AEP 4230: Classical statistical mechanics

Contents

In this part of the course, we move from describing systems in terms of a *macrostate*, described by a relatively small number of thermodynamic coordinates (e.g., temperature, volume, particle number) to considering the complete *microstate* of a given system. We will use this microscopic picture to *derive* the laws of thermodynamics, giving these laws a rigorous microscopic backing. As discussed in the first part of the course on thermodynamics, it is essentially impossible be it analytically or computationally, to follow the dynamical evolution of microstates of a macroscopic number of particles. Therefore, it may seem a fool's errand to think about microstates. However, there are key simplifications that occur which make it possible to make general statements about microstates that allow us to predict thermodynamic properties of systems.

1. The thermodynamic properties of systems do not rely on the full dynamical state of a system: instead, we only need to know the *probability* that a system is in a given microstate. Probabilities show up because of a lack of knowledge about the detailed microstate of the system. As an example of a system, consider a gas of N particles in a container. The microstate of the system is described by $6N$ coordinates ($3N$ positions and $3N$ momenta). In classical physics, the large deal of information required to specify the microstate (knowing the positions and momenta of every particle in your box is a tall order!). Therefore, even though the dynamics are deterministic, the final microstate is *random* because of the lack of knowledge of the initial condition.

   Therefore, when thinking about a macroscopic system, we will introduce a hypothetical *ensemble* consisting of many copies of that system. In the language of our gas in a container, you could imagine an ensemble of boxes of the same volume, filled with the same number of gas molecules of the same species. Each could be imagined as starting in some possible initial microstate $\mu = (\mathbf{q}_1 \cdots \mathbf{q}_N, \mathbf{p}_1 \cdots \mathbf{p}_N)$. At some specified time, each member of the ensemble is in a different microstate, pulled from some probability distribution of microstates. In statistical mechanics the primary question is: for a given macrostate M of a system, what is the probability $p_M(\mu)$ of microstate μ being observed?

2. Relatedly, we are only interested in the probability distribution at thermal equilibrium. When our system of interest is started from some non-equilibrium distribution, it will generically equilibrate (there are exceptions). In other words, after some timescale, related to an *interaction* timescale, the probability distribution of microstates will converge to some value. The thermal equilibrium state should be thought of as a dynamic equilibrium. For any given member of the ensemble (for example, our gas in a container), the microstate changes in time.

Of course, in the real physical system we are trying to analyze (our gas in a container), we do not have access to an ensemble of identically prepared systems. We have only one. The ensemble would only be a useful device if somehow the ensemble average of any observable quantity of interest (for example, the pressure) was equal to the time average of that same property, in our one system. This remarkable property is called *ergodicity* and holds for a wide variety of macroscopic physical systems. It does not hold for some special, finely tuned, or sufficiently simple systems, but for most cases of interest in statistical mechanics, it does hold. Ergodicity is easy to state, and typically very hard to prove - so we do not attempt to do so here.

I. THE MICROCANONICAL ENSEMBLE AND THE CENTRAL POSTULATE OF STATISTICAL MECHANICS

Let us consider an ensemble of identical systems that is adiabatically and mechanically isolated from the rest of the Universe (and isolated from each other). This is called a *microcanonical* ensemble. If each system has energy E, it is conserved. Its generalized coordinates $\mathbf{x}$ are also conserved. We assume that there are no other conserved quantities.

The central postulate of statistical mechanics is that in this ensemble, all microstates of equal energy are equally probable. Therefore, the probability density of microstates can be written as

$$p_{E,\mathbf{x};\Delta E}(\mu) = \frac{1}{\Omega(E,\mathbf{x})}\delta_{H(\mu)=E\pm\Delta E/2}, \tag{1}$$

where $\delta_{H(\mu)=E\pm\Delta E/2}$ is a function that is 1 if the energy $H(\mu)$ of the state is in the range $[E-\Delta E/2, E+\Delta E/2]$ and zero otherwise. Since $p_{E,\mathbf{x};\Delta E}(\mu)$ is a probability distribution, it is normalized, and therefore

$$\Omega(E,\mathbf{x}) = \sum_{\mu}\delta_{H(\mu)=E\pm\Delta E/2}, \tag{2}$$

is simply the number of microstates that are in the energy shell of width ΔE. The sum over microstates is a generalized sum: for continuous systems, it represents an integration, as will be made clear by example.

