

Chapter 3. Ideal and Not-So-Ideal Gases

In this chapter we find statistical properties of gases: systems of free or almost-free identical, indistinguishable particles.

3.1. Ideal Classical Gas: The Maxwell Distribution

A dilute gas is an example of a system of similar particles, which do not interact explicitly. Its main peculiarity is that there are no means to distinguish the particles, and this fact needs to be taken into account at the statistical description. Let us start with a “classical” gas which may be defined as having small average occupancy $\langle n_k \rangle \ll 1$ of each quantum state.

$$\langle n_k \rangle = c \exp\left\{-\frac{\varepsilon_k}{T}\right\}$$

At no external forces, and no internal degrees of freedom,

$$\varepsilon_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m},$$

and the Boltzmann formula is reduced to the *Maxwell distribution* (which was put forward earlier, in 1860):

$$dw = c \exp\left\{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}\right\} dp_x dp_y dp_z,$$

or equivalently

$$dw' = c \exp\left\{-\frac{p^2}{2mT}\right\} 4\pi p^2 dp.$$

Normalization:

$$1 = c \int_0^\infty \exp\left\{-\frac{p^2}{2mT}\right\} 4\pi p^2 dp$$

gives:

$$c = (2\pi mT)^{-3/2}.$$

Average energy per particle:

$$\langle \varepsilon \rangle = \int_{p \text{ space}} \frac{p^2}{2m} dw = 4\pi c \int_0^\infty \frac{p^2}{2m} \exp\left\{-\frac{p^2}{2mT}\right\} p^2 dp = 3 \int_{-\infty}^{+\infty} dp_x \frac{p_x^2}{2m} \left[\int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z \frac{dw}{dp_x dp_y dp_z} \right] = \frac{3}{2} T.$$

This means that the r.m.s. velocity of the particles is

$$\langle v^2 \rangle^{1/2} = \left(3 \frac{T}{m}\right)^{1/2}.$$

For a typical gas (say, N_2): $m \sim 30 m_p \sim 6 \times 10^{-26}$ kg at 300K ($E = k_B T_K \approx 4 \times 10^{-21}$ J), this velocity is about 4.5 km/s, about 10 times faster than a typical handgun bullet.

Explicit calculation of work for the Maxwell's Demon system (Fig. 2.3):

$$\langle v_x^2 \rangle = \frac{T}{m}.$$

Momentum transferred at single collision with the partition: $2mv_x$. Average pressure force:

$$\langle F \rangle = \left\langle \frac{2mv_x}{\tau} \right\rangle = \left\langle \frac{2mv_x}{2x/v_x} \right\rangle = \frac{m}{x} \langle v_x^2 \rangle = \frac{T}{x},$$

where x is the length of the cylinder's part containing the molecule. Work:

$$\int_{L/2}^L \langle F \rangle dx = \int_{L/2}^L \frac{T}{x} dx = T \ln 2.$$

(Confirms our general result for this particular case.)

Gas in an external field:

$$\varepsilon_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + U(x, y, z).$$

Distribution:

$$dw = c \exp \left\{ -\frac{p_x^2 + p_y^2 + p_z^2}{2mT} - \frac{U(x, y, z)}{T} \right\} dx dy dz dp_x dp_y dp_z.$$

If we are not interested in momentum distribution:

$$dw = c \exp \left\{ -\frac{U(x, y, z)}{T} \right\} dx dy dz \int \exp \left\{ -\frac{p^2}{2mT} \right\} d^3 p = c' \exp \left\{ -\frac{U(x, y, z)}{T} \right\} dx dy dz.$$

Example: Earth's gravity field: $U = mgz + \text{const}$. Density of molecules (number per unit volume $dV = dx dy dz$):

$$n \equiv \frac{dw}{dV} = n_0 \exp \left\{ -\frac{mgz}{T} \right\} = n_0 \exp \left\{ -\frac{z}{z_0} \right\}. \quad (*)$$

(the "barometric formula"). For a typical gas (N_2) at $T_K = 300$ K, $z_0 \equiv k_B T_K / mg \approx 7$ km. This gives the right order of magnitude of the Earth atmosphere's thickness, though the exact law differs from Eq. (*) because of the drop of temperature with height.

