

## Thermodynamics of a Classical Ideal Gas—C.E. Mungan, Spring 2000

The purpose of this note is to remind one how to calculate the entropy  $S$  and chemical potential  $\mu$  of a classical ideal gas. First consider a monatomic ideal gas consisting of  $N$  identical atoms of mass  $m$  each having  $\nu = 3$  translational degrees of freedom and obeying the ideal gas law,

$$pV = NkT. \quad (1)$$

This law implicitly assumes that the atoms are point particles and interact only by elastic hard-sphere collisions. On the other hand, a classical gas is one which obeys classical statistics for the partition function of the system,

$$Z = \frac{1}{N!} \zeta^N \quad (2)$$

where the translational partition function of a single particle is

$$\zeta = \zeta_{TR} = \sum_{\text{translational states}} \exp\left(-\beta \frac{p^2}{2m}\right). \quad (3)$$

(A degeneracy factor would have to be included if the sum were over the levels rather than over the individual states.) Recall that Eq. (2) is obtained by assuming that the probability that any particle occupies a state is independent of that for all other particles and furthermore that the particles densities are sufficiently low that no states are multiply occupied. It is possible for a gas to be ideal but not classical (e.g. helium under high pressure) or alternatively classical but not ideal (e.g. phonons in a high-temperature solid).

Equation (3) can be converted into an integral and evaluated by noting that the number of states in some elementary volume of phase space is equal to  $d^3r d^3p / h^3$ , because  $h^3$  is the phase-space volume of a single quantum state according to Heisenberg's Uncertainty Principle. This gives

$$\begin{aligned} \zeta_{TR} &= \iint \frac{d^3r d^3p}{h^3} \exp\left(-\beta \frac{p^2}{2m}\right) = \frac{4\pi V}{h^3} \int_0^\infty p^2 e^{-\beta p^2 / 2m} dp = -\frac{2\pi V}{h^3} \frac{d}{d\alpha} \int_{-\infty}^{+\infty} e^{-\alpha p^2} dp \\ &= -\frac{2\pi V}{h^3} \frac{d}{d\alpha} \sqrt{\frac{\pi}{\alpha}} = V \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \end{aligned} \quad (4)$$

using  $\alpha \equiv \beta/2m$  and the integral of a Gaussian. Substitute this into Eq. (2) and use the standard relation between  $Z$  and  $S$ ,

$$S = k \ln Z + \frac{E}{T} \quad (5)$$

as given for example by Eq. (21.11) of Stowe, where  $E$  is the total internal energy of the gas. Invoking the equipartition theorem as

$$E = \nu N \cdot \frac{1}{2} kT \quad (6)$$

and Stirling's approximation for large  $N$  in the form

$$\ln N! \cong N \ln N - N \quad (7)$$

gives the final result,

$$S = Nk \left[ \ln \left( \frac{\zeta}{N} \right) + \frac{\nu + 2}{2} \right] = Nk \left[ \frac{5}{2} + \ln \frac{V(2\pi mkT)^{3/2}}{Nh^3} \right] \quad (8)$$

known as the Sackur-Tetrode equation.

To find the chemical potential, we can use another standard relation,

$$\mu = -kT \ln \frac{\zeta}{N}. \quad (9)$$

which is Eq. (21.19) of Stowe. From this it follows that

$$\mu = kT \ln \frac{Nh^3}{V(2\pi mkT)^{3/2}}, \quad (10)$$

thereby completing what we originally set out to find.

These results can be cast into forms which are easier to remember. The entropy per particle is

$$s = c_p - \mu/T \quad (11)$$

where  $c_p$  is the heat capacity per particle at constant pressure. The chemical potential is

$$e^{\mu/kT} = o \quad (12)$$

where I have introduced the average occupancy of available states,

$$o \equiv \frac{N}{\zeta} = \frac{N}{V} \times V_{state} \quad (13)$$

since the volume per quantum state in real space is

$$V_{state} = \frac{h^3}{(2\pi mkT)^{3/2}} \quad (14)$$

i.e., the volume in phase space divided by the volume in momentum space. An estimate for the latter is

$$V_p \equiv p_{rms}^3 = (3mkT)^{3/2} \quad \text{since} \quad \frac{p_{rms}^2}{2m} = \frac{E}{N} = \frac{3kT}{2}. \quad (15)$$

Equation (13) therefore has the simple interpretation that the average number of particles per state is simply the product of the number of particles per unit volume and the volume per state. Our results here are valid provided  $o \ll 1 \Rightarrow \mu \ll -kT$  so that the gas is classical.