From this ensemble, let us now connect to thermodynamics. The easiest thing that we can do is calculate the information theoretic entropy of this distribution. It is

$$S(E, \mathbf{x}; \Delta E) = -k_B \sum_{\mu} p_{E,\mathbf{x};\Delta E}(\mu) \ln p_{E,\mathbf{x};\Delta E}(\mu) = k_B \ln \Omega(E, \mathbf{x}), \tag{3}$$

where we have multiplied by k_B to express the units of entropy as those of thermodynamic entropy.

The introduction of the width ΔE is required to make Ω a dimensionless quantity, having the interpretation of a number of states. Had we replaced $\delta_{H(\mu)=E\pm\Delta E/2}$ by a tight delta function $\delta(H(\mu) - E)$, Ω would have dimensions $[\Omega] = [\text{energy}]^{-1}$. That said, carrying around the ΔE is occasionally cumbersome, especially since for most systems, provided $\Delta E \ll E$, the thermodynamic predictions we will make do not depend on ΔE. Therefore, it is sometimes convenient to define a classical *density of microstates*:

$$\rho(E) = \sum_{\mu} \delta(H(\mu) - E) \tag{4}$$

related to the number of microstates by

$$\Omega(E; \Delta E) = \int_{E-\Delta E/2}^{E+\Delta E/2} dE' \, \rho(E'), \tag{5}$$

where we have omitted the generalized coordinate labels.

A. Deriving the laws of thermodynamics in the microcanonical ensemble

We now show how this simple probability distribution reproduces the laws of thermodynamics.

1. *The zeroth law*

Let us consider two systems which were once isolated, with energies E_1 and E_2, and put them into contact, allowing them to exchange heat but not work. Therefore the generalized coordinates of the two systems are fixed to their initial values prior to contact, and we will not keep track of them in what follows. Because of the heat exchange, the energy of each subsystem is not exactly defined. However, the total energy of the system is still known: it is $E = E_1 + E_2$. Importantly, if the interaction between the two systems is small, then the space of microstates of the joint system is the product space of the microstates of the individual systems. We could write that a generic microstate $\mu = \mu_1 \otimes \mu_2$, where $\mu_{1,2}$ are microstates of the initially isolated systems. The joint system is in a microcanonical ensemble of energy E, and we may write the microstate probability distribution in terms of the number of microstates in the system $\Omega(E; \Delta E)$. We express the number of microstates in terms of the density of microstates

$$\rho(E) = \int d\mu_1 d\mu_2\ \delta(H(\mu_1) + H(\mu_2) - E), \tag{6}$$

where we have expressed the sum over microstates as an integral, assuming the micro-coordinates to be continuous. We may write this as

$$\rho(E) = \int d\mu_1 d\mu_2\ \delta(H(\mu_1) + H(\mu_2) - E) \int dE'\ \delta(H(\mu_1) - E'), \tag{7}$$

or equivalently

$$\rho(E) = \int d\mu_1 d\mu_2 dE'\ \delta(E' + H(\mu_2) - E)\delta(H(\mu_1) - E') = \int dE' \rho_1(E')\rho_2(E - E'), \tag{8}$$

where $\rho_{1,2}$ are the density of states of the individual systems. The number of microstates is simply $\Omega(E; \Delta E) = \rho(E)\Delta E$ provided that ΔE is sufficiently small.

We may now express the entropy of the system as

$$S(E) = k_B \ln \int \Omega_1(E'; \delta E)\Omega_2(E - E'; \Delta E) - S_0, \tag{9}$$

with $S_0 = -k_B \ln \Delta E$. Expressed in terms of the subsystem entropies, we may write:

$$S(E) = k_B \ln \int dE'\ \exp\left[(S_1(E'; \Delta E) + S_2(E - E'; \Delta E))/k_B\right] - S_0. \tag{10}$$