3.2. Ideal Classical Gas: Thermodynamics

Since the entropy is a measure of information about a statistical system, in order to calculate it (and hence all other thermodynamic variables) we have to make a more accurate calculations than we did in the previous section. First, for any system of independent particles (no explicit interaction energy), we can present the full internal energy of the system as

$$E = \sum_{j=1}^N \varepsilon_{k(j)}$$

If the particles are exactly the same, their eigenstate spectrum $\{\varepsilon_k\}$ is the same, and it is tempting to calculate the statistical sum using an apparent (but **WRONG**) formula:

$$Z = \sum_n \exp\left\{-\frac{E_n}{T}\right\} = \left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\}\right)^N,$$

where the summation is over the states of one particle. Most results (e.g. the equation of state $p = p(T, V)$) obtained from this formula would be correct, but it would lead to a wrong expression for entropy and, as a result, to the gas mixing paradox (see below). Instead, for indistinguishable particles (first, internally similar, and, second, not fixed in particular spatial locations) one should use the “correct Boltzmann counting”

$$Z = \frac{1}{N!} \left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\}\right)^N.$$

which treats all states which differ by particle permutations as one.

For the translational degrees of freedom, the summation may be reduced to integration:

$$\sum_k \rightarrow \frac{1}{(2\pi\hbar)^3} \int d^3q \int d^3p.$$

If the averaged quantity (e.g., $p^2/2m$) does not depend on q_j and the direction of vector \vec{p} , then

$$\frac{1}{(2\pi\hbar)^3} \int d^3q \int d^3p = \frac{V}{(2\pi\hbar)^3} 4\pi \int_0^\infty p^2 dp.$$

Taking into account the internal degrees of freedom:

$$\varepsilon_k = \frac{p^2}{2m} + \varepsilon'.$$

As a result,

$$Z = \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3} 4\pi \int_0^\infty p^2 \exp\left\{-\frac{p^2}{2mT}\right\} dp \times \sum_{\varepsilon'} \exp\left\{-\frac{\varepsilon'}{T}\right\} \right)^N.$$

The integral is the same as we had in Sec. 1, and we get

$$Z = \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3} (2\pi mT)^{3/2} \times \sum_{\varepsilon'} \exp\left\{-\frac{\varepsilon'}{T}\right\} \right)^N,$$

so that, using the Stirling formula,

$$F = -T \ln Z = -NT \ln \frac{eV}{N} + Nf(T),$$

with

$$f(T) = -T \ln \left[\left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \times \sum_{\varepsilon'} \exp \left\{ -\frac{\varepsilon'}{T} \right\} \right].$$

If the internal degrees of freedom are “frozen” ($T \ll \varepsilon'$), the last sum equals 1.

Now using the general thermodynamics formula, we get:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{NT}{V},$$

i.e. regardless of $f(T)$, we have the equation of state

$$pV = NT.$$

Next,

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = N \left[\ln \frac{eV}{N} - f'(T) \right].$$

(Without the “correct Boltzmann counting”, we would get a wrong result under the logarithm.)

$$E = F + TS = N[f(T) - Tf'(T)].$$

The average energy per molecule, $\langle \varepsilon \rangle = E/N$ is a function of temperature alone.

$$W = E + pV = N[f(T) - Tf'(T) + T]$$

$$c_p - c_v = \left(\frac{\partial W}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_V = \frac{\partial(NT)}{\partial T} = N.$$

$$G = F + pV = N[T \ln p + \chi(T)],$$

i.e.

