# 25 Feb.

Logistics: HW1 due 3 March – tutorial
Typo fixed

## Recap.

Ideal gas in canonical ensemble
Non-rel., classical, in box $V = L^3$
↳ Discrete energy levels
$\vec{p} = \frac{\hbar\pi}{L}(n_x, n_y, n_z)$ $n_i \geq 0$

What are the corresponding results for the case of distinguishable particles, where the partition function $Z_D$ is given by Eq. 50?

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$$F_D = -\frac{3}{2} NT \log\left(\frac{mTL^2}{2\pi\hbar^2}\right)$$

$$\langle E \rangle_D = \frac{3}{2} NT$$

$$S_D = \frac{3}{2} N + N \log\left(\frac{V}{\lambda_{th}^3}\right)$$

You should find that the energy is insensitive to whether or not we can label the particles:

$$\langle E \rangle_D = \langle E \rangle_I = \frac{3}{2} NT. \checkmark \tag{52}$$

This is in contrast to the spin system we considered in Section 3.4.[9] The entropy, however, does reflect the extra information that distinguishability provides:

$$S_D = \frac{3}{2}N + N\log\left(\frac{V}{\lambda_{\text{th}}^3}\right) \qquad\qquad S_I = \frac{5}{2}N + N\log\left(\frac{V}{N\lambda_{\text{th}}^3}\right). \checkmark \tag{53}$$

Because $N \log N > N$ for $N \gg 1$, we have $S_D > S_I$, as expected. We can also note that $\lambda_{\text{th}} \to \infty$ as the temperature approaches absolute zero, $T \to 0$, apparently producing negative entropies for fixed $V$. This is a warning sign that our classical assumptions are breaking down in this regime, and quantum effects would need to be taken into account.

$$\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mT}}$$

## 4.3 The mixing entropy and the 'Gibbs paradox'

Back in Section 2.4 we considered what would happen if we allowed two micro-canonical systems to exchange energy, and then re-isolated them. We saw that this procedure obeys the second law of thermodynamics — the entropy never decreases, though we have to be careful to account for all of the entropy after re-isolating the two systems.

We can now carry out a similar thought experiment of allowing two *canonical* systems to exchange *particles*, and then re-separating them. We demand

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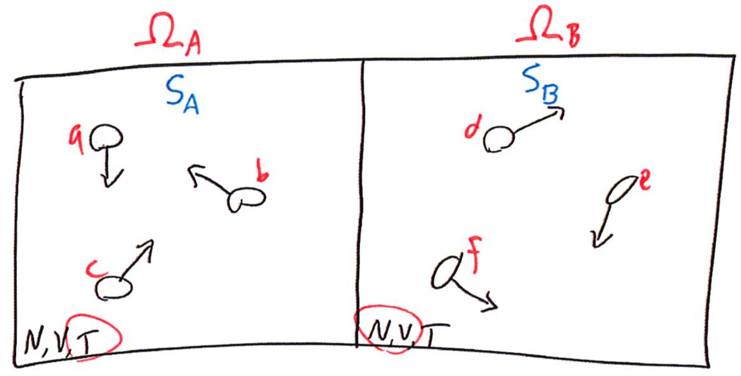
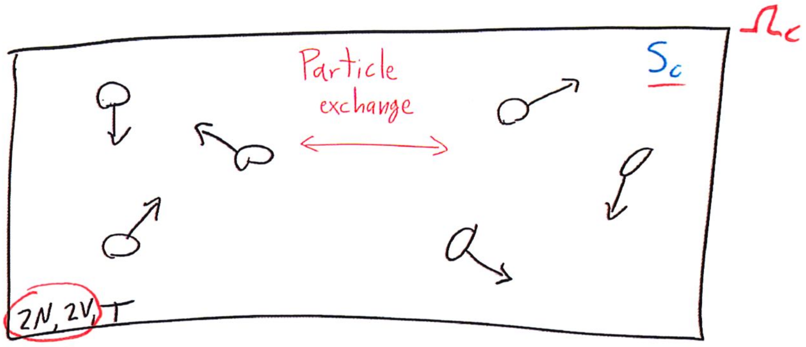
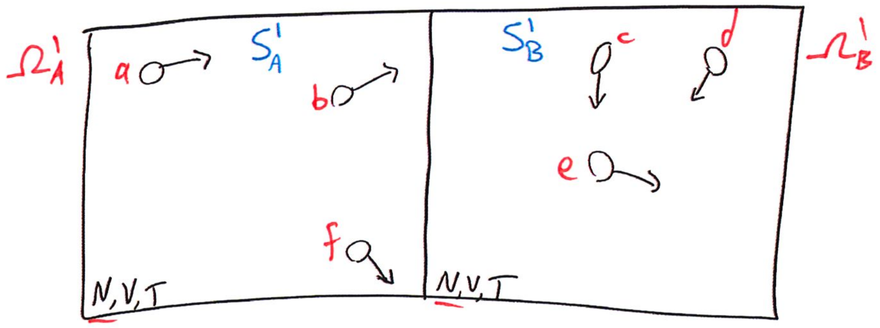
[9] The ultimate origin of this contrast is that each ideal gas micro-state $\omega_i$ in the indistinguishable case corresponds to $N!$ micro-states in the distinguishable case, independent of the energy $E_i$. For the spin system this factor is $\binom{N}{n_+}$ and varies with the energy $E_{n_+}$.