The idea is now as follows: suppose there is a maximum in the argument of the exponential (there typically will be): if this maximum is large, and it is in the thermodynamic limit, since it is a number of states (which grows with system size), the integral will be dominated by this maximum. Therefore, the integral is dominated by contributions from energy E^* such that

$$\left.\frac{\partial S_1(E')}{\partial E'}\right|_{E'=E^*} - \left.\frac{\partial S_2(E')}{\partial E'}\right|_{E'=E-E^*} = 0. \tag{11}$$

Recall that for a thermodynamic system, the first law of thermodynamics reads:

$$dU = TdS + \mathbf{J} \cdot d\mathbf{x} + \mu dN, \tag{12}$$

and that the thermodynamic temperature is related to the thermodynamic entropy via

$$T = \frac{\partial U}{\partial S}\bigg|_{\mathbf{x},N} \implies T^{-1} = \frac{\partial S}{\partial U}\bigg|_{\mathbf{x},N}. \tag{13}$$

This relation is suggestive: if we take the information theoretic entropy of the microcanonical ensemble to be equivalent to the thermodynamic entropy, and the energy of each subsystem E to be equivalent to the internal energy U, then the equality in Eq. (11) could be restated as

$$\frac{1}{T_1(E^*)} = \frac{1}{T_2(E - E^*)}, \tag{14}$$

where T plays the role of a temperature. This result is suggestive of a zeroth law of thermodynamics, because it establishes that when two systems are placed into contact and equilibrate, they reach some common value of a state variable. It is also clear that if we take a third system at the same "temperature" T, the equilibration temperature of this system with either of the two subsystems 1 or 2 will also simply be T. If it had entropy $S_3(E)$ such that $\partial S_3(E')/\partial E'\big|_{E^*} = 1/T$, then the total entropy of systems 1 + 3 or 2 + 3 would still be maximized.

This derivation gives a picture of microscopic, and *statistical* picture of equilibration. Equilibration happens because each system, in the presence of interactions, is optimizing for an energy with the largest number of states available to the total system. In the microcanonical ensemble defined by systems 1+2, any state with the same energy is equally probable, and the system can dynamically access those states equally easily. But, the number of states depends on energy. As systems 1 and 2 interact, they can exchange energy. Since energy is conserved, the energy of one system will increase (say system 1 without loss of generality) while the energy of the other system increases. This process will occur until the systems find a common energy that has the largest number of states. Since the contributions to entropy are exponentially dominated by the entropy maximum, and because that entropy maximum grows with the number of particles, the claim is that in the thermodynamic limit ($N \to \infty$), the joint system 1+2 is exponentially more likely to be in energy state $(E^*, E - E^*)$ for systems 1 and 2 than any other energy pair.

2. *The first law*

Let's ask what happens when we do work on the system, changing the generalized coordinates *reversibly* from $\mathbf{x}$ to $\mathbf{x}+\delta\mathbf{x}$. The change in energy is

$$E = E(S,\mathbf{x},N) \to E + \left.\frac{\partial E}{\partial S}\right|_{\mathbf{x},N} \left.\frac{\partial S}{\partial \mathbf{x}}\right|_{N} \cdot \delta\mathbf{x} + \left.\frac{\partial E}{\partial \mathbf{x}}\right|_{S,N} \cdot \delta\mathbf{x}. \tag{15}$$

Note that the entropy changes since the number of microstates associated with a given energy also changes. For example, in an ideal gas, if we change the volume of its container, the number of states increases since there are more places to arrange the molecules consistent with the energy of the gas. The change in energy can be written as

$$dE = TdS + \mathbf{J}\cdot d\mathbf{x}, \tag{16}$$

using the results from the discussion of the zeroth law, and identifying the external force $\mathbf{J}$ with the change in energy with respect to generalized coordinates (which requires only mechanics to establish). While this derivation looks trivial, there are a few things to appreciate.

1. The relation $E = E(S,\mathbf{x},N)$ is important in the derivation. This follows from the fact that the number of microstates, and thus, the entropy, depends on $E,\mathbf{x},N$, allowing us to write $S = S(E,\mathbf{x},N)$, from which we can write $E = E(S,\mathbf{x},N)$.

2. The change in the generalized coordinates leads to a heat $dQ = T\left.\frac{\partial S}{\partial \mathbf{x}}\right|_{N}\cdot\delta\mathbf{x}$, which results from the fact that the number of microstates changes when we change the generalized coordinates. For example, if we consider an ideal gas in a container whose volume is controlled by a piston, if we increase the volume of the container, the entropy increases, and so heat is generated in the process.