$$\mu = T \ln p + \chi(T),$$

where

$$\chi(T) = f(T) - T \ln T.$$

In particular, for a gas with the internal degrees of freedom frozen,

$$\mu = T \ln \left[\frac{N}{V} \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2} \right].$$

Since

$$\langle n_k \rangle = \exp\left\{\frac{\mu - \varepsilon_k}{T}\right\},$$

in order to satisfy the classicity condition $\langle n_k \rangle \ll 1$ with the choice $\varepsilon_0 = 0$, it suffices to have

$$-\mu \gg T.$$

This means $T \ll T_0$, where

$$T_0 \equiv \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{2/3} = \frac{\hbar^2}{mr^2},$$

where r is the average distance between the molecules. Physical sense of T_0 : thermal energy becomes comparable to the zero-point quantum (kinetic) energy scale.

Another important formula for the case of no internal degrees of freedom: since in this case $f(T) - Tf'(T) = 3/2$, then

$$E = \frac{3}{2} NT.$$

Since in this case $E = m\langle v^2 \rangle / 2$, this formula could be also obtained from the Maxwell distribution.

3.3. Ideal Fermi and Bose Gases

In the previous section, we have derived the Fermi and Bose distributions, which may be presented by one formula:

$$\langle n_k \rangle = \frac{1}{\exp\{(\varepsilon_k - \mu)/T\} \pm 1}.$$

(Everywhere in this section, the top sign is for the Fermi gas, lower for the Bose gas.) Now let us apply these distributions to gases of free particles: $\varepsilon_k = p^2/2m$.

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3.4. Degenerate Fermi Gas

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3.5. Bose-Einstein Condensation

Let us explore in more detail the equation discussed Sec. 4, for the case of Bose gas:

$$\frac{N}{V} = g \frac{m^{3/2} T^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{z^{1/2} dz}{e^{z-y} - 1}, \quad y \equiv \frac{\mu}{T}.$$

For the normalized temperature $t \equiv T/T_0$ this equation gives:

$$t = \left[\frac{g}{\sqrt{2\pi^2}} \int_0^\infty \frac{z^{1/2} dz}{e^{z-y} - 1} \right]^{-2/3}$$

The plot of this result (Fig. 4a) shows that $\mu \rightarrow 0$ at some finite temperature t . Condition $\mu = 0$ yields:¹

$$t = t_c = \left[\frac{g}{\sqrt{2\pi^2}} \int_0^\infty \frac{z^{1/2} dz}{e^z - 1} \right]^{-2/3} = \left[\frac{g}{\sqrt{2\pi^2}} \Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right) \right]^{-2/3} \approx 3.313 g^{-2/3}.$$

