

Tarea 5: Estadísticas de Boltzmann, Fermi-Dirac y Bose-Einstein

4-5. For an ideal gas, show that the relation

$$P = \frac{2}{3} \frac{E_{\text{kin}}}{V}$$

holds irrespective of its statistics, where E_{kin} is the total kinetic energy.

4-7. Recall that the equation of state for an ideal quantum gas is

$$pV = kT \ln \Xi = \pm kT \sum_j \ln [1 \pm \lambda e^{-\epsilon_j/kT}]$$

where $\lambda = e^{\mu/kT}$. Using the fact that the summation over states can be replaced by an integration over energy levels

$$\omega(\epsilon) d\epsilon = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} V \epsilon^{1/2} d\epsilon$$

derive the quantum virial expansion

$$\frac{p}{kT} = \mp \frac{1}{\Lambda^3} \sum_{j=1}^{\infty} \frac{(\mp 1)^j \lambda^j}{j^{5/2}}$$

where $\Lambda = (h^2 \cdot 2\pi m kT)^{1/2}$.

4-8. Show that the entropy of an ideal quantum gas can be written as

$$S = -k \sum_j [\bar{n}_j \ln \bar{n}_j \pm (1 \mp \bar{n}_j) \ln (1 \mp \bar{n}_j)]$$

4-9. Show that $pV \geq \langle N \rangle kT$ for fermions, and $pV \leq \langle N \rangle kT$ for bosons.

4-12. Consider a system of N distinguishable independent particles, each of which can be in the state $+\varepsilon_0$ or $-\varepsilon_0$. Let the number of particles with energy $\pm\varepsilon_0$ be N_{\pm} , so that the energy is

$$E = N_+ \varepsilon_0 - N_- \varepsilon_0 = 2N_+ \varepsilon_0 - N\varepsilon_0$$

Evaluate the partition function Q by summing $\exp(-E/kT)$ over levels and compare your result to $Q = q^N$. Do not forget the degeneracy of the levels, which in this case is the number of ways that N_+ particles out of N can be in the $+$ state. Calculate and plot the heat capacity C_V for this system.

4-13. The vibrational energy levels of a diatomic molecule can be approximated by a quantum mechanical harmonic oscillator. The fundamental vibrational frequency ν is $0(10^{13} \text{ sec}^{-1})$ for many diatomic molecules. Calculate the fraction of molecules in the first few vibrational levels in an ideal diatomic gas at 25°C . Derive a closed expression for the fraction of molecules in all excited states.

4-18. Derive the equation

$$C_V = \frac{N}{kT^2} [\overline{\varepsilon^2} - \bar{\varepsilon}^2]$$

for independent particles and show that fluctuations of molecular energies are not at all negligible.

Tarea 6: Gases ideales y Estadística Clásica

5-2. By considering the special case of an ideal gas, determine the order of magnitude of E , A , G , S , C_V , and μ . Express your answers in terms of N , kT , or Nk , whichever is appropriate.

5-18. Consider a monatomic ideal gas of N particles in a volume V . Show that the number n of particles in some small subvolume v is given by the Poisson distribution

$$\begin{aligned} P_n &= (\lambda q)^n \frac{e^{-\lambda q}}{n!} \\ &= (\bar{n})^n \frac{e^{-\bar{n}}}{n!} \end{aligned}$$

Hint: Use the grand canonical ensemble and particularly the result that $\Xi = \exp(\lambda q)$.

5-17. Evaluate the isothermal-isobaric partition function of a monatomic ideal gas by converting the summation over V in Eq. (3-17) to an integral. The result is

$$\Delta(N, p, T) = \left(\frac{kT}{p\Lambda^3} \right)^N$$

Using the fact that $G = -kT \ln \Delta$, derive expressions for S and V .

6-2. The dissociation energy D_0 of H_2 is 103.2 kcal/mole, and its fundamental vibrational frequency $\bar{\omega}$ is 4320 cm^{-1} . From this information, calculate D_0 and $\bar{\omega}$ for D_2 , T_2 , and HD , assuming the Born-Oppenheimer approximation.

6-13. What is the most probable value of the rotational quantum number J of a gas phase N_2 molecule at 300°K? What is the most probable vibrational quantum number n for this same situation?