3. Chemical work can readily be incorporated into this derivation, establishing the μdN term in the first law.

3. The second law

The second law follows almost immediately from the discussion of the zeroth law. Consider two initially adiabatically and mechanically isolated systems at initial temperatures T_1 and T_2 which are allowed to equilibrate. Without loss of generality, assume $T_2 > T_1$. We have already established that they come to a common temperature T. The temperature was determined by the condition that the joint entropy reaches a maximum. If the joint entropy is $S_1(E^*) + S_2(E - E^*)$ after equilibration, and $S_1(E_1) + S_2(E_2)$ before equilibration, then maximization of the joint entropy implies that

$$\delta S = S_1(E^*) + S_2(E - E^*) - (S_1(E_1) + S_2(E_2)) > 0. \tag{17}$$

Stated differently, the entropy spontaneously increases in the absence of mechanical work when heat flows from one body to another. This is suggestive of the second law of thermodynamics.

In most systems, temperature increases with increasing energy, and therefore it also follows that $T > T_1$ and $T < T_2$, as is expected. In other words, heat flows from the hotter body to the colder body. However, as we will see in the next section, for two-level systems, the temperature can in fact *decrease* with energy, and even be negative.

4. Stability criterion

The argument that the entropy is dominated by the entropy maximum requires that the second derivative of the entropy needs to be negative. Otherwise, the integral in Eq. (10) would diverge. Therefore, we require

$$\frac{\partial^2 S(E)}{\partial E^2} = \left.\frac{\partial^2 S_1(E')}{\partial E'^2}\right|_{E'=E^*} + \left.\frac{\partial^2 S_1(E')}{\partial E'^2}\right|_{E'=E-E^*} < 0. \tag{18}$$

The result of these derivations is that by identifying the information theoretic entropy with the thermodynamic entropy, and the energy with the internal energy, the laws of thermodynamics follow from the equlibrium probability distribution associated with the microcanonical ensemble. The information theoretic entropy, like the thermodynamic entropy of Chapter 1, has the property that it acts as a thermodynamic potential that spontaneously increases, and defines a thermodynamic temperature.

II. CALCULATING THERMODYNAMIC PROPERTIES IN THE MICROCANONICAL ENSEMBLE

We now apply the microcanonical ensemble to compute the thermodynamic properties of two systems of interest: an arrangement of two-level systems, and the ideal gas.

A. Two-level systems

Consider N so-called two-level systems (such as quantum spin 1/2 systems) which are immobile: they could be defects embedded in a solid matrix, but they do not move around. We will call each of these two-level systems atoms for convenience. Each of these two-level systems is called such because they can exist in one of two states: state 1 (the ground state) with energy 0 and state 2 (the excited state) with energy ϵ. The total energy is dictated by the number N_1 of these atoms in excited states. $E = N_1\epsilon$. Let us now compute the entropy, temperature, internal energy, and specific heat of this system, assuming that it is in thermal equilibrium. As illustrated in the derivations of the previous section, the entropy is the main starting point.

The entropy is the number of states consistent with a given energy $E = N_1\epsilon$. It is equal to the number of states with N_1 excited atoms. This is simply

$$\Omega(E) = \frac{N!}{N_1!(N-N_1)!}. \tag{19}$$

The corresponding entropy is

$$S(E)/k_B = \ln\frac{N!}{N_1!(N-N_1)!} \tag{20}$$

We will consider the case where $N, N_1, N-N_1 \gg 1$. Then, the entropy may be approximated by Stirling's approximation as

$$S/k_B = -N[x\ln x + (1-x)\ln(1-x)], \tag{21}$$

where $x = E/N\epsilon = N_1/N$. The temperature immediately follows as

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_N = -\frac{k_B}{\epsilon} \ln \frac{E}{N\epsilon - E}. \tag{22}$$

This may be re-arranged to find the internal energy, yielding

$$E(T) = \frac{N\epsilon}{e^{\epsilon/k_BT} + 1}. \tag{23}$$

Finally, the specific heat is given by

$$C = \frac{\partial E}{\partial T}\bigg|_N = Nk_B \left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\epsilon/k_BT}}{(e^{\epsilon/k_BT} + 1)^2}. \tag{24}$$

We do not have to specify whether the specific heat is taken at constant generalized coordinate or constant generalized force, since there is no notion of work in this system.

