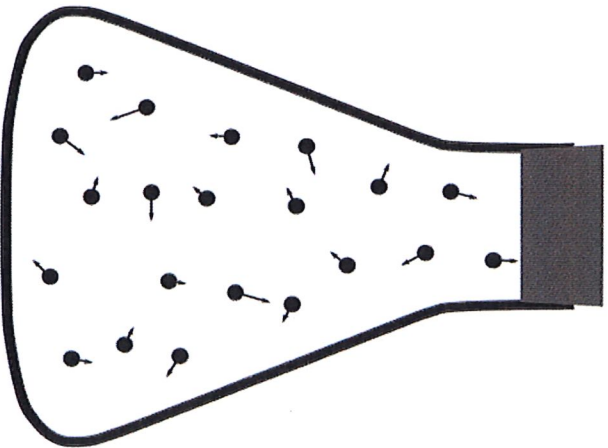
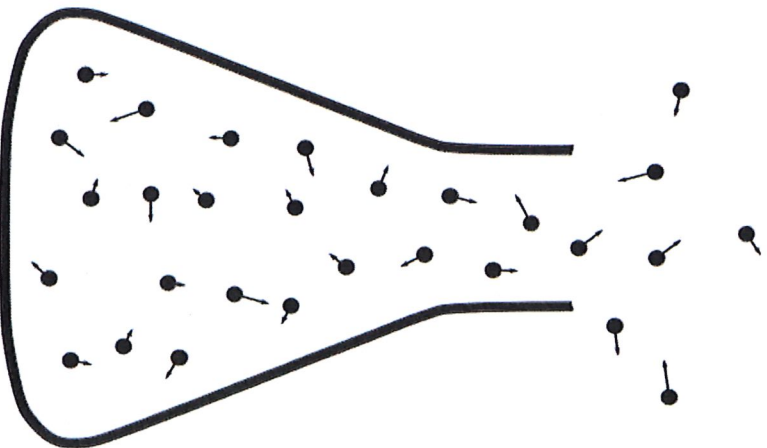


Microcanonical
(const. N E)



Canonical
(const. N T)



Grand Canonical
(const. μ T)

Unit 6: Grand-canonical ensemble

6.1 The particle reservoir and chemical potential

Now that we have had some fun with applications of the canonical ensemble, we will complete our more formal development of statistical ensembles by considering the grand-canonical ensemble. Recall that statistical ensembles are probability spaces describing the micro-states that a system can adopt as it evolves in time, subject to certain constraints. Back in Unit 2 we first considered the micro-canonical ensemble, for which these constraints are conservation of the internal energy E and particle number N . We then introduced the canonical ensemble in Unit 3 by allowing the system's internal energy to fluctuate, while keeping its temperature T fixed through thermal contact with a large external thermal reservoir.

Building on this pattern, the next step is to allow both the system's energy and its particle number to fluctuate. Generalizing our earlier work on the canonical ensemble, these fluctuations occur through contact between the system and a large external reservoir. This is now a particle reservoir, with which the system can exchange both energy and particles.

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In the same way that energy exchange leads to a fixed temperature, we expect there to be some quantity that will be fixed due to particle exchange. Recall that we initially defined the temperature in the context of the micro-canonical ensemble in thermodynamic equilibrium (Eq. 22), as the dependence of the entropy on the internal energy for a fixed number of degrees of freedom:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_N.$$

The quantity we are now interested in comes from the complementary analysis interchanging the roles of E and N .

In thermodynamic equilibrium, the chemical potential in the micro-canonical ensemble is defined by

$$\mu = -T \left. \frac{\partial S}{\partial N} \right|_E. \quad (67)$$

This definition is not terribly intuitive, and unlike the temperature the chemical potential is not a familiar concept from everyday experiences. To gain some insight into the chemical potential, we can first note that μ has dimensions of energy. It is also an intensive quantity, like the temperature — it is independent of the extent of the system, and remains the same if we consider only a part of a larger system. Finally, we can expect the chemical potential to be negative, at least for 'natural' systems with positive temperatures. This is because the partial derivative $\frac{\partial S}{\partial N}$ is generally positive, since systems with more degrees of freedom typically have more entropy, reflecting the greater amount of information they can

contain even with the energy fixed. This can be checked explicitly from Eq. 24 for the micro-canonical spin system we considered in Section 2.3.