that both canonical ensembles are in thermodynamic equilibrium with each other, for instance by sharing the same thermal reservoir with temperature $T$. This procedure is illustrated below, where we simplify the setup by taking the two initial systems to have equal volumes, $V_A = V_B = V$, and numbers of particles, $N_A = N_B = N$.







We can represent the process of combining and then re-separating these systems by writing

$$\Omega_A + \Omega_B \longrightarrow \Omega_C \longrightarrow \Omega'_A + \Omega'_B.$$

What is the entropy for each of these three stages? Since the entropies depend on whether or not the particles in the gas are distinguishable from each other, let's first consider the case of *indistinguishable* particles.

The initial entropy is the sum of the contributions from the two canonical systems, $S_A + S_B$, both of which are the same thanks to our simplification above, and are given by Eq. 53:

$$S_A + S_B = 2S_I(N, V) = 2\left(\frac{5}{2}N + N\log\left(\frac{V}{N\lambda_{th}^3}\right)\right)$$
$$= 5N + 2N\log\left(\frac{V}{N\lambda_{th}^3}\right)$$

To find the entropy $S_C$ of the combined system, we just need to consider what happens when we double the volume and also double the number of particles:

$$S_C = S_I(2N, 2V) = \frac{5}{2}(2N) + (2N)\log\left(\frac{2V}{2N\lambda_{th}^3}\right)$$
$$= 5N + 2N\log\left(\frac{V}{N\lambda_{th}^3}\right)$$

You should find $S_C = S_A + S_B$, which is consistent with the second law of thermodynamics.

Things are more complicated when we re-separate the systems. Analogously to our considerations in Section 2.4, we need to sum over all the possible ways of dividing the $2N$ indistinguishable particles between the two re-separated boxes. In particular, we need to perform this sum at the stage of computing the partition function $Z'$ for $\Omega'_A + \Omega'_B$, since this is the fundamental quantity from which the entropy is then derived as $S = \frac{\partial}{\partial T}(T\log Z')$. In other words, we have to consider a logarithm of a sum rather than a sum of logarithms.

If $\nu$ particles end up in system $\Omega'_A$, then the other system $\Omega'_B$ must contain the remaining $2N - \nu$ particles, giving us

$$Z_I(\nu!) \qquad Z_\nu = \underset{\Omega_A'}{\frac{1}{\nu!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{\nu}} \times \underset{\Omega_B'}{\frac{1}{(2N-\nu)!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N-\nu}} = \frac{1}{\nu!\,(2N-\nu)!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N}.$$

Summing over all possible values of $0 \le \nu \le 2N$,

$$Z' = \sum_{\nu=0}^{2N} Z_\nu = \left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N}\sum_{\nu=0}^{2N}\frac{1}{\nu!\,(2N-\nu)!} = \left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N}\frac{1}{(2N)!}\sum_{\nu=0}^{2N}\binom{2N}{\nu}$$
$$\Longrightarrow S'_A + S'_B = 2N\frac{\partial}{\partial T}\left(T\log\left[\frac{V}{\lambda_{\text{th}}^3}\right]\right) - \log[(2N)!] + \log\left[\sum_{\nu=0}^{2N}\binom{2N}{\nu}\right].$$

This is a complicated expression. We can simplify it with an approximation considered by J. Willard Gibbs in the 1870s, which we have already motivated in some of our tutorial discussions. For large $N \gg 1$, we saw that the entropy of two

$P_i = e^{-E_i/T}$

subsystems in thermal contact is nearly saturated by the case in which the energy is divided roughly evenly between the two subsystems, rather than being mostly in one of them. The same thing happens for two systems that are allowed to exchange particles: there are far more micro-states with particles divided roughly evenly between the two subsystems, $N'_A \approx N'_B \approx N$, compared to the particles being mostly in one of them.

So we declare $N'_A = N'_B = N$, as drawn in the illustration above. This suffices to establish $\Omega'_A = \Omega_A$ and $\Omega'_B = \Omega_B$, producing a final entropy of $S'_A + S'_B = S_A + S_B$ that satisfies the second law of thermodynamics:

$$S'_A + S'_B = S_C = S_A + S_B.$$

This is just what we would expect from everyday experience: opening a door between two identical rooms doesn't produce any dramatic effects, nor does reversing that process by closing the door.