The reader is encouraged to fill out the algebraic details leading to these results. Let us analyze these different thermodynamic expressions, starting with the entropy.

The entropy is properly extensive, and, for $x < 1/2$ increases with energy. The entropy reaches a maximum at $x = 1/2$, corresponding to half of the atoms being excited. Beyond this point, the entropy *decreases* with increasing energy. The origin of this phenomenon is clear: in a system with discrete states (such as ground and excited), there is an absolute maximum energy the system can have. The absolute maximum energy has only a single microstate, corresponding to all atoms excited, and is the maximally ordered state. It is as ordered as the state with zero energy which also only has one microstate. Both the maximally unexcited and maximally excited states are zero entropy. Because the entropy decreases with energy for $x > 1/2$, the temperature of states with energy $E > N\epsilon/2$ is *negative*. This is an unusual circumstance because adding energy (heat) to the system causes it to become more ordered (cool down) while removing energy makes the system less ordered. Some systems can be described as effectively having a negative temperature, such as atoms in a laser crystal, which can be placed in a state where there are more excited atoms than ground state atoms, but this description is only effective, as such states are not in thermal equilibrium.

The specific heat has the property that it goes to zero exponentially as $T \to 0$ ($C \sim T^{-2}e^{-\epsilon/kT}$ for $T \ll \epsilon/k_B$). This is a typical property for systems with an *energy* *gap*, a finite energy difference between the lowest-energy and second-lowest-energy states. The interpretation is that, at low temperatures, the addition of energy $kT \ll \epsilon$ is not enough to add an energy ϵ to the system, and so the energy increases very little: in this case exponentially. At high temperatures, the specific heat is also suppressed, scaling like $C \sim T^{-2}$. This is because, at high temperatures, the system has approximately $N/2$ excited atoms, which is the highest entropy state. The system can theoretically accept more energy, but it does not "want to" because it would need to move to a more ordered state.

Another interesting quantity is the unconditional probability that one atom is excited. In other words, irrespective of the state of all of the other atoms in the system, what is the probability that a particular atom (say atom 1) is excited? Before embarking on this calculation, since we will perform a similar one for the ideal gas, it is useful to derive a general result for the unconditional one-body probability density, derived in the subsection below. It follows that the probability that atom 0 is in the ground state (denoted m=0) is

$$p_1(m=0) = \Omega(E;\Delta E, N-1)/\Omega(E;\Delta E, N) = \frac{N-N_1}{N} = 1 - \frac{N_1}{N}, \tag{25}$$

while $p_1(m=1) = N_1/N$ follows from normalization. This result is of course expected because the atoms are independent of each other. It is also easy to show that for N independent atoms with this probability density, the entropy is given by N times the single atom entropy which is $-k_B(x\ln x + (1-x)\ln(1-x))$ with $x = N_1/N$.

1. *Unconditional probability densities in the microcanonical ensemble*

Suppose we have an arrangement of non-interacting systems with one-body Hamiltonian $H(m)$ with m denoting the degrees of freedom relevant to the system description. For a particle in a potential, $m = (\mathbf{q}, \mathbf{p})$ while for a two-level system, the degree of freedom is the excitation index, e.g., 0 or 1. The probability distribution for a microstate of the total system is given by

$$p(\mu) = \frac{1}{\Omega(E;\Delta E)}\delta(H(\mu) = E \pm \Delta E/2), \tag{26}$$

where we have indicated the argument of the discrete delta function by parentheses for clarity. The joint microstate can be specified in the product space of the individual systems as $\mu = m_1, m_2, \cdots m_N$. The conditional one-body probability density is given by

$$p_1(m_1) = \sum_{m_2\cdots m_N} p(m_1, m_2, \cdots, m_N) = \frac{1}{\Omega(E;\Delta E)} \sum_{m_2\cdots m_N} \delta(H(\mu) = E \pm \Delta E/2). \quad (27)$$