The presence of the negative sign in Eq. 67 is really a choice we have made. The motivation for this choice comes from considering a net flow of particles between two systems Ω_A and Ω_B with the same temperature $T > 0$ but different

$$\left(\frac{\partial S}{\partial N}\right)_A > \left(\frac{\partial S}{\partial N}\right)_B > 0 \quad \implies \quad \underline{\mu_A < \mu_B}.$$

Due to the negative sign in Eq. 67, the system with the larger partial derivative has the smaller (more-negative) chemical potential. According to the second law of thermodynamics, if there is any net flow of particles, it must be from Ω_B to Ω_A . We can see this by considering

$$\underline{\Delta S_A} = \left(\frac{\partial S}{\partial N}\right)_A \Delta N > \left(\frac{\partial S}{\partial N}\right)_B \Delta N = \underline{\Delta S_B},$$

meaning that more entropy is gained by adding ΔN particles to system Ω_A than is lost by removing them from system Ω_B . This ensures that the process increases the total entropy of the universe, $\underline{\Delta S = |\Delta S_A| - |\Delta S_B| > 0}$.

In other words, the choice of sign in Eq. 67 ensures that particles flow from systems with larger chemical potentials to systems with smaller chemical potential. This provides a useful analogy to heat flowing from hotter systems with larger temperatures to colder systems with smaller temperatures, allowing us to reuse our intuition based on the temperature. Had we instead chosen to make μ positive for natural systems, we would have ended up with counter-intuitive flow of particles from small to large chemical potential.

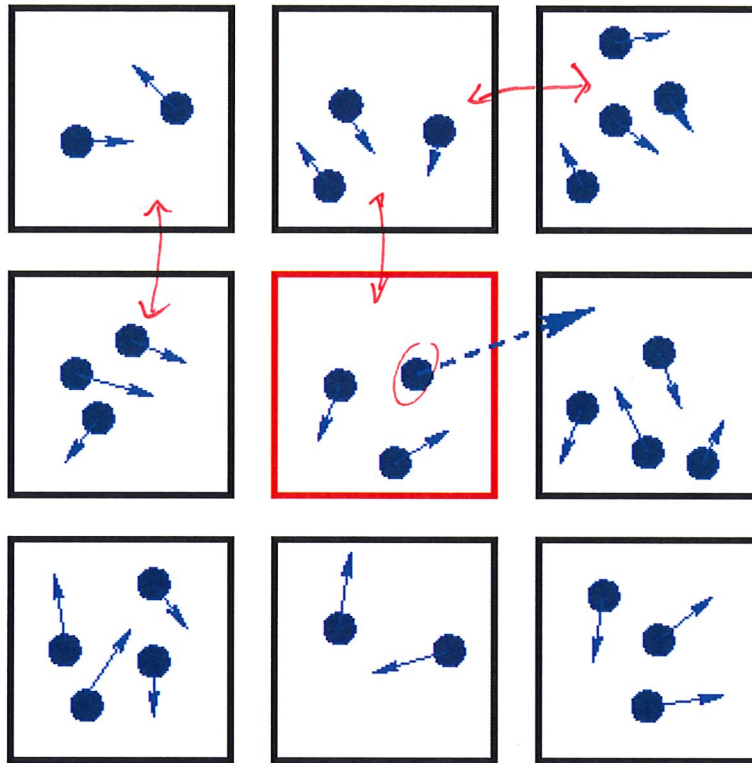
We are now able to define the **grand-canonical ensemble** to be a statistical ensemble characterized by its fixed temperature T and fixed chemical potential μ , with the temperature and chemical potential held fixed through contact with a particle reservoir.

6.2 The grand-canonical partition function

Let's now place the grand-canonical ensemble on a more concrete mathematical foundation, by following the same procedure we used for the canonical ensemble. That is, we introduce a well-motivated ansatz for the form of the particle reservoir Ω_{res} , then show that the form of the reservoir is ultimately irrelevant. This will allow us to work directly with the system of interest, Ω , independent of the details of the particle reservoir that fixes its temperature and chemical potential.

As before, our ansatz is to take $\Omega_{\text{tot}} = \Omega_{\text{res}} \otimes \Omega$ to consist of many ($R \gg 1$) identical replicas of the system Ω that we're interested in. All of these replicas are in thermodynamic equilibrium, and can exchange both energy and particles with each other. The overall system Ω_{tot} is governed by the micro-canonical ensemble,

with conserved total energy E_{tot} and conserved total particle number N_{tot} . An extremely small example of this setup is illustrated by the figure below, where the system of interest is an ideal gas in a volume V . In this unit we will consider only indistinguishable particles, so that we don't need to keep track of which particular particles are exchanged between the replicas, only the overall number.



