THE UNIVERSITY OF BRITISH COLUMBIA

Physics 122 Assignment # 2 SOLUTIONS:
KINETIC THEORY OF GASES

Wed. 09 Jan. 2002 — finish by Wed. 16 Jan.

1. **One-Dimensional Ideal Gas**

Making use of the EQUIPARTITION THEOREM, derive an equation analogous to the familiar 3D IDEAL GAS LAW ($pV = N\tau$) for an ideal gas confined to a **one**-dimensional "box" of length L. (Some examples would be N electrons moving freely along a single DNA molecule, a *trans*-polyacetylene chain or a "nanowire" made from GaAs/AlGaAs structures.)

ANSWER: The arguments developed for the time-averaged *force* exerted on one wall of a cubical 3D container apply equally well for the force acting on the boundary of a 1D "box" — namely, for a *single* particle bouncing back and forth, $\langle F_1 \rangle = m\langle v_x^2 \rangle / L$, where L is the length of the "box". In this case there is only one direction of motion (degree of freedom) so we can drop the $_x$ subscript on v_x. The EQUIPARTITION THEOREM says that the *thermal* average of the kinetic energy $E_1 = \frac{1}{2}mv^2$ associated with this translational degree of freedom is $\langle E_1 \rangle \equiv \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}\tau$, giving $m\langle v^2 \rangle = \tau$. If we substitute this back into the formula for $\langle F_1 \rangle$ we get $\langle F_1 \rangle = \tau/L$. For N particles all doing this at the same time, we just multiply by N, giving $\langle F \rangle = N\tau/L$ or (ignoring the fact that the actual force F at any instant fluctuates minutely about the average force $\langle F \rangle$) $\boxed{FL = N\tau}$. This is the 1D equivalent of the IDEAL GAS LAW. Note that the only difference between this derivation and the one for a 3D box is that here we didn't have to introduce the notion of pressure as the force per unit area. This is simpler!

2. **One-Dimensional Maxwellian Speed Distribution**

(*a*) What is the thermal speed distribution $\mathcal{D}(v)$ [in the textbook's notation, $N(v)/N$, as in Eq. (22-14) on p. 503] for an ideal gas confined to a **one**-dimensional "box"? It would be nice if you could find the right leading factors (involving temperature and various constants) to *normalize* the distribution so that

$$\int_0^\infty \mathcal{D}(v)\, dv \;=\; 1 \,,$$

but I am mainly looking for its *dependence on the speed* v.

Hint: Use de Broglie's hypothesis ($\lambda = h/p$) and think in terms of *standing waves*.

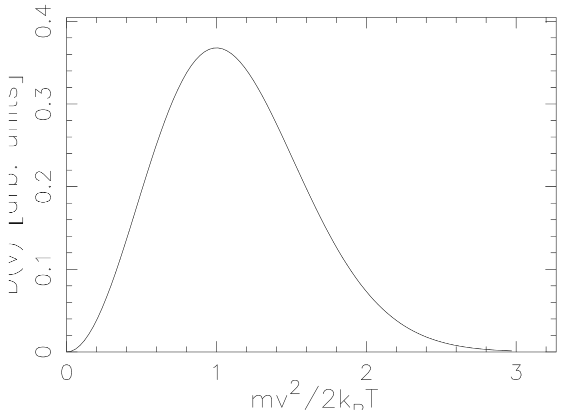
ANSWER: Again the 1D case is much *simpler* than the 3D case because we don't have to worry about composing v^2 out of $v_x^2 + v_y^2 + v_z^2$ (or $\vec{k}$ out of k_x, k_y and k_z). There is just one direction, just one velocity component, one momentum component and one wavelength to worry about making commensurate with the length of the "box". Thus the requirement that an integer n half-wavelengths fit evenly into ℓ gives $\lambda_n = 2\ell/n$ and so $p_n = h/\lambda_n = nh/2\ell = mv_n$ or $v_n = n(h/2m\ell)$. Thus *the possible values of the speed v are evenly spaced every $(h/2m\ell)$* and the distribution of speeds varies only as the Boltzmann factor $\exp(-\frac{1}{2}mv^2/\tau)$. This gives immediately $\boxed{\mathcal{D}_{1D}(v) = A\, e^{-mv^2/2\tau}}$ where A is a normalization constant that does not depend on v. You get full credit for this result, but here's how to get A: Let $y \equiv mv^2/2\tau$ where τ is treated as a constant. Now, $v^2 = (2\tau/m)y$ or $v = \sqrt{2\tau/m}\, y^{1/2}$ so $dv = \frac{1}{2}\sqrt{2\tau/m}\, y^{-1/2} dy$ and we have $\int_0^\infty \mathcal{D}(v)\, dv \;=\; 1 \;=\; A\sqrt{\frac{\tau}{2m}} \int_0^\infty y^{-1/2}\, e^{-y}\, dy$. You can look up the definite integral; its value is $\sqrt{\pi}$, giving $\boxed{A = \sqrt{2m/\pi\tau}}$.

(*b*) *Sketch* this distribution for a given temperature and compare its shape with that shown in the Figures on p. 503 of the textbook. **ANSWER**: See next page.

