

# Notes on Thermal Physics

## Kinetic theory of gases

**Pressure:** for non-interacting particles, the only change in momentum is the collision with the walls:  $\Delta p_x = -mv_x - mv_x = -2mv_x$ . The time between two successive collisions of one particle with one particular wall is  $\Delta t = 2L/v_x$ . The

force on the particle is  $F_{x,\text{part}} = \frac{\Delta p_x}{\Delta t} = \frac{-2mv_x}{2L/v_x} = -\frac{mv_x^2}{L}$ . The force on the

wall is (Newton's third law)  $F_x = mv_x^2/L$ . For  $N$  identical particles, we have the

total average force  $\bar{F}_{x,\text{tot}} = \frac{m \sum_{i=0}^N \bar{v}_{x,i}^2}{L}$ , but  $\bar{v}_{x1}^2 + \bar{v}_{x2}^2 + \dots = N\bar{v}_x^2$ . But the  $x$  direction is not

preferential:  $\bar{v}_x = \bar{v}_y = \bar{v}_z$  and then  $\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 = 3\bar{v}_x^2$  which means that the force is

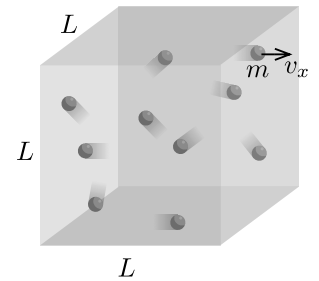
$\bar{F} = \frac{Nm\bar{v}^2}{3L}$ . Finally, the pressure on the wall of area  $L^2$  is  $P = \frac{\bar{F}}{L^2} = \frac{Nm\bar{v}^2}{3L^3} = \frac{Nm\bar{v}^2}{3V}$ .

**Equation of state and internal energy:** from thermodynamics (experiment),  $PV = Nk_B T$ .

Then,  $PV = N \left( \frac{1}{3} m \bar{v}^2 \right) = Nk_B T$ ,  $\implies \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T := \bar{E}_{\text{one particle}}$ . And the total

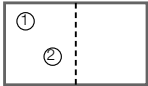
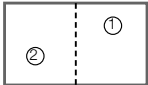
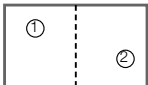
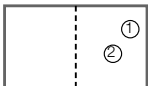
internal energy of the gas  $\bar{E}_{\text{int,tot}} := U = \frac{3}{2} Nk_B T = \frac{3}{2} nRT$ . The 3 is because of the three

degrees of freedom ( $x, y, z$ ). The *equipartition theorem* says that in equilibrium, the energy of one particle is  $\frac{1}{2} k_B T$  per degree of freedom.



# Foundations on Statistical Physics

## Example: particles in the two halves of a box

	macrostate	probability	
microstates		all in the left	1/4
		half in the left	2/4 = 1/2
		<i>the most disordered state is more probable</i>	
		none in the left	1/4

4 particles in two halves of a box

1	2	3	4	$n$	$n'$	$C_N(n)$
L	L	L	L	4	0	1
L	L	L	R	3	1	4
L	L	R	L	3	1	
L	R	L	L	3	1	
R	L	L	L	3	1	
L	L	R	R	2	2	6
L	R	L	R	2	2	
L	R	R	L	2	2	
R	L	L	R	2	2	
R	L	R	L	2	2	
R	R	L	L	2	2	
L	R	R	R	1	3	4
R	L	R	R	1	3	
R	R	L	R	1	3	
R	R	R	L	1	3	
R	R	R	R	0	4	1

**Example: spins:** system of 3 particles with two spins (+,-) without any external fields.

**Number of microstates  $\Omega$ , probability  $P$ :** from the previous examples, we see that the total number of microstates with two options (L/R, +/-) can be calculated as  $2^N$ . The number of microstates that corresponds to a particular macrostate  $i$ ,  $\Omega_i$ , can be calculated with combinatorics. The probability of finding the system in the macrostate  $i$  is  $P_i = \Omega_i/\Omega$ .

