free to move in x, y, and z. The freedoms to move in each direction are independent of the other directions. So you can develop the statistics associated with each degree independently. For example, you can say what the probability is that the particle's moving with a certain v_x regardless of what it's doing in y and z. So, the math looks just like it would if you had 3 1-D particles instead of 1 3-D particle. In this way he suggests that each degree of freedom be treated as a 'system' for us to analyze.
        -
- We'll start by finding the partition function, and from there we'll find the average energy.
    - $Z = \sum_{state} e^{-E_q b} = \sum_{state} e^{-cq^2 b} = \frac{1_{state}}{\sqrt{cb}\Delta q} \sum_q e^{-cq^2 b}\left(\sqrt{cb}\,\Delta q\right) = \frac{1}{\sqrt{cb}\,\Delta q} \sum_x e^{-x^2}\Delta x$
    - I've rewritten this in terms of $x = \sqrt{cb}\,q$ because, as long as the step size in q is quite small in comparison to kT/c, we have $\Delta x = \sqrt{cb}\,\Delta q << 1$, then it's not much of a stretch of the imagination to let it become differentially small, i.e., turn the discrete sum into a continuous one.
    - $Z \approx \frac{1}{\sqrt{cb}\,\Delta q} \int_{x=-\infty}^{x=\infty} e^{-x^2} dx$
    - **How to do this integral: Appendix B.1**
        - This is awfully cute

$$\int_{-\infty}^{\infty} e^{-x^2}dx = \sqrt{\left(\int_{-\infty}^{\infty} e^{-x^2}dx\right)^2} = \sqrt{\int_{-\infty}^{\infty} e^{-x^2}dx \int_{-\infty}^{\infty} e^{-y^2}dy} = \sqrt{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\left(y^2+x^2\right)}dxdy}$$

$$\int_{-\infty}^{\infty} e^{-x^2}dx = \sqrt{\int_0^{\infty}\int_0^{2p} e^{-r^2}rdfdr} = \sqrt{\int_0^{\infty} 2pe^{-r^2}rdr} = \sqrt{2p\left(-\frac{1}{2}e^{-r^2}\right)\Big|_0^{\infty}} = \sqrt{2p\left(0-\frac{-1}{2}\right)} = \sqrt{p}$$

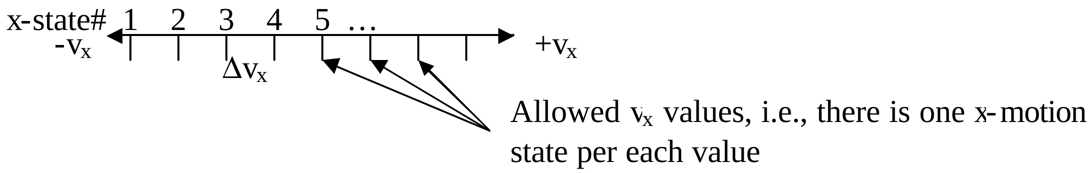
- So, $Z \approx \frac{1}{\sqrt{cb}\Delta q}\sqrt{p}$.
- Now $\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial b} = -\sqrt{\frac{cb}{p}}\Delta q \frac{\sqrt{p}}{\sqrt{c}\Delta q}(-1/2)\frac{1}{b^{3/2}} = \frac{1}{2}\frac{1}{b} = \frac{1}{2}kT$
- Tada!
- **Don't forget the approximation.** This result followed from the condition that $\Delta x = \sqrt{cb}\Delta q << 1$. If this is not true, the discrete sum looks nothing like the continuous integral. Rewriting this condition gives $c(\Delta q)^2 << kT \to \Delta E_q << kT$. Only if the energy steps are quite small compared to kT is the partition theorem valid. This makes sense because, even if the heat-bath would happily *give* a particle kT of energy, the particle can only accept discrete multiples of ΔE, no less and nothing in between.

* **Prep. For 6.31** You will do something similar, but for a linear degree of freedom.

6.4 The Maxwell Speed Distribution

* **Prep for 6.41.** You will repeat this following work for 2-D instead of a 3-D gas.
* Translational kinetic energy is $\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, each of these three represents a degree of freedom, and each depends quadratically, so leads to a ½ kT. For example, if we make the substitutions $\frac{1}{2}m \to c$ and $v_x \to q$, then we get exactly what we just proved ½ kT.
$\left\langle K.E.\right\rangle = \left\langle \frac{1}{2}mv^2\right\rangle = \left\langle \frac{1}{2}mv_x^2\right\rangle + \left\langle \frac{1}{2}mv_y^2\right\rangle + \left\langle \frac{1}{2}mv_z^2\right\rangle = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$
* $\sqrt{\left\langle v^2\right\rangle} = \sqrt{\frac{3kT}{m}}$
* But what does the whole distribution look like? For that, we return to the expression $\overline{X} = \sum_s X_s \frac{e^{-E_s b}}{Z}$, where $X = v$, the speed. We'll build up the equation and thus see how a given speed weighs into the average. $\overline{v} = \sum_s |v| \frac{e^{-\frac{1}{2}mv^2 b}}{Z}$ (absolute value sign since we're interested in *speed* which is just a magnitude). Now we must sum over the *states*. Considering each component of velocity as a separate degree of freedom, we can independently sum over states of x-motion, y-motion, and z-motion.