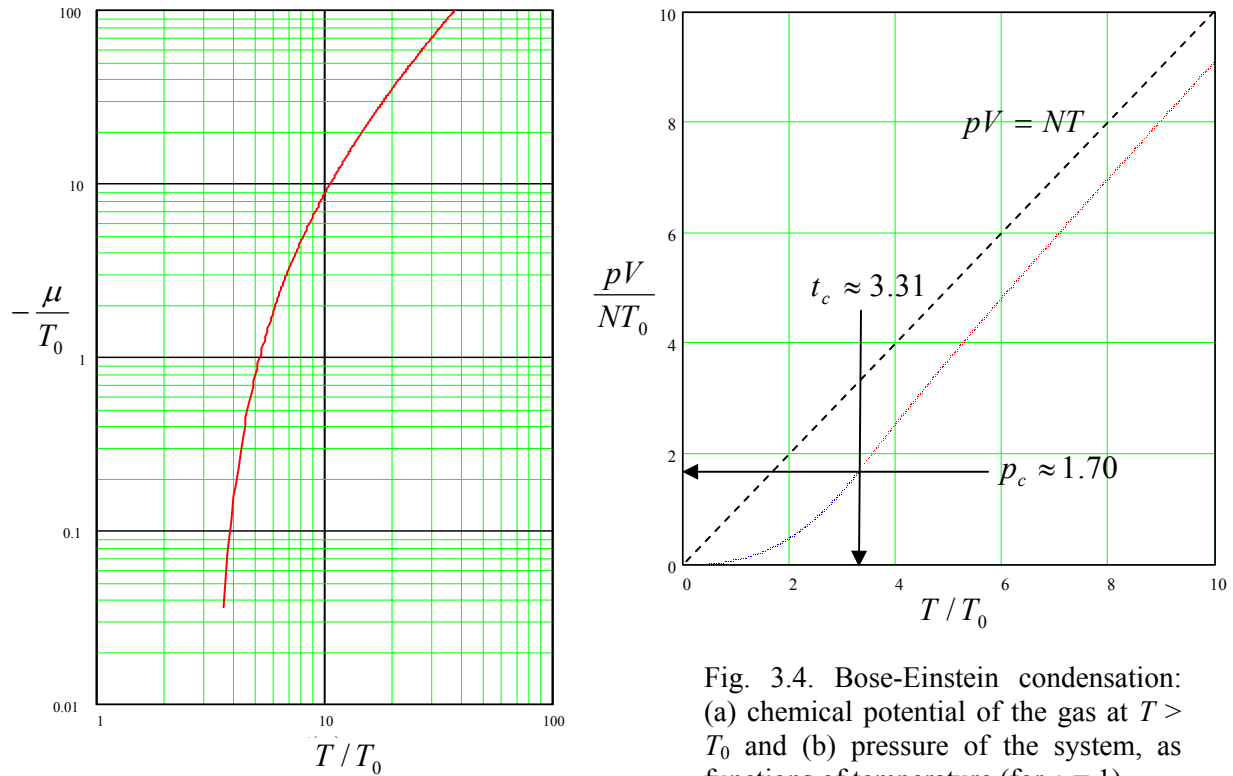


Fig. 3.4. Bose-Einstein condensation: (a) chemical potential of the gas at $T > T_0$ and (b) pressure of the system, as functions of temperature (for $g = 1$).

At $0 < T \leq T_c = t_c T_0 \approx 3.313 g^{-2/3} T_0$: chemical potential μ may only equal zero (otherwise the integral for N diverges), but then that equation cannot be satisfied. The only possible

¹ Math box: $\int_0^\infty \frac{z^{\alpha-1} dz}{\exp\{z\} - 1} = \Gamma(\alpha) \zeta(\alpha)$, $\Gamma(\alpha) \equiv \int_0^\infty z^{\alpha-1} e^{-z} dz$ (Gamma-function), $\zeta(\alpha) \equiv \sum_{n=0}^\infty \frac{1}{n^\alpha}$

(Riemann's zeta-function). Important properties and values: $\Gamma(n) = (n-1)!$,

$$\Gamma\left(n + \frac{1}{2}\right) = \Gamma\left(\frac{1}{2}\right) \frac{1 \cdot 3 \cdot 7 \dots (2n-1)}{2^n}, \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}, \quad \zeta\left(\frac{3}{2}\right) \approx 2.612, \quad \zeta\left(\frac{5}{2}\right) \approx 1.341.$$

resolution of the paradox: a fraction (N_0 of N) particles are in the ground state (with $\varepsilon = p^2/2m = 0$). This is the *Bose-Einstein condensate*.

Equation for finding N_0 :

$$N - N_0 = gV \frac{m^{3/2} T^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{z^{1/2} dz}{e^z - 1}.$$

On the other hand, the equation for T_c may be re-written as

$$N = gV \frac{m^{3/2} T_c^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{z^{1/2} dz}{e^z - 1}.$$

Dividing these two equations, we get a very simple result:

$$\frac{N - N_0}{N} = \frac{T^{3/2}}{T_c^{3/2}},$$

giving finally

$$N_0 = N \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right].$$

Figure 4 shows this function together with the first experimental results $N_0(T)$ for the Bose-Einstein condensation of a dilute gas of neutral atoms.