**Temperature:** let the parameter  $\beta := \frac{\partial \ln \Omega}{\partial E}$ , by definition. The number of microstates of a system depends on the energy (the more energy, the more microstates available), and this contributes a factor for each degree of freedom  $f$  (number of particles, directions of motion, etc.). Then,  $\Omega \propto (E - E_0)^f$ , where  $E_0$  is the ground state energy.

$\implies \ln \Omega(E) = f \ln(E - E_0) + \text{const}$ , which means that  $\beta \approx \frac{f}{E - E_0}$ . For the ideal gas in thermal equilibrium, for example,  $E_0 = 0$ ,  $E = \bar{E}$ . Then,  $\beta = \frac{f}{\bar{E}} \implies \bar{E} = \frac{f}{\beta}$ . But from kinetic theory and thermodynamics,  $\bar{E} = f k_B T$ , which means that  $\beta = \frac{1}{k_B T}$ .

3 particles with spin +,-

1	2	3	$n$	$n'$	$C_N(n)$
+	+	+	3	0	1
+	+	-	2	1	3
+	-	+	2	1	
-	+	+	2	1	
+	-	-	1	2	3
-	+	-	1	2	
-	-	+	1	2	
-	-	-	0	3	1

**Entropy:** consider a box divided in two compartments, each with an ideal gas of thermodynamical coordinates  $(E_1, V_1, N_1)$  and  $(E_2, V_2, N_2)$ . The number of microstates of the total system is  $\Omega(E, V, N) = \Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2)$ . The differential of this equation is

$$d\Omega = \Omega_2 d\Omega_1 + \Omega_1 d\Omega_2 \implies \frac{d\Omega}{\Omega} = \frac{d\Omega_1}{\Omega_1} + \frac{d\Omega_2}{\Omega_2} \implies d \ln \Omega = d \ln \Omega_1 + d \ln \Omega_2.$$

Now, the entropy of such a system from a purely thermodynamical point of view is

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2), \text{ with total differential } dS = dS_1 + dS_2.$$

Comparing, we get a relation of proportionality:  $S(E, V, N) = k_B \ln \Omega(E, V, N)$ . We need to show that the proportionality constant is indeed the Boltzmann's constant  $k_B$ . The full proof involves the calculation of  $\Omega$ . We take the very particular case of the free expansion of an ideal gas from its original volume  $V_1$  to the volume  $V_2$ . From thermodynamics, we know that one can calculate the change in entropy with an isothermal process, yielding

$$\Delta S = \int_1^2 \frac{dQ}{T_1} = \int_1^2 \frac{dW}{T_1} = \int_1^2 \frac{pdV}{T_1} = \int_1^2 \frac{Nk_B \mathcal{T}_1 dV}{\mathcal{T}_1 V} = Nk_B \ln \frac{V_2}{V_1}.$$

Now, with statistical physics. We can say that the number of microstates is proportional to the volume (the more volume, the more microstates available), multiplied  $f$  times ( $f$ : degrees of freedom, like number of particles, directions of motion, etc.):  $\Omega \propto V^N$ . Then,  $\Delta S = k_B \ln \frac{V_2^N}{V_1^N} = Nk_B \ln \frac{V_2}{V_1}$ . The two

expressions are equal, and we conclude that the constant of proportionality is indeed  $k_B$ . The entropy is the amount of disorder of a system. In the examples of the particles in a box or the spins, the macrostates with higher randomness have also higher  $\Omega_i$ , and thus, higher entropy.

## Probabilities and averages

**Normalization condition:**  $\sum_i P_i = 1$ , which means that  $0 < P_i < 1$

**"or":** the probability that a system is in a state  $i$  or a state  $j$  is  $P(i \text{ or } j) = \frac{N_i + N_j}{N} = P_i + P_j$

**"and":** the probability that a system is both  $i$  and  $j$ , when they are *statistically independent variables* are calculated as follows. Number of states in  $i$  is modified by the probability of

finding the system in  $j$ :  $N_{ij} = N_i P_j$ . Then,  $P_{ij} = \frac{N_{ij}}{N} = \frac{N_i P_j}{N} = P_i P_j$ .