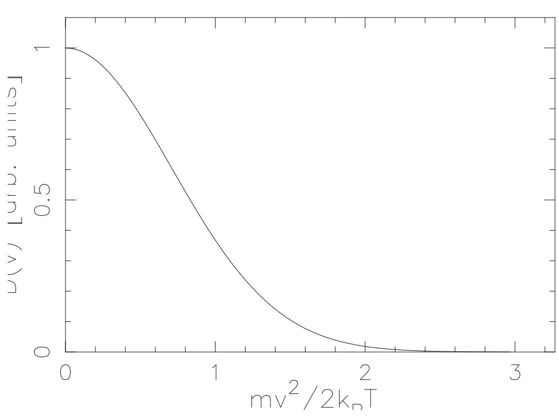
(*c*) What can you say about the *most probable speed* $v_{\rm p}$ in the two different cases?

ANSWER: As stated in the textbook, the most probable speed for an ideal gas molecule in 3D is $\boxed{v_p^{3D} = \sqrt{2\tau/m}}$ (*i.e.* when $mv^2/2\tau = 1$). For the 1D gas, however, $\mathcal{D}_{1D}(v)$ is missing that extra factor of v^2 that forces its value to zero at $v = 0$, so the resultant speed distribution has its *maximum* at $v = 0$: $\boxed{v_p^{1D} = 0}$.

3D:



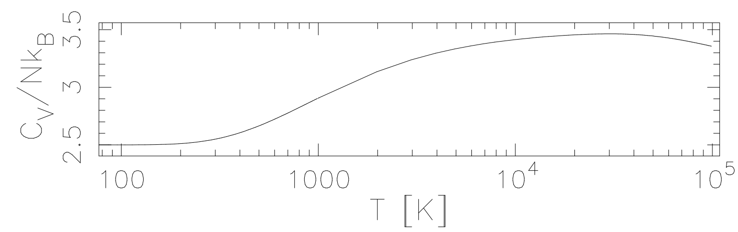
1D:



3. Heat Capacity of Nitrogen Gas

Sketch (including axis labels *and scales*) the *heat capacity per molecule*, C_1, of an ideal gas of diatomic nitrogen (N_2) molecules in an isolated closed vessel of fixed volume, as a function of temperature τ from room temperature[1] up to a temperature high enough to dissociate the molecules into separate atoms. You may have to make some estimates based on simple mechanics and common sense.

ANSWER: The *qualitative* picture was drawn in class; this is all about *quantitative estimates* of how hot the gas has to get before rotational and vibrational degrees of freedom are excited. For this you need to remember that (i) the energy of either is always given by $\varepsilon = \hbar\omega$ where $\hbar \equiv h/2\pi = 1.05458 \times 10^{-34}$ J-s; and (ii) that the lowest nonzero angular momentum allowed for any object (including a molecule) is $L_{\rm min} = \hbar$. You already know how to find the resonant frequency of a pair of masses connected by a spring; you need only the effective "spring constant" for the N_2 bond, namely $k_{\rm eff} \approx 300$ N/m, and the mass of a ^{14}N atom: $m = (14 \times 1.67 = 23.38) \times 10^{-27}$ kg. So $\omega_{\rm vibr} = \sqrt{k_{\rm eff}/m} \approx 1.2 \times 10^{14}$ s^{-1}. The corresponding energy is $\varepsilon_{\rm vibr} = \hbar\omega_{\rm vibr} = 1.2 \times 10^{-20}$ J $= k_{\rm B}T_{\rm vibr}$ giving $\boxed{T_{\rm vibr} \approx 900 \text{ K}}$. At lower temperatures the vibrational degrees of freedom will not be thermally excited. Now for the rotational ones: the distance between the two ^{14}N nuclei in an N_2 molecule is about 1 Å $\equiv 10^{-10}$ m. Crudely representing the molecule as two point masses an Angstrom apart, the moment of inertia is about $I_{N_2} = 2mr^2 = 2 \times 2.34 \times 10^{-26} \times (0.5 \times 10^{-10})^2 = 164 \times 10^{-47}$ J-s^2. Now, $L_{\rm min} = \hbar = I_{N_2}\omega_{\rm min}$ gives $\omega_{\rm min} = \hbar/I_{N_2} = 1.05458 \times 10^{-34}/1.64 \times 10^{-45} = 0.643 \times 10^{11}$ s^{-1} and so $\varepsilon_{\rm min} = \hbar\omega_{\rm min} = 0.678 \times 10^{-23}$ J. A state with this size energy will get excited only if the temperature is comparable to or greater than $\varepsilon_{\rm min}/k_{\rm B}$ or $T_{\rm rot} = 0.678 \times 10^{-23}/1.38 \times 10^{-23} = 1.08$ K. Hmm, looks like I was mistaken when I said in class that the rotational degrees of freedom are only excited at high temperature. Considering that nitrogen freezes solid at 68 K, it is safe to say that N_2 *gas* has its rotational heat capacity at *all* temperatures, giving a total heat capacity of $\boxed{C_V(T \ll 900 \text{ K}) = \frac{5}{2}k_{\rm B}}$ from room temperature up to about 900 K, and then $\boxed{C_V(T \gg 900 \text{ K}) = \frac{7}{2}k_{\rm B}}$. The binding energy of an N_2 molecule is around 11 eV (or 1.8×10^{-18} J) so at temperatures above about $\boxed{T_{\rm dissoc} \approx 130{,}000 \text{ K}}$ the molecules will dissociate into nitrogen atoms. Then each atom will contribute only its translational degrees of freedom, giving $\boxed{C_V(T \gg 10^5 \text{ K}) = \frac{6}{2}k_{\rm B}}$. (I'm not sure I believe this myself; at any rate the atoms are apt to *ionize* by that temperature.) **Sketch**: [2]



[1] At atmospheric pressure, solid nitrogen melts at 68 K and liquid nitrogen boils at 77 K.

[2] I hope you don't take any of these numbers too seriously. . . . *Believe me not!*