In the right-hand side, the sum is evaluated as follows: it is the number of states consistent with being in the energy shell $E \pm \Delta E/2$ *and* the state of subsystem 1 being m_1 with energy $E(m_1)$. That number is the same as the number of microstates of $N-1$ particles consistent with an energy $E - E(m_1) \pm \Delta E/2$. Therefore, the unconditional one-body probability density is

$$p_1(m_1) = \Omega(E - E(m_1); \Delta E, N-1)/\Omega(E; \Delta E, N) \quad (28)$$

III. THE IDEAL GAS: AN INCORRECT APPROACH

Now we consider the ideal gas from the perspective of the microcanonical ensemble. It turns out that a naive approach to applying the microcanonical ensemble gets most of the thermodynamics of the ideal gas correct, but incorrectly predicts a non-extensive entropy. The error will require quantum mechanical considerations to fix, and the fix leads to a simple modification of the incorrect approach. Thus, we still pursue the "wrong" way.

The number of states in the system is found as follows: first, evaluate the density of microstates, which is

$$\rho(E, V, N) = \frac{1}{h^{3N}} \int \left(\prod_{n=1}^{N} d^3 q_i d^3 p_i \right) \delta\left(\sum_{i=1}^{N} \frac{p_i^2}{2m} - E \right). \quad (29)$$

In this expression, we have introduced a constant h which is currently unspecified, but has units of action $[h] = [qp]$. This is needed to make the expression $\frac{1}{h^3}\int d^3q d^3p$ dimensionless, which is needed if we want that to represent a sum over states (the number of states is dimensionless). Classical statistical mechanics will not give us any way to actually know what this quantity is: at this stage, it can only be introduced as a way to get the units right. It turns out that in quantum statistical mechanics, we will be able to determine that this constant h is the Planck constant.

Note that the number of states has a volume dependence by virtue of the limits of integration of the positions of the different particles: we are only interested in states of energy E which correspond to all N particles being in a box of volume V. Therefore:

$$\rho(E,V,N) = \left(\frac{2m}{h^2}\right)^{3N/2} V^N \int \left(\prod_{n=1}^{N} d^3\tilde{p}_i\right) \delta\left(\sum_{i=1}^{N} \tilde{p}_i^2 - E\right), \tag{30}$$

where we have rescaled coordinates to simplify matters. The remaining integral is simplified by going into $3N$-dimensional spherical coordinates. The quantity $r^2 \equiv \tilde{p}_i^2$ is the squared radius in $3N$ dimensions. We may change variables into spherical coordinates, writing the integral as

$$\rho(E,V,N) = \left(\frac{2m}{h^2}\right)^{3N/2} V^N S_{3N} E^{3N/2-1} \int d\tilde{r}\, \tilde{r}^{3N-1} \delta(\tilde{r}^2 - 1), \tag{31}$$

with $\tilde{r} = r/\sqrt{E}$. where S_{3N} is the surface area of a sphere of radius 1. We quote the result here: $S_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}$. The remaining integral is simply $1/2$, and so we have

$$\rho(E,V,N) = \frac{(2m\pi E/h^2)^{3N/2} V^N}{(3N/2-1)!E} \tag{32}$$

and the number of microstates is

$$\Omega(E,V,N) = \frac{(2m\pi E/h^2)^{3N/2} V^N}{(3N/2-1)!E} \Delta E. \tag{33}$$

The entropy is

$$S = k_B \ln \Omega(E,V,N) = k_B \left(N \ln\left((2m\pi E/h^2)^{3/2} V\right) - \ln(3N/2-1)! + \ln \Delta E/E\right), \tag{34}$$

which, using Stirling's approximation, and neglecting terms that are subleading in N, we have

$$S \approx N k_B \ln\left(V\left(\frac{4\pi m e E}{3Nh^2}\right)^{3/2}\right). \tag{35}$$

The temperature is given by

$$\frac{1}{T} = \frac{3Nk_B}{2E} \implies E = \frac{3}{2} N k_B T. \tag{36}$$

The heat capacity at constant volume is simply $3/2Nk_B$. The ideal gas law is found by finding a relation for the pressure from the first law of thermodynamics:

$$dE = TdS - pdV + \mu dN. \tag{37}$$

Suppose we perform a thermodynamic transformation at constant temperature and particle number: the energy does not change by the above equation, and so

$$\frac{\partial S}{\partial V}\bigg|_{N,E} = \frac{p}{T}, \tag{38}$$

which implies that

$$p = Nk_BT/V, \tag{39}$$

as expected.