**binomial distribution:** for our system of spins,  $1/\Omega = 1/2^N = (1/2)^{n+n'}$ . In general, the  $1/2$  is the intrinsic probability that each spin appear (if isolated, it is indeed  $1/2$ , but if they are in the presence of a magnetic field, for example, some spins align with it and it is no longer  $1/2$ ). In general,  $1/\Omega = p^n q^{n'}$ , where  $q = 1 - p$ . Then,  $P_N(n) = C_N(n) p^n q^{N-n}$ . But

$$C_N(n) = \frac{N!}{n!(N-n)!}$$

**Proof of the combinations formula:** first there are  $N$  choices for spin such that the total number of spin ups is  $n$ . Let's say we choose spin up ( $U_1$ ) for the first particle; there are  $(N - 1)$  choices left. We continue so that  $U_1, U_2, \dots, U_{n-1}$  is reached, so we have to choose  $U_n$  (the maximum allowed number of spins up), and there are  $(N - n + 1)$  choices left (we write this in terms of factorials by multiplying and dividing  $(N - n)!$ ). But the choice  $U_1, U_2, x, x, \dots$  is the same as the choice  $U_2, U_1, x, x, \dots$ , so we also have to divide the number of choices by  $n!$  (permutations of the subindices).

**Weighted average:**  $\bar{x} := \frac{\sum_i N_i x_i}{N} = \sum_i P_i x_i$

**Properties of averages:**  $\overline{f + g} = \bar{f} + \bar{g}$ ;  $\overline{cf} = c\bar{f}$  ( $c$ : constant);  $\overline{fg} = \bar{f}\bar{g}$  (if  $f, g$  are statistically independent);  $\overline{u^2} \geq \bar{u}^2$ .

## Partition function

**Canonical ensemble:** consider a system A in contact with a reservoir A'; the combined system is A\*. The conservation of energy when A is in the state  $i$  states that  $E^* = E_i + E' = \text{const}$   
 $\implies E' = E^* - E_i$ . The fact that A' is a reservoir means that the fluctuations in energy  $E_i$  are very small compared to  $E^*$ . When A is in  $i$ ,  $\Omega$  for A\* is just  $\Omega'$  for A' (the same also for A), and then, the probability  $P_i \propto \Omega'(E^* - E_i)$ . Expanding around  $E' = E^*$ ,

$$\ln \Omega'(E^* - E_i) = \ln \Omega'(E^*) - \frac{\partial \ln \Omega'}{\partial E'} E_i = \ln \Omega'(E^*) - \beta E_i$$

$\implies \Omega'(E^* - E_i) = \Omega'(E^*) e^{-\beta E_i}$ . The probability is then  $P_i = C e^{-\beta E_i}$ ; normalizing,

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

using Maxwell-Boltzmann statistics ( $Z = \sum_i e^{-\beta E_i}$ )

**Macrocanonical ensemble:** consider the canonical ensemble, but we now allow for the exchange of particles between the subsystems. By relaxing the restriction on the number of particles, we now can measure their number at a certain energy. We do this by introducing a *chemical potential*  $\mu$ . The fundamental thermodynamic relation is then

$$dU = TdS - pdV + \mu N. \text{ The partition function ends up being } \Xi = \sum_i e^{-\beta(E_i - \mu N_i)}.$$