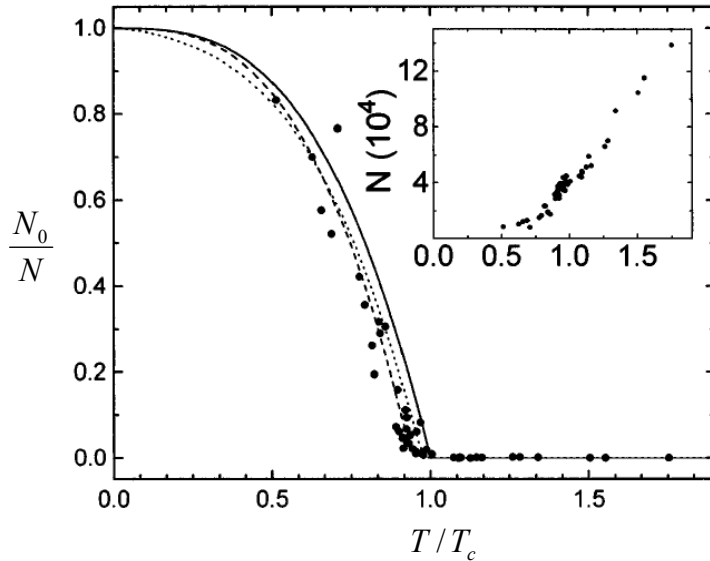


Fig. 3.5. The total number N of trapped ^{87}Rb atoms (inset) and their ground-state fraction N_0/N , as functions of the ratio T/T_c in the experiment by J. Ensher *et al.* (1996). In this experiment, T_c was as low as 0.28×10^{-6} K. The solid line shows our simple theoretical dependence $N(T)$, while other lines correspond to more complex theories taking into account the trapping potential and the finite number of trapped atoms.

Thus, energy E (and hence pressure p) should be calculated separately in two temperature ranges. At $T > T_c$,

$$E(T) = gV \frac{m^{3/2} T^{5/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{z^{3/2} dz}{e^{z-y} - 1}, \quad p(T) = \frac{2}{3} \frac{E(T)}{V}.$$

Red points in Fig. 4b show the dependence $p(T)$ numerically calculated from this equation. At the critical temperature (where $\mu \rightarrow 0$),

$$E(T_c) = gV \frac{m^{3/2} T_c^{5/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{z^{3/2} dz}{e^z - 1} = gV \frac{m^{3/2} T_c^{5/2}}{\sqrt{2\pi^2 \hbar^3}} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right).$$

Now, using the above equation for T_c , we can reduce this expression to

$$E(T_c) = \frac{\Gamma(5/2) \zeta(5/2)}{\Gamma(3/2) \zeta(3/2)} NT_c = \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)} NT_c \approx 0.7701 NT_c \approx 2.551 g^{-2/3} NT_0,$$

so that

$$p(T_c) = \frac{2}{3} \frac{E(T_c)}{V} = \frac{\zeta(5/2)}{\zeta(3/2)} \frac{N}{V} T_c \approx 0.5134 \frac{N}{V} T_c \approx 1.701 g^{-2/3} \frac{N}{V} T_0.$$

On the other hand at $T < T_c$,

$$E(T) = gV \frac{m^{3/2} T^{5/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{z^{3/2} dz}{e^z - 1} = E(T_c) \left(\frac{T}{T_c}\right)^{5/2}, \quad p(T) = p(T_c) \left(\frac{T}{T_c}\right)^{5/2}.$$