Before moving on, we also derive the one-particle conditional probability density. It is

$$p_1(\mathbf{q},\mathbf{p}) = \Omega(E-\frac{p^2}{2m}, V, N-1)/\Omega(E,V,N) = \left(\frac{2m}{h^2}\right)^{-3/2} \frac{(3N/2-1)!}{(3N/2-3/2-1)!}\frac{V^{N-1}}{V^N}\frac{(E-\frac{p^2}{2m})^{3N/2-1-3/2}}{E^{3N/2-1}}, \tag{40}$$

which simplifies to

$$p_1(\mathbf{q},\mathbf{p}) = \left(\frac{2m}{h^2}\right)^{-3/2} V^{-1}(3N/2)^{3/2}(E-\frac{p^2}{2m})^{-3/2}\left(1-\frac{p^2}{2mE}\right)^{3N/2}. \tag{41}$$

Using $E = 3/2Nk_BT$, this simplifies to

$$p_1(\mathbf{q},\mathbf{p}) = V^{-1}(h^2/2m\pi k_BT)^{3/2}\left(1-\frac{p^2}{3mk_BT}\right)^{3N/2} = \frac{1}{V}\left(\frac{h^2}{2\pi mk_BT}\right)^{3/2} e^{-\frac{p^2}{2mk_BT}}. \tag{42}$$

in the limit of $N \to \infty$. This is the so-called Maxwell-Boltzmann distribution. Typically, it is not seen with the h^3 factor: the conventional form is realized by omitting the h^3 and changing the integration from $\frac{1}{h^3}\int d^3q d^3p$ to $\int d^q d^3p$. Additionally, since the position dependence is trivial (a gas molecule is equally likely to be anywhere in the box), the distribution is typically expressed as a momentum probability density only. Thus, we may write that the one-body momentum probability density is

$$p_{\mathrm{MB}}(\mathbf{p}) = \left(\frac{1}{2\pi mk_BT}\right)^{3/2} e^{-\frac{p^2}{2mk_BT}}, \tag{43}$$

with the property that $\int d^3p\; p_{\mathrm{MB}} = 1$.

IV. GIBBS PARADOX AND ENTROPY OF MIXING

As discussed in the unit on thermodynamics, entropy is an extensive quantity, meaning that if we scale up all intensive variables upon which it depends by a factor

λ, the entropy will also increase by λ (not to be confused with the thermal de Broglie wavelength): $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$. The ideal gas entropy we have derived *does not* have this property. In fact, we find that $S(\lambda E, \lambda V, \lambda N) = \lambda S + Nk_B \ln \lambda$. This error happens to be related to the entropy of mixing of the gas.

Suppose we have a container with two chambers $1, 2$ separated by a partition. Chamber 1 contains an ideal gas of particles with mass m_1, number of particles N_1, and volume V_1, while Chamber 2 contains an ideal gas of particles with mass m_2, number of particles N_2, and volume V_2. Both gases are at the same temperature T. Intuitively, we expect that if the partition is removed, the two gases will mix in an irreversible fashion, suggesting an increase in entropy relative to the two unmixed gases. This is called the entropy of mixing: let's calculate it.

The entropy of the individual gases is given from our calculation above by:

$$S_i = N_i k_B \ln\left(V_i \left(\frac{2\pi m_i e k_B T}{N_i h^2}\right)^{3/2}\right) \equiv N_i k_B \left(\ln\left(\frac{V_i}{\lambda_i^3}\right) + \frac{3}{2}\right), \tag{44}$$

where we have defined $\lambda_i = h/\sqrt{2\pi m_i k_B T}$. The entropy of the mixture is found by counting the states available to the two gases. The computation is simplified by the fact that the two gases are at the same temperature, and therefore there is no energy exchange in the two gases. The energy of each gas is $N_1 k_B T$ and $N_2 k_B T$. Therefore, the total number of microstates of the mixture of the two gases, Ω_{12}, is

$$\Omega_{12} = \Omega_A(E_1 = N_1 k_B T, V, N_1)\Omega_B(E_2 = N_2 k_B T, V, N_2), \tag{45}$$

and the entropy is

$$S_{12} = k_B \ln \Omega_{12} = N_1 k_B \left(\ln\left(\frac{V}{\lambda_1^3}\right) + \frac{3}{2}\right) + N_2 k_B \left(\ln\left(\frac{V}{\lambda_2^3}\right) + \frac{3}{2}\right). \tag{46}$$

