Assignment 10

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PC2135
Thermodynamics and Statistical Mechanics

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Problem 1

[13 pts] In class, we have learnt Maxwell's speed distribution of a particle in an ideal gas. However, speed is just the magnitude of the velocity, and the velocity is a 3-component vector. In this problem, we discuss the velocity distribution of a particle in an ideal gas. We will consider an ideal gas made of particles with mass m, and we assume that the gas is in equilibrium with temperature T.

(1) (5 points) Denote the probability distribution function of the particles' velocity by $f(v_x, v_y, v_z)$. Namely, the probability of finding a particle that has a velocity lying in the range $(v_x, v_x + \mathrm{d}v_x)$, $(v_y, v_y + \mathrm{d}v_y)$ and $(v_z, v_z + \mathrm{d}v_z)$ for the three components is $f(v_x, v_y, v_z)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$. Show that, according to the Boltzmann statistics,

$$f(v_x, v_y, v_z) = \mathcal{N} e^{-\beta m(v_x^2+v_y^2+v_z^2)/2} \tag{1}$$

where $\beta = 1/(kT)$ and $\mathcal{N}$ is a normalisation constant. Calculate $\mathcal{N}$.

(2) (4 points) From $f(v_x, v_y, v_z)$, calculate the probability density of the speed, i.e., the magnitude of the velocity. You should obtain the result we have discussed in class.

(3) (4 points) At room temperature $T = 300$ K, what fraction of the nitrogen molecules in the air are moving at less than 300 m/s? You need to look up the mass of a nitrogen molecule by yourself, and use a computer to get the numerical value of the result.

Solution

Part (1): Velocity distribution and normalisation

The kinetic energy of a single particle is

$$E = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \tag{2}$$

By the Boltzmann distribution, the probability of a microstate with energy E is proportional to $e^{-\beta E}$. The velocity components (v_x, v_y, v_z) fully specify the kinetic state, so the probability density for finding a particle with velocity in a small volume $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$ is

$$f(v_x, v_y, v_z) = \mathcal{N} e^{-\beta m(v_x^2+v_y^2+v_z^2)/2} \tag{3}$$

where $\mathcal{N}$ is fixed by normalisation to unity. The exponential factorises into three identical Gaussian integrals:

$$\mathcal{N}\left[\int_{-\infty}^{\infty} e^{-\beta m v_x^2/2}\,\mathrm{d}v_x\right]^3 = 1 \tag{4}$$

Each one-dimensional integral is a standard Gaussian $\int_{-\infty}^{\infty} e^{-\alpha v^2}\,\mathrm{d}v = \sqrt{\pi/\alpha}$ with $\alpha = \beta m/2$:

$$\int_{-\infty}^{\infty} e^{-\beta m v_x^2/2}\,\mathrm{d}v_x = \sqrt{\frac{2\pi kT}{m}} \quad\Longrightarrow\quad \mathcal{N}\left(\frac{2\pi kT}{m}\right)^{3/2} = 1 \quad\Longrightarrow\quad \mathcal{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \tag{5}$$

$$f\big(v_x, v_y, v_z\big) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/(2kT)} \tag{6}$$

Part (2): Speed distribution

The speed is $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. To obtain the probability density for the speed, we convert to spherical coordinates in velocity space: $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z = v^2 \sin\theta\,\mathrm{d}v\,\mathrm{d}\theta\,\mathrm{d}\varphi$. Integrating over all directions:

$$D(v) = \int_0^{\pi}\int_0^{2\pi} f(v) v^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi = 4\pi v^2 f(v) \tag{7}$$

since f depends only on $|\boldsymbol{v}|$ and $\int \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi = 4\pi$:

$$D(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/(2kT)} \tag{8}$$

This is the Maxwell speed distribution.

Part (3): Fraction of N_2 below 300 m/s

For a nitrogen molecule, $m = 28\ \mathrm{u} = 28 \times 1.661 \times 10^{-27}\ \mathrm{kg} = 4.651 \times 10^{-26}\ \mathrm{kg}$. In an ideal gas mixture at thermal equilibrium, each species samples the bath temperature independently, so the velocity distribution of N_2 depends only on m_{N_2} and T; the presence of O_2, Ar, and CO_2 makes no difference. At $T = 300$ K, the most probable speed is

$$v_p = \sqrt{\frac{2kT}{m}} \approx 422\ \ \mathrm{m/s} \tag{9}$$

so 300 m/s is well below the peak of the distribution. The cumulative probability is