- $\bar{v} = \sum_{x-state}\sum_{y-state}\sum_{z-state} |v| \frac{e^{-\frac{1}{2}mv^2\beta}}{Z}$



- So we can switch from summing over states to summing over their corresponding velocity components. We'd say that there's 1 state of x-motion per Δv_x , one state of y-motion per…, so we have sum over these three independent states of motion individually: $\bar{v} = \sum_{v_x}\sum_{v_y}\sum_{v_z} |v| \frac{e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)\beta}}{Z} \frac{1_{x-state}}{\Delta v_x}\frac{1_{y-state}}{\Delta v_x}\frac{1_{z-state}}{\Delta v_z}\Delta v_x \Delta v_y \Delta v_z$.

- Just as in our equipartition argument, if the temperature is high enough, we can approximate these three sums with three integrals:

$$\bar{v} \approx \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{1}{Z}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |v| e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)\beta} dv_x dv_y dv_z$$

$$\bar{v} \approx \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{8}{Z}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty} v e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)\beta} dv_x dv_y dv_z$$

  - o Range: The integrals would be over all values of the velocity components, but since I'm just interested in the speed, I can multiply by 8 and confine myself to considering just the positive octant.

- Now, we have three, orthogonal variables, not unlike x, y, and z. For that matter $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, quite similar to $r = \sqrt{x^2 + y^2 + z^2}$. Borrowing a procedure from real space, we can transform from 'Cartesian' to 'polar' coordinates.

- $\bar{v} = \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{8}{Z}\int_{v=0}^{\infty}\int_{\theta=0}^{\frac{\pi}{2}}\int_{\phi=0}^{\frac{\pi}{2}} v e^{-\frac{1}{2}mv^2\beta} dv \cdot v\sin\theta d\phi \cdot v d\theta = \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{4\pi}{Z}\int_{v=0}^{\infty} v^3 e^{-\frac{1}{2}mv^2\beta} dv$

- **Determining Pre-factor**
  - o Before going any further, we can pause and figure out exactly what $\Delta v_x \Delta v_y \Delta v_z Z$ is so we can get rid of these unsightly variables. Looking back where we started from, $\bar{v} = \sum_s |v| \frac{e^{-\frac{1}{2}mv^2\beta}}{Z}$, if we just didn't have that $|v|$ in there, we'd simply have Z/Z which of course is 1. $\sum_s \frac{e^{-\frac{1}{2}mv^2\beta}}{Z} = \frac{Z}{Z} = 1$. So tracing back through our work, that means if we remove one factor of v from our integrand, we'll have Z/Z, i.e., 1.

    $$1 = \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{4\pi}{Z}\int_{v=0}^{\infty} v^2 e^{-\frac{1}{2}mv^2\beta} dv$$

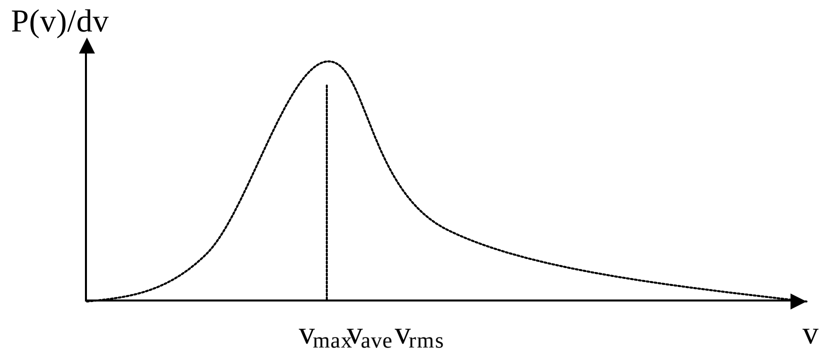
    - ▪ Evaluating the integral: back to Appendix B.