Although we draw a box around each replica (and colour one red to pick out the system Ω we will consider), these boxes are now merely mental constructions, and don't interfere with particles moving from one replica to another. For example, we could take our system to be a cubic centimetre of air in a room, with the rest of the room forming its reservoir. As in Section 3.1.1, we assume that this system $\Omega = \{\omega_1, \omega_2, \dots, \omega_M\}$ has a finite number of M possible micro-states, where now different micro-states may involve different numbers of particles.

This again allows us to analyze the overall system of R replicas in terms of occupation numbers n_i and the corresponding occupation probabilities p_i . Recall that n_i is the number of replicas that adopt the micro-state $\omega_i \in \Omega$ in any given micro-state of the overall system Ω_{tot} , so that $\sum_i n_i = R$. Similarly, $p_i = n_i/R$ is the probability that a randomly chosen replica will be in micro-state ω_i , with $\sum_i p_i = 1$ as usual. In terms of n_i and p_i , the total number of micro-states of Ω_{tot} , and the corresponding entropy, are the same as we derived in Section 3.1.2,

$$M_{\text{tot}} = \frac{R!}{n_1! n_2! \dots n_M!} \quad \longrightarrow \quad S(E_{\text{tot}}, N_{\text{tot}}) = -R \sum_{i=1}^M p_i \log p_i,$$

assuming $R \gg 1$ and $n_i \gg 1$ for all $i = 1, \dots, M$. In this expression, the dependence on both E_{tot} and N_{tot} now enters through the occupation probabilities p_i ,

since the micro-states ω_i may involve different numbers of particles in addition to different energies.

Continuing as before, we want to determine the (intensive) temperature and chemical potential of Ω_{tot} through Eqs. 22 and 67, which requires expressing $S(E_{\text{tot}}, N_{\text{tot}})$ directly in terms of E_{tot} and N_{tot} . We again do this by maximizing the entropy subject to the constraints on the conserved quantities of the micro-canonical overall system Ω_{tot} . Labelling the energy and particle number of each replica E_r and N_r , respectively, as in Eq. 27 we can again rearrange sums over replicas into sums over the micro-states of Ω :

$$\begin{aligned} 1 &= \sum_{i=1}^M p_i & E_{\text{tot}} &= \sum_{r=1}^R E_r = \sum_{i=1}^M n_i E_i = R \sum_{i=1}^M p_i E_i \\ N_{\text{tot}} &= \sum_{r=1}^R N_r = \sum_{i=1}^M n_i N_i = R \sum_{i=1}^M p_i N_i, \end{aligned} \quad (68)$$

where E_i and N_i are the energies and particle numbers of the M micro-states $\omega_i \in \Omega$. The first two constraints, on the occupation probabilities and the total energy, are the same as we had in Section 3.1.2. The third constraint, on the total particle number, is the new ingredient for us to incorporate.

Writing everything in terms of occupation probabilities, we see that we need to maximize the modified entropy

$$\begin{aligned} \bar{S} &= -R \sum_{i=1}^M p_i \log p_i + \alpha \left(\sum_{i=1}^M p_i - 1 \right) \\ &\quad - \beta \left(R \sum_{i=1}^M p_i E_i - E_{\text{tot}} \right) + \gamma \left(R \sum_{i=1}^M p_i N_i - N_{\text{tot}} \right), \end{aligned}$$

adding the Lagrange multiplier γ to the α and (negative) β we previously had in Section 3.1.2. What is the occupation probability p_k that maximizes \bar{S} ?

$$\begin{aligned} 0 &= \frac{\partial \bar{S}}{\partial p_k} = -R \left(\log p_k + 1 \right) + \alpha - \beta R E_k + \gamma R N_k \\ \log p_k &= -1 + \frac{\alpha}{R} - \beta E_k + \gamma N_k \\ p_k &= \exp \left[-1 + \frac{\alpha}{R} - \beta E_k + \gamma N_k \right] = \frac{\exp \left[-\beta E_k + \gamma N_k \right]}{\exp \left(1 - \frac{\alpha}{R} \right)} \\ &= \frac{1}{Z_g} e^{-\beta E_k + \gamma N_k} \end{aligned}$$

You should find a probability of the form

$$p_k = \frac{1}{Z_g} e^{-\beta E_k + \gamma N_k}, \quad (69)$$

defining $Z_g = \exp \left[1 - \frac{\alpha}{R} \right]$ to work in terms of the parameters $\{Z_g, \beta, \gamma\}$. As usual, we fix these three parameters by demanding that the three constraints above are satisfied. Using the first constraint, what is Z_g in terms of β and γ ?

$$\underline{1} = \sum_{i=1}^M p_i = \frac{1}{Z_g} \sum_i e^{-\beta E_i + \gamma N_i} \rightarrow Z_g = \sum_i e^{-\beta E_i + \gamma N_i}$$