$$P(v < v_{\max}) = \int_0^{v_{\max}} D(v)\,\mathrm{d}v = \operatorname{erf}(a) - \frac{2a}{\sqrt{\pi}} e^{-a^2} \tag{10}$$

where $a = v_{\max}\sqrt{m/(2kT)}$. With $v_{\max} = 300$ m/s:

$$a = 300 \times \sqrt{\frac{4.651 \times 10^{-26}}{2 \times 1.381 \times 10^{-23} \times 300}} \approx 0.711 \tag{11}$$

$$P(v < 300\ \ \mathrm{m/s}) \approx 0.201 \approx 20.1\% \tag{12}$$

About one-fifth of the nitrogen molecules in the air at room temperature have speeds below 300 m/s.

Problem 2

[14 pts] In class, we have applied the partition function approach to study a paramagnet and ideal gas. In this problem, we apply it to an Einstein solid made of N harmonic oscillators. Recall that the energy of each harmonic oscillator takes the form $q\hbar\omega$, where q is a non-negative integer and ω is the frequency of the oscillator.

(1) (4 points) What is the partition function of one such harmonic oscillator?

(2) (5 points) What is the partition function of the entire Einstein solid that consists of N such harmonic oscillators? Think through whether there is any issue related to overcounting states.

(3) (5 points) What is the energy, entropy and heat capacity of this Einstein solid? At high temperatures, what is the approximate value of the heat capacity? Does the result agree with the equipartition theorem? At low temperatures, what is the behaviour of the heat capacity (keep the dominant temperature dependence in this calculation)? Does the result agree with the third law of thermodynamics?

Solution

Part (1): Single-oscillator partition function

The energy levels of one oscillator are $E_q = q\hbar\omega$ with $q = 0, 1, 2, ...$ The partition function is the sum over all states:

$$Z_1 = \sum_{q=0}^{\infty} e^{-\beta q\hbar\omega} = \sum_{q=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^q = \frac{1}{1 - e^{-\beta\hbar\omega}} \tag{13}$$

where the last step uses the geometric series $\sum_{q=0}^{\infty} r^q = 1/(1-r)$ for $|r| < 1$, which holds since $e^{-\beta\hbar\omega} < 1$ for any finite T.

Zero-point energy: The question sets $E_q = q\hbar\omega$ with no zero-point term. A real quantum harmonic oscillator has $E_q = (q + 1/2)\hbar\omega$, which would multiply Z_1 by an overall factor $e^{-\beta\hbar\omega/2}$ and shift the internal energy by a constant $+N\hbar\omega/2$. But S and C do not change, since they depend only on energy **differences** between levels, not on the absolute zero of energy.

Part (2): N-oscillator partition function

The atoms in a crystal are fundamentally identical quantum particles, but each one is bound in a deep potential well at a specific lattice site. The spatial wavefunctions of neighbouring sites have essentially zero overlap, so exchange interactions are negligible. This means we can treat the oscillators as effectively distinguishable by position, and no $1/N!$ Gibbs correction is needed. In an ideal gas the molecules are fully delocalized, so the same argument does not apply.

The total partition function is just the product of independent single-oscillator partition functions:

$$Z_N = Z_1^N = \frac{1}{\left(1 - e^{-\beta\hbar\omega}\right)^N} \tag{14}$$

Part (3): Thermodynamic quantities

Define the dimensionless ratio $x = \beta\hbar\omega = \hbar\omega/(kT)$ for compactness.

Energy:

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -N\frac{\partial}{\partial \beta}\left[-\ln\left(1 - e^{-\beta\hbar\omega}\right)\right] = \frac{N\hbar\omega\, e^{-x}}{1 - e^{-x}} = \frac{N\hbar\omega}{e^x - 1} \tag{15}$$

Entropy:

The free energy is $F = -kT \ln Z_N = NkT \ln(1 - e^{-x})$. The entropy follows from $S = -\frac{\partial F}{\partial T}$, or equivalently $S = (U - F)/T$:

$$S = \frac{U}{T} + Nk \ln Z_1 = Nk\left[\frac{x}{e^x - 1} - \ln(1 - e^{-x})\right] \tag{16}$$

Heat capacity:

$$C = \frac{\partial U}{\partial T} = Nkx^2 \frac{e^x}{(e^x - 1)^2} \tag{17}$$

High-temperature limit ($T \gg \hbar\omega/k$, i.e. $x \to 0$):

For small x, $e^x \approx 1 + x + x^2/2$, so $e^x - 1 \approx x$ and

$$C \approx Nk\frac{x^2(1 + x)}{x^2} \approx Nk \tag{18}$$

This is the equipartition result: each oscillator has two quadratic degrees of freedom (kinetic and potential), each contributing $kT/2$, so $U \approx NkT$ and $C = Nk$. Here N is the number of oscillators, not atoms. A real 3D solid has $3N$ independent oscillators (one per spatial direction per atom), giving $C \to 3Nk$ in the classical limit, which is the Dulong–Petit law. The factor of 3 is absent here only because the problem is stated for N one-dimensional oscillators.