6–25. Consider a system of independent diatomic molecules constrained to move in a plane, that is, a two-dimensional ideal diatomic gas. How many degrees of freedom does a two-dimensional diatomic molecule have? Given that the energy eigenvalues of a two-dimensional rigid rotor are

$$\varepsilon_J = \frac{\hbar^2 J^2}{2I} \quad J = 0, 1, 2, \dots$$

with a degeneracy $\omega_J = 2$ for all J except $J = 0$, calculate the rotational partition function. I is the moment of inertia of the molecule. The vibrational partition function is the same as for a three-dimensional diatomic gas. Write out

$$q(T) = q_{\text{trans}}(T)q_{\text{rot}}(T)q_{\text{vib}}(T)$$

and derive an expression for the average energy of this two-dimensional ideal diatomic gas.

7–4. Consider a classical ideal gas enclosed in an infinitely tall cylinder in a gravitational field. Assuming that the temperature is uniform up the cylinder, derive the barometric formula

$$p(z) = p(0)\exp\left(\frac{-mgz}{kT}\right)$$

From this calculate the atmospheric pressure at the top of Mt. Everest.

7–6. Consider a perfect gas of molecules with permanent electric dipole moments μ in an electric field \mathcal{E} . Neglecting the polarizability of the molecules, the potential energy is

$$U = -\mu\mathcal{E} \cos \theta$$

where θ is the angle between μ and \mathcal{E} . Using classical mechanics, derive an expression for the additional effect of \mathcal{E} on the energy E and heat capacity of the gas.

7–8. It is possible to determine the value of Boltzmann’s constant by observing the distribution of suspended Brownian particles in a gravitational field as a function of their height z . Given that the particles have a mass of 1.0×10^{-14} g, that the temperature is 300°K , and the following data:

z(cm)	Number of particles
0.0000	100
0.0025	55
0.0050	31
0.0075	17
0.0100	9

calculate the value of the Boltzmann constant.

7–13. Consider a system of N interacting molecules, whose vibrational degrees of freedom are treated quantum mechanically and whose translational and rotational degrees of freedom are treated classically with Hamiltonian

$$H_{\text{class}} = K_{\text{trans}} + K_{\text{rot}} + U$$

where K represents kinetic energy, and U represents potential energy. Substitute this into Eq. (7–19); integrate over all the coordinates except the $3N$ translational momentum coordinates; and derive

$$\text{prob}\{K_{\text{trans}}\} = \frac{e^{-K_{\text{trans}}/kT} dp_{\text{trans}}}{\int e^{-K_{\text{trans}}/kT} dp_{\text{trans}}}$$

Now realize that

$$K_{\text{trans}} = \sum_{j=1}^N \frac{1}{2m} (p_{xj}^2 + p_{yj}^2 + p_{zj}^2)$$

and derive the normalized Maxwell-Boltzmann distribution, namely,

$$f(p_x, p_y, p_z) dp_x dp_y dp_z = (2\pi mkT)^{-3/2} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z \quad (7-40)$$

One can derive all of the usual expressions of the kinetic theory of gases from this.

7-15. Convert Eq. (7-40) (see Problem 7-13) from a Cartesian coordinate to a spherical coordinate representation by writing

$$\begin{aligned} p^2 &= p_x^2 + p_y^2 + p_z^2 \\ p_z &= p \cos \theta \\ p_x &= p \sin \theta \cos \phi \\ p_y &= p \sin \theta \sin \phi \\ dp_x dp_y dp_z &\rightarrow p^2 \sin \theta dp d\theta d\phi \end{aligned}$$

and integrating over θ and ϕ to get

$$f(p) dp = 4\pi(2\pi mkT)^{-3/2} p^2 e^{-p^2/2mkT} dp$$

for the fraction of molecules with momentum between p and $p + dp$. By substituting $p = mv$, we get the fraction of molecules with *speeds* between v and $v + dv$:

$$f(v) dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv$$

7-20. According to Problem 1-35, the speed of sound in an ideal gas is given by

$$c_0 = \left(\gamma \frac{RT}{M} \right)^{1/2}$$

where M is the molecular weight of the gas, and $\gamma = C_p/C_v$. Show that $c_0 = 0.81\bar{v}$ for an ideal monatomic gas.

7-32. Consider a two-dimensional harmonic oscillator with Hamiltonian

$$H = \frac{1}{2m} (p_x^2 + p_y^2) + \frac{k}{2} (x^2 + y^2)$$

According to the principle of equipartition of energy, the average energy will be $2kT$. Now transform this Hamiltonian to plane polar coordinates to get

$$H = \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{k}{2} r^2$$

What would you predict for the average energy now? Show by direct integration in plane polar coordinates that $\bar{\epsilon} = 2kT$. Is anything wrong here? Why not?