Analogously to Eq. 31 in Section 3.1.2, the other two constraints

$$E_{\text{tot}} = R \sum_i p_i E_i \quad N_{\text{tot}} = R \sum_i p_i N_i$$

now produce complicated relations between $\{\beta, \gamma\}$ and $\{E_{\text{tot}}, N_{\text{tot}}\}$:

$$\underline{E_{\text{tot}}} = R \frac{\sum_{i=1}^M E_i e^{-\beta E_i + \gamma N_i}}{\sum_{j=1}^M e^{-\beta E_j + \gamma N_j}} = -R \frac{\partial}{\partial \beta} \log Z_g(\beta, \gamma) \quad (70)$$

$$\underline{N_{\text{tot}}} = R \frac{\sum_{i=1}^M N_i e^{-\beta E_i + \gamma N_i}}{\sum_{j=1}^M e^{-\beta E_j + \gamma N_j}} = R \frac{\partial}{\partial \gamma} \log Z_g(\beta, \gamma). \quad (71)$$

Here we take the opportunity to relate E_{tot} and N_{tot} to partial derivatives of $\log Z_g$, which will prove useful when we consider the partial derivatives of the entropy that define the temperature and chemical potential. Of course, in order to consider those partial derivatives, we need to express the entropy itself in terms of E_{tot} , N_{tot} and the parameters

$$\{Z_g(\beta, \gamma), \beta(E_{\text{tot}}, N_{\text{tot}}), \gamma(E_{\text{tot}}, N_{\text{tot}})\}$$

that we have now related to E_{tot} and N_{tot} . What do you obtain upon inserting Eq. 69 for p_i into the formula for the entropy?

$$\begin{aligned} \underline{S(E_{\text{tot}}, N_{\text{tot}})} &= -R \sum_{i=1}^M p_i \log p_i = -R \sum_i p_i \left(-\log Z_g - \beta E_i + \gamma N_i \right) \\ &= R \log Z_g + \beta E_{\text{tot}} - \gamma N_{\text{tot}} \end{aligned}$$

$$Z_g(\beta, \gamma)$$

Taking the derivative of the resulting entropy with respect to E_{tot} , keeping N_{tot} fixed, gives the temperature from Eq. 22. Thanks to Eqs. 70 and 71, the result should simplify in a pleasant way:

$$\begin{aligned} \frac{1}{T} = \left. \frac{\partial S}{\partial E_{\text{tot}}} \right|_{N_{\text{tot}}} &= R \left(\underbrace{\frac{\partial \beta}{\partial E}}_{-E} \frac{\partial}{\partial \beta} \log Z_g + \underbrace{\frac{\partial \gamma}{\partial E}}_N \frac{\partial}{\partial \gamma} \log Z_g \right) + E \frac{\partial \beta}{\partial E} + \beta - N \frac{\partial \gamma}{\partial E} \\ &= \cancel{\frac{\partial \beta}{\partial E} (-E)} + \cancel{\frac{\partial \gamma}{\partial E} (N)} + \cancel{E \frac{\partial \beta}{\partial E}} + \beta - \cancel{N \frac{\partial \gamma}{\partial E}} = \beta \\ &\beta = \frac{1}{T} \end{aligned}$$

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In the same way, the derivative with respect to N_{tot} , keeping E_{tot} fixed, gives the chemical potential with similar simplifications:

$$\mu = -T \left. \frac{\partial S}{\partial N_{\text{tot}}} \right|_{E_{\text{tot}}} =$$

In the end you should find

$$\beta = \frac{1}{T} \qquad \gamma = \beta \mu = \frac{\mu}{T} \qquad (72)$$

and the desired result that all information about the particle reservoir has dropped out, with no remaining reference to R , E_{tot} or N_{tot} . This large external reservoir is still present to fix the temperature T and chemical potential μ that characterize the grand-canonical system Ω , but beyond that nothing about it is relevant (or even knowable) in the grand-canonical approach.

Every aspect of Ω can now be specified in terms of its fixed temperature T and chemical potential μ , starting with the parameters $\beta = 1/T$ and $\gamma = \mu/T$. In particular, the probability—in thermodynamic equilibrium—that Ω adopts microstate ω_i with (non-conserved) internal energy E_i and particle number N_i is

$$p_i = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)} = \frac{1}{Z_g} e^{-(E_i - \mu N_i)/T}. \qquad (73)$$

Since the particle number N_i is dimensionless, the combination $E_i - \mu N_i$ that appears here reflects our observation below Eq. 67 that the chemical potential μ has dimensions of energy.