Low-temperature limit ($T \ll \hbar\omega/k$, i.e. $x \to \infty$):

For large x, $e^x \gg 1$, so $e^x - 1 \approx e^x$ and

$$C \approx Nkx^2 e^{-x} = Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/(kT)} \tag{19}$$

The heat capacity vanishes exponentially as $T \to 0$, consistent with the third law. All oscillators freeze into the $q = 0$ ground state because the thermal energy kT is far below the gap $\hbar\omega$ to the first excited level, so $S \to 0$ and $C = T\frac{\partial S}{\partial T} \to 0$.

Problem 3

[13 pts] In class, we have discussed the partition function and its applications to a monatomic ideal gas. In this problem, we apply the same idea to a diatomic ideal gas. For a diatomic gas made of identical atoms near room temperature, the internal partition function is simply the rotational partition function computed last week ($Z_{\text{rot}} = kT/(2\varepsilon)$ where ε is the characteristic rotational energy scale), multiplied by the degeneracy Z_e of the electronic ground state (the number of all such electronic ground states). That is, the internal partition function is $Z_{\text{int}} = Z_e Z_{\text{rot}}$.

(1) (7 points) Show that the entropy in this case is

$$S = Nk\left[\ln\left(\frac{V}{N}\frac{Z_e Z_{\text{rot}}}{v_Q}\right) + \frac{7}{2}\right] \tag{20}$$

Calculate the entropy of a mole of oxygen molecules ($Z_e = 3$) at room temperature (300 K) and atmospheric pressure. The value of ε for an oxygen molecule is about 0.00018 eV, and you need to look up the mass of an oxygen molecule by yourself.

(2) (6 points) Calculate the chemical potential of oxygen in earth's atmosphere near sea level, at room temperature. Express the answer in electron-volts.

Solution

Part (1): Entropy of a diatomic ideal gas

For N identical diatomic molecules, the total partition function is

$$Z = \frac{Z_1^N}{N!} \tag{21}$$

where the $1/N!$ corrects for the indistinguishability of identical molecules (Gibbs factor), and Z_1 is the single-molecule partition function. This factorises into translational and internal parts:

$$Z_1 = Z_{\text{tr}} \times Z_{\text{int}} = \frac{V}{v_Q} \times Z_e Z_{\text{rot}} \tag{22}$$

where $v_Q = \left(h^2/(2\pi mkT)\right)^{3/2}$ is the quantum volume.

The free energy is

$$F = -kT \ln Z = -kT[N \ln Z_1 - \ln N!] \tag{23}$$

Using Stirling's approximation ($\ln N! \approx N \ln N - N$):

$$F = -NkT\left[\ln\left(\frac{V}{N}\frac{Z_e Z_{\text{rot}}}{v_Q}\right) + 1\right] \tag{24}$$

The entropy is $S = -\frac{\partial F}{\partial T}$. The T-dependent factors in Equation 24 are $Z_{\text{rot}} = kT/(2\varepsilon) \propto T$ and $v_Q \propto T^{-3/2}$:

$$\ln\left(\frac{V Z_e Z_{\text{rot}}}{N v_Q}\right) = \ln V + \ln Z_e + \ln Z_{\text{rot}} - \ln N - \ln v_Q \tag{25}$$

$$\frac{\partial}{\partial T}\ln\left(\frac{V Z_e Z_{\text{rot}}}{N v_Q}\right) = \frac{1}{T} + \frac{3}{2T} = \frac{5}{2T} \tag{26}$$

$$S = -\frac{\partial F}{\partial T} = Nk\left[\ln\left(\frac{V}{N}\frac{Z_e Z_{\text{rot}}}{v_Q}\right) + 1\right] + NkT \cdot \frac{5}{2T} \tag{27}$$

$$S = Nk\left[\ln\left(\frac{V}{N}\frac{Z_e Z_{\text{rot}}}{v_Q}\right) + \frac{7}{2}\right] \tag{28}$$

This is the diatomic version of the Sackur–Tetrode equation. The 7/2 instead of 5/2 comes from the two additional rotational degrees of freedom.