Something interesting happens when we repeat this analysis for the case of *distinguishable* particles, using our result for $S_D(N, V)$ in Eq. 53. If we consider the difference between the combined entropy $S_C$ and the initial entropy $S_A + S_B$,

$$\begin{aligned} \Delta S_{\text{mix}} &= S_C - (S_A + S_B) = S_D(2N, 2V) - 2S_D(N, V) \\ &= 3\cancel{N} + 2N \log\left(\frac{2V}{\lambda_{\text{th}}^3}\right) - \left[3\cancel{N} + 2N \log\left(\frac{V}{\lambda_{\text{th}}^3}\right)\right] = 2N \log 2 > 0, \end{aligned} \qquad (54)$$

we find that the entropy increases upon combining the two initial systems. This $\Delta S_{\text{mix}} > 0$ is known as the **mixing entropy**.

This result $S_C > S_A + S_B$ is what we would expect from the second law of thermodynamics. However, repeating the argument above—that we should have $N'_A \approx N'_B \approx N$ and therefore $S'_A + S'_B = S_A + S_B$ after re-separating the systems—would imply $S'_A + S'_B < S_C$, indicating a *decrease* in the entropy by $\Delta S_{\text{mix}}$ and an apparent violation of the second law. This is known as the 'Gibbs paradox', though Gibbs himself explained how a paradox is avoided.

The explanation is that because the particles are now distinguishable, $N'_A = N_A$ no longer suffices to establish $\Omega'_A = \Omega_A$ and $S'_A = S_A$. Recovering $\Omega_A$ would additionally require that the $N'_A$ particles in the re-separated system are the *same* distinguishable particles that were initially in $\Omega_A$. While we can still expect $N'_A \approx N'_B \approx N$, the vast majority of the resulting micro-states will not correspond to micro-states of $\Omega_A$ and $\Omega_B$. Summing over these additional possibilities ensures $S'_A + S'_B > S_A + S_B$, and it turns out $S'_A + S'_B \geq S_C$ as well, obeying the second law of thermodynamics.

These thought experiments provide another example of behaviour that differs depending only on the intrinsic information content of the system — whether or not the particles in an ideal gas can be distinguished from each other in principle. Mixing gases of distinguishable particles introduces a positive mixing entropy, Eq. 54, but for gases of indistinguishable particles there is no change in entropy when we let two subsystems mix, or when we reverse that process and

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re-separate them. Due to the second law of thermodynamics, processes that produce an increase in entropy are irreversible.

## 4.4 Pressure, ideal gas law, and equations of state

Below Eq. 50 we emphasized that the ideal gas partition function depends on the volume of the gas, $V$, in addition to the fixed temperature $T$ and conserved particle number $N$ that always characterize systems governed by the canonical ensemble. Parameters like $V$ that appear in the partition function are called **control parameters**, with the idea that they can (in principle) be controlled in experiments. Control parameters generally enter the partition function through the definition of the energies $E_i$ for the micro-states $\omega_i$. Another example is the magnetic field strength $H$ for the spin systems we considered earlier.

Focusing on ideal gases for now, we see that all dependence on $V$ drops out in our results for the average internal energy, Eq. 52. On the other hand, the entropies in Eq. 53 do depend on the volume. For both cases of distinguishable and indistinguishable particles, the entropy $S$ depends on the same combination of volume and temperature: $V\lambda_{\text{th}}^{-3} \propto VT^{3/2}$. If we keep $N$ fixed and consider using our experimental control to change the volume and the temperature of the system, the entropy will typically change as a consequence, unless the following relation is satisfied:

$$VT^{3/2} = \text{constant} \qquad \Longrightarrow \qquad S = \text{constant}.$$

Such **constant-entropy (or isentropic) processes** will be important in our upcoming analyses of thermodynamic cycles.[10] These cycles will involve making changes to control parameters, which is a topic we have already started to consider through the micro-canonical temperature (Eq. 22) and the canonical heat capacity (Eq. 36). The pressure of an ideal gas is similarly connected to a change in its volume, which we can motivate by thinking about squeezing an inflated balloon into a small box.

The **pressure** is defined to be

$$P = -\frac{\partial}{\partial V}\left\langle E\right\rangle\Big|_S, \qquad (55)$$

with constant entropy $S$. In words, the pressure is the isentropic response of the system's internal energy to a change in its volume.

In Unit 5 we will look in detail at processes that change some or all of the pressure, volume, temperature, or internal energy of an ideal gas, with $N$ fixed. Although changing the temperature departs from the assumptions of the canonical ensemble, we will be able to understand such a process as a change from

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[10] The term *isentropic* is based on the Greek word $\iota\sigma o\varsigma$ ("isos"), meaning "equal".