**Average energy and number of particles:** first, we take  $\ln \Xi = \ln[\sum_i e^{-\beta(E_i - \mu N_i)}]$ . The

derivative with respect to  $-\beta$  is

$$\frac{\partial \ln \Xi}{\partial(-\beta)} = \frac{\partial \ln \Xi}{\partial \Xi} \frac{\partial \Xi}{\partial(-\beta)} = \frac{1}{\Xi} \sum_i \frac{\partial}{\partial(-\beta)} e^{-\beta(E_i - \mu N_i)} = \frac{1}{\Xi} \sum_i E_i e^{-\beta(E_i - \mu N_i)} = \bar{E}. \text{ And, the}$$

derivative with respect to  $\mu$  is

$$\frac{\partial \ln \Xi}{\partial(\beta\mu)} = \frac{\partial \ln \Xi}{\partial \Xi} \frac{\partial \Xi}{\partial(\beta\mu)} = \frac{1}{\Xi} \sum_i \frac{\partial}{\partial(\beta\mu)} e^{-\beta(E_i - \mu N_i)} = \frac{1}{\Xi} \sum_i N_i e^{-\beta(E_i - \mu N_i)} = \bar{N}$$

**Maxwell-Boltzmann distribution of velocities:** the probability of finding a particle with energy between  $E$  and  $E + dE$  is  $P(E)dE = e^{-E/(k_B T)} / \int_0^\infty e^{-E/(k_B T)} dE$ . For velocities, the probability of finding a particle with velocities between  $\vec{v}$  and  $\vec{v} + d\vec{v}$  is

$$f(\vec{v})dv_x dv_y dv_z = \frac{e^{-mv^2/(2k_B T)}}{\int_0^\infty e^{-mv_x^2/(2k_B T)} dv_x \int_0^\infty e^{-mv_y^2/(2k_B T)} dv_y \int_0^\infty e^{-mv_z^2/(2k_B T)} dv_z}. \text{ Each integral}$$

in the denominator is  $\sqrt{a/\pi}$ , with  $a = m/(2k_B T)$ . Then,

$$f(\vec{v})dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/(2k_B T)} dv_x dv_y dv_z. \text{ In spherical coordinates,}$$

$$dv_x dv_y dv_z = v^2 \sin\theta dv d\theta d\phi. \text{ Integrating in } \theta \text{ and } \phi,$$

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

## Pseudo-quantum statistics

**Fermions (Fermi-Dirac statistics):** there is one particle per energy level (other degeneracies can be added later). The system is just one energy level, and its possible states are "with" or "without" particle; in contact with the rest of the physical system, allowing particles to be or not in an energy level. We write

$$E_i = \sum_r \epsilon_r n_r; N_i = \sum_r n_r \text{ (in the example of the figure, } E_i = \epsilon_1 + \epsilon_2 + \epsilon_4 \text{ and}$$

$N_i = 3$ . We use the macrocanonical ensemble to get

$$\Xi = \sum_{n_1, n_2, \dots = 0}^1 \exp \left[ -\beta \sum_r n_r (\epsilon_r - \mu) \right]; \text{ for Fermi-Dirac statistics, } n_r = 0, 1$$

only. Then,  $\Xi = e^{0 \cdot \beta(\mu - \epsilon)} + e^{1 \cdot \beta(\mu - \epsilon)} = 1 + e^{\beta(\mu - \epsilon)}$  and, finally, for the average occupation number,  $\bar{n}_i = \frac{e^{\beta(\mu - \epsilon_i)}}{1 + e^{\beta(\mu - \epsilon_i)}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$ .

**Bosons (Bose-Einstein statistics):** the grand canonical function is

$$\Xi = \sum_{N=0}^{\infty} \exp [\beta N(\mu - \epsilon)] = \sum_{N=0}^{\infty} \left( \exp [\beta(\mu - \epsilon)] \right)^N. \text{ Now, we are}$$

considering an energy with unlimited particles in it. Using the geometrical

sum formula,  $\Xi = \frac{1}{1 - e^{\beta(\mu - \epsilon)}}$ . The average occupation number is

$$\bar{n}_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}. \text{ (In the singularity } \mu = \epsilon_i \text{, the result is the Bose-Einstein condensate).}$$

**Gibbs's factor:**  $1/N!$  term that arises from the limit from quantum mechanics with a Fermi gas to classical mechanics.

## References

- Greiner, W., Neise, L., Stöcker, H. (1995) *Thermodynamics and Statistical Mechanics*, Springer.
- Chandler, D. (1987) *Introduction to Modern Statistical Mechanics*, Oxford U. Press.

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