Two things are worth clarifying before the numbers. First, the $Z_{\text{rot}} = kT/(2\varepsilon)$ given in the question already includes the symmetry number $\sigma = 2$ in the denominator. For a homonuclear molecule like O_2, exchanging the two identical nuclei does not produce a new microstate, so half of the rotational states are forbidden by quantum statistics. This gives $Z_{\text{rot}} = kT/(\sigma\varepsilon)$ with $\sigma = 2$, rather than kT/ε for a heteronuclear molecule. Second, vibrational modes are omitted. The characteristic vibrational temperature for O_2 is $\Theta_{\text{vib}} \approx 2256$ K, far above $T = 300$ K, so the Boltzmann factor $e^{-\Theta_{\text{vib}}/T} \approx 0.0005$ and $Z_{\text{vib}} \approx 1$ to well within 0.1%. Including vibration would make no measurable difference here.

Numerical evaluation for O_2:

The mass of an O_2 molecule is $m = 32$ u $= 5.315 \times 10^{-26}$ kg. At $T = 300$ K:

Thermal de Broglie wavelength: $\lambda = h/\sqrt{2\pi mkT} = 1.781 \times 10^{-11}$ m
Quantum volume: $v_Q = \lambda^3 = 5.652 \times 10^{-33}$ m^3
Volume per molecule at 1 atm: $V/N = kT/P = 4.090 \times 10^{-26}$ m^3
Rotational partition function: $Z_{\text{rot}} = kT/(2\varepsilon) = 0.02586/(2 \times 0.00018) \approx 71.8$
Internal partition function: $Z_{\text{int}} = Z_e Z_{\text{rot}} = 3 \times 71.8 = 215.5$

Therefore

$$\ln\left(\frac{V}{N}\frac{Z_{\text{int}}}{v_Q}\right) = \ln\left(\frac{4.090 \times 10^{-26} \times 215.5}{5.652 \times 10^{-33}}\right) = \ln(1.559 \times 10^9) \approx 21.17 \tag{29}$$

For one mole:

$$S = N_A k(21.17 + 3.5) = R \times 24.67 \approx 205.1 \ \text{J/(mol·K)} \tag{30}$$

This agrees well with the experimental value of 205.0 J/(mol · K) for O_2 at standard conditions.

Part (2): Chemical potential

The chemical potential is $\mu = \frac{\partial F}{\partial N}_T$, or equivalently $\mu = G/N$ for an ideal gas. Differentiating Equation 24 with respect to N (for an ideal gas at fixed P and T, $V/N = kT/P$ does not depend on N):

$$\mu = -kT\ln\left(\frac{V}{N}\frac{Z_e Z_{\text{rot}}}{v_Q}\right) \tag{31}$$

We can also get this from the Gibbs free energy: $G = F + PV = F + NkT$, so $\mu = G/N = -kT\left[\ln\left(VZ_{\text{int}}/(Nv_Q)\right) + 1\right] + kT$, which simplifies to Equation 31.

The question is about O_2 **in Earth's atmosphere**, not a pure sample. In the atmosphere O_2 makes up about 21% of the total, so its partial pressure is $P_{O_2} \approx 0.21 P_{\text{atm}} \approx 2.13 \times 10^4$ Pa. This is the pressure that sets the volume per O_2 molecule:

$$\frac{V}{N} = \frac{kT}{P_{O_2}} = \frac{1.381 \times 10^{-23} \times 300}{2.13 \times 10^4} \approx 1.948 \times 10^{-25} \ \text{m}^3 \tag{32}$$

Part (1) uses a pure O_2 sample at 1 atm as stated, so $V/N = kT/P_{\text{atm}}$ is still correct there.

The internal partition function $Z_{\text{int}} = 215.5$ is unchanged:

$$\ln\left(\frac{V}{N}\frac{Z_{\text{int}}}{v_Q}\right) = \ln\left(\frac{1.948\times10^{-25}\times215.5}{5.652\times10^{-33}}\right) = \ln(7.42\times10^{9}) \approx 22.73 \tag{33}$$

$$\mu = -kT\times22.73 = -0.02586\ \text{ eV}\times22.73 \approx -0.588\ \text{ eV} \tag{34}$$

The shift from the pure-O_2 value (-0.547 eV) is exactly $-kT\ln(1/0.21) \approx -0.040$ eV, reflecting the extra translational entropy each molecule gains from the larger volume available at the lower partial pressure. The chemical potential is negative because there are far more available quantum states than there are molecules.