Next, we can extend these results to a classical diatomic ideal gas. We assume that the temperatures are low enough that the potential and kinetic vibrational degrees of freedom are

frozen out, so that the molecules are rigid dumbbells of moment of inertia  $I$ . In that case,  $\nu = 5$  due to the addition of 2 rotational degrees of freedom. Equation (3) must now be corrected to include the rotational partition function,

$$\zeta = \zeta_{TR} \zeta_{ROT} \quad (16)$$

where

$$\begin{aligned} \zeta_{ROT} &= \sum_{\substack{\text{rotational} \\ \text{states}}} \exp\left(-\beta \frac{L^2}{2I}\right) = \sum_{l=0}^{\infty} (2l+1) e^{-\beta \hbar^2 l(l+1)/2I} \\ &= \int_0^{\infty} (2l+1) e^{-\beta \hbar^2 l(l+1)/2I} dl = \int_0^{\infty} e^{-x \hbar^2 / 8\pi^2 IkT} dx = \frac{8\pi^2 IkT}{\hbar^2} \end{aligned} \quad (17)$$

using  $x \equiv l^2 + l$  and where the  $2l + 1$  values of  $m_l$  were summed over in the second step. Equation (8) thus becomes

$$S = Nk \left[ \frac{7}{2} + \ln \frac{V(2\pi mkT)^{5/2} 4\pi I / m}{Nh^5} \right] \quad (18)$$

and Eq. (10) becomes

$$\mu = kT \ln \frac{Nh^5}{V(2\pi mkT)^{5/2} 4\pi I / m}. \quad (19)$$

Equations (11)–(13) thus continue to hold provided that we redefine

$$V_{state} = \frac{h^3}{(2\pi mkT)^{3/2}} \cdot \frac{h^2}{8\pi^2 IkT}. \quad (20)$$

To interpret this, consider an extended phase space  $V_r V_p V_\Omega V_L$  where  $V_r = V_{state}$  is the volume of a quantum state in real space,  $V_\Omega = 4\pi$  is the volume in solid-angle space, and an estimate for the volume in angular-momentum space is

$$V_L \cong L_{rms}^2 = 2IkT \quad \text{since} \quad \frac{L_{rms}^2}{2I} = \frac{2kT}{2}. \quad (21)$$

The volume of a quantum state in this extended phase space is now  $h^5$ , leading directly to Eq. (20).

To make this concrete, let's substitute numerical values into these expressions. Consider say helium and dry air at 1 atm ( $p = 101$  kPa) and RT ( $T = 300$  K). We have

$$c_P = \frac{\nu + 2}{2}k \quad \text{with} \quad \nu = \begin{cases} 3 & \text{for He} \\ 5 & \text{for air} \end{cases}$$

$$\frac{N}{V} = \frac{p}{kT}$$

$$m = \frac{A(0.001 \text{ kg})}{6.022 \times 10^{23}} \quad \text{where} \quad A = \begin{cases} 4 & \text{for He} \\ 0.79 \times 28 + 0.21 \times 32 & \text{for air} \end{cases}$$

$$I \cong \frac{1}{4}mr^2 \quad \text{where} \quad r \cong 1.2 \text{ \AA} \quad \text{for air}$$

so that

$$s = \begin{cases} 1.3 \text{ meV/K} & \text{for He} \\ 2.1 \text{ meV/K} & \text{for air} \end{cases} \quad \text{and} \quad \mu = \begin{cases} -0.33 \text{ eV} & \text{for He} \\ -0.53 \text{ eV} & \text{for air} \end{cases} .$$