The entropy of mixing is defined as

$$\Delta S_{\text{mix}} = S_{12} - S_1 - S_2 = N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2}, \tag{47}$$

which is positive since $V > V_1, V_2$, as expected.

Let's consider the case where the two gases are identical: they are made of the same substance (e.g., oxygen) and have the same density and temperature (and therefore pressure). Removing the partition separating these gases does not change the thermodynamic state of the system. The box still looks like a gas of density n at temperature T, and there is nothing one can do to tell that anything has changed when the partition is removed. The entropy change should be zero. The expression above gives a positive non-zero answer.

In fact, our calculation of microstates of the ideal gas is in error. This could have also been anticipated by the non-extensivity of the predicted entropy. The problem is as follows: consider an ideal gas of N atoms of the same species (e.g., oxygen). When we count microstates, we perform integrations such as $\int d^3q_1 \cdots d^3q_N$ (and similar for momentum). In this integration, if we interchange or permute the coordinates of the N particles, that contribution from the integrand is counted: this is how we get a V^N in doing the position-space integrations. The reality however is that there is no way to tell a difference if we take our N particles and permute them: there is no classical operation that can distinguish this situation, and in fact there is no quantum mechanical way to distinguish them either. Therefore, we have overcounted by $N!$ and the entropy is overcounted by $\ln N! \approx N \ln N - N$. The corrected entropy of the ideal gas is therefore

$$S_i = N_i k_B \left(\ln \left(\frac{V_i}{N_i \lambda_i^3} \right) + \frac{5}{2} \right) \equiv N_i k_B \left(\ln \left(\frac{1}{n_i \lambda_i^3} \right) + \frac{5}{2} \right), \tag{48}$$

which is the so-called Sackur-Tetrode formula for the ideal gas entropy.

Let us re-evaluate the entropy of mixing for two gases now. If the gases are distinct, the reader should convince themselves that the entropy of mixing is the same as previously derived. That is because the microstates of two distinct gases $1, 2$ are distinguishable and we simply multiply the number of microstates available to the two gases. In the case of mixing two *identical* gases, the entropy becomes

$$\Delta S_{\text{mix}} \to N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2} - k_B \ln(N_1 + N_2)! + k_B \ln N_1! + k_B \ln N_2!, \tag{49}$$

which, using Stirling's approximation, yields:

$$\Delta S_{\text{mix}} \to N_1 k_B \ln n_1 + N_2 k_B \ln n_2 - (N_1 + N_2) k_B \ln(n_{12}), \tag{50}$$

with $n_{12} = (N_1 + N_2)/V$. This expression vanishes if $n_1 = n_2 = n_{12}$.

A. The ideal gas: the correct approach

The result of all this is that when counting microstates for an N particle system where the particles are indistinguishable, we should write

$$\sum_{\mu} = \frac{1}{N!} \int \prod_{i=1}^{n} \frac{d^3 q_i d^3 p_i}{h^3}. \tag{51}$$

Previous results for intensive quantities such as temperature, pressure and the one-particle probability density do not need to be corrected. The reader is encouraged to show for example that the chemical potential is correctly found as $\mu = k_B T \ln n\lambda^3$ and that the extensivity relation $E = TS - PV + \mu N$ holds.

V. ALTERNATIVE ENSEMBLES

In the beginning of this chapter, we discussed that due to a lack of knowledge in large thermodynamic systems, we need to take a probabilistic approach, and ask questions about the theoretical probability (subjective probability) of observing a system to be in some particular microstate. The notion of probability brought up the notion of an ensemble of identically prepared systems of which each member of the ensemble has a state at a given time