The latter dependence is shown by blue points in Fig. 4b. We see that for all temperatures the pressure is below that of the classical gas (equal to NT/V), thus confirming the asymptotic analysis of Sec. 5. On the other hand, for the specific heat below T_c we get the result

$$C_V(T) \equiv \left(\frac{\partial E}{\partial T}\right)_{N,V} = E(T_c) \frac{5}{2} \frac{T^{3/2}}{T_c^{5/2}},$$

so that at critical temperature it equals

$$C_V(T_c) = E(T_c) \frac{5}{2} \frac{T_c^{3/2}}{T_c^{5/2}} \approx 1.925 N,$$

i.e. is 28% above that of the classical gas (1.5 N). An analysis of the equation for $E(T)$ shows that both this function and its derivative (C_V) are continuous everywhere, including the critical point $T = T_c$. Since at $T \gg T_c$ the specific heat has to approach the classical value, it must decrease at $T > T_c$, forming a ‘‘cusp’’ in the critical point. Such a cusp is good indication of the critical temperature, with particle interactions (unaccounted for in our simple theory) making this singularity even more substantial.

Historically, such singularity (the so-called λ -point) in the $C_V(T)$ dependence was the first noticed (though not immediately understood) sign of the Bose-Einstein condensation (found in liquid ^4He by H. Kamerlingh-Onnes in 1908). Other milestones of the Bose-Einstein condensation studies include:

- the discovery of superconductivity in metals by the same H. Kamerlingh-Onnes (1911);
- the development of Bose statistics by S. Bose (for photons, 1924) and A. Einstein (for massive particles, 1925);
- the discovery of superfluidity of the Bose-Einstein condensate in ^4He by J. Allen, P. Kapitza, and D. Misener (1938);

- the explanation of superconductivity as a result of the Bose-Einstein condensation of electron pairs by J. Bardeen, L. Cooper, and J. Schrieffer (1957);

- the first observation of the Bose-Einstein condensation in dilute gases (^{87}Rb by E. Cornell *et al.* and ^{23}Na by W. Ketterle) in 1995.

The importance of the last achievement (and the continuing intensive work in this direction) is that in contrast to all other Bose-Einstein condensates, in dilute gases (with $N/V \sim 10^{14} \text{ cm}^{-3}$) the particles interact very weakly, and hence the results are very close to the simple theory described above – see, e.g., Fig. 4. On the other hand, the importance of prior experimental observations of the Bose-Einstein condensation should not be overlooked.

The most important feature of any Bose-Einstein condensate is that all the condensed particles have exactly the same wavefunction which thereby describes the whole condensate. As a result, the “strange” behaviors predicted by the quantum mechanics are not averaged out as in the usual particle ensembles (see, e.g., the discussion in Sec. 2.2), but may be directly revealed in the behavior of the condensate. The prominent examples of these “macroscopic quantum effects” include superfluidity, superconductivity, Josephson effect, quantized vortices, magnetic flux quantization, etc.

Exercises

3.1. Find all thermodynamic properties of an ideal classical gas of $N \gg 1$ identical and indistinguishable atoms of mass m , contained in volume V at temperature T , starting from the microcanonical distribution. (Neglect the internal energies of the atoms.)

3.2. An ideal classical gas, confined in a container with the linear size scale L , had been in thermal equilibrium at temperature T . Then a small hole of size a was opened in the wall of the container for a short time interval t such that $a \ll v_0 t \ll L$, where v_0 is the r.m.s. velocity of the molecules in equilibrium, given by Eq. (?). Find the r.m.s. velocity of the escaped molecules. Compare it with v_0 . On the basis of the comparison, what would be the most immediate observable effect of the gas emission?

3.3. A round cylinder of radius R , containing an ideal classical gas in thermal equilibrium at temperature T , is rotated about its symmetry axis with angular velocity ω . Gas pressure at the cylinder axis is p_a . Find the pressure near the cylinder wall.

3.4. Find the effective latent heat $\Lambda \equiv -(\partial Q / \partial N_0)_{N, V}$ of evaporation of the Bose-Einstein condensate as a function of temperature T . Here Q is the heat absorbed by the (condensate + gas) system as a whole, while N_0 is the number of particles in the condensate alone.

3.5. Prove that the specific heat C_V of the Bose gas is a continuous function of temperature in the critical point T_c .