- Note that $\int_{v=0}^{\infty} v^2 e^{-\frac{1}{2}mv^2 b}\,dv = -\frac{d}{d\left(\frac{1}{2}mb\right)}\left(\int_{v=0}^{\infty} e^{-\frac{1}{2}mv^2 b}\,dv\right)$ but
$$\int_{v=0}^{\infty} e^{-\frac{1}{2}mv^2 b}\,dv = \frac{1}{\sqrt{\frac{1}{2}mb}}\int_{x=0}^{\infty} e^{-x^2}\,dx = \frac{1}{\sqrt{\frac{1}{2}mb}}\frac{\sqrt{p}}{2}$$
- So,
$$\int_{v=0}^{\infty} v^2 e^{-\frac{1}{2}mv^2 b}\,dv = -\frac{d}{d\left(\frac{1}{2}mb\right)}\left(\frac{1}{2}\sqrt{\frac{p}{\frac{1}{2}mb}}\right) = \frac{1}{4}\sqrt{\frac{p}{\left(\frac{1}{2}mb\right)^3}} = \sqrt{\frac{p}{2(mb)^3}}$$

  - $1 = \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{4p}{Z}\int_{v=0}^{\infty} v^2 e^{-\frac{1}{2}mv^2 b}\,dv = \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{4p}{Z}\left(\frac{p}{2(mb)^3}\right)^{1/2} \Rightarrow \frac{1_{state}}{\Delta v_x \Delta v_x \Delta v_z}\frac{1}{Z} = \left(\frac{mb}{2p}\right)^{3/2}$

- So, $\bar{v} = \left(\frac{mb}{2p}\right)^{3/2} 4p \int_{v=0}^{\infty} v^3 e^{-\frac{1}{2}mv^2 b}\,dv$.
- **Results.**
  - **Average Speed.** Sure, we can evaluate this integral, with the help of a change of variables to $q = \sqrt{\frac{1}{2}mb}\,v$ and appendix B, to find $\bar{v} = \sqrt{\frac{8T}{pm}}$.
  - **Probabilities.** We can also find the probabilities of each speed. Since $\bar{v} = \sum vP(v)$ we can rewrite the integral in this form and read off what's playing the roll of *P(v)*. $\bar{v} = \sum v \cdot \left[4p\left(\frac{mb}{2p}\right)^{3/2} v^2 e^{-\frac{1}{2}mv^2 b}\,dv\right]$, I've rewritten the integral symbol as the sum symbol to make the two equations more parallel. Clearly $P(v) = 4p\left(\frac{mb}{2p}\right)^{3/2} v^2 e^{-\frac{1}{2}mv^2 b}\,dv$. It is worth noting that dv is an infinitesimally small constant, thus so is the probability of having any specific velocity (since, classically speaking, there are infinite different velocities to choose from, the probability of any specific one is 0). But it's really the *relative* probabilities of different speeds that we're interested in, so we'll just consider *dv* as a constant.
  - **Most Probable Speed.** Then the most probable speed can be found by maximizing the probability function (taking its derivative and setting equal to 0.) this yields $v_{\max/\min} = (0, \sqrt{2kT/m}, \infty)$. Plugging these three values back in reveals that 0 and infinity are minima, where the probability goes to 0.

- **Distribution.**



Prep for 6.36. You will find fill in some of the math to actually evaluate the average speed. I recommend doing a change of variable or two to make the integral look like stuff* $\int_0^\infty ye^{-y}dy$ which can be integrated by parts or like other.stuff* $\int_0^\infty ye^{-ay}dy$, in which case you can use the "increadibly handy" trick employed in appendix B.1

6.5 Partition Functions and Free Energy

- So far, we've applied the Boltzmann formalism directly to single-member, or *micro*-systems. But even for these simple systems, we sometimes found that more than one micro-state had the same energy, so we got used to dealing with a degeneracy: $Z = \sum_{state} e^{-E_{state}b} = \sum_E \Omega(E)e^{-Eb}$. Of course, $\Omega(E) = e^{S(E)/k}$ so $Z = \sum_{state} e^{-E_{state}b} = \sum_E \Omega(E)e^{-Eb} = \sum_E e^{-(E-ST)b} = \sum_E e^{-F(E)b} = \sum_F e^{-Fb}$
- Now here's the shortcut to the book's result. Let's apply the Boltzmann formalism not to a single-member, *micro*-system, but to a whole *macro*-system at energy U and temperature T. Why not?
  - Then the partition function for the whole system must be $Z(U,T) = \sum_{state} e^{-E_{state}b} = \sum_E \Omega(E)e^{-Eb}$, but of course every micro-state of the macro-system has the *same* energy, U, since we decided to only look at such micro-states. So there's just one term in the sum over energy, $Z(U,T) = \Omega(U)e^{-Ub} = e^{S/k}e^{-Ub} = e^{-(U-TS)b} = e^{-Fb} \Rightarrow F = -kT\ln Z(U,T)$.
- Recall, for a system at constant T, a process that reduces its F increases the universe's entropy, thus is a favorable process. Another way to put it, the macrostate with lowest F is the most probable.
- Z is something like a (weighted) count of states. We can see by this new relationship that reducing F increases Z, as would be expected.
- This F – Z relationship is useful because we can often figure out Z, and because we have partial derivatives of F for finding S, P, and μ.
  - $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ $m = \left(\frac{\partial F}{\partial N}\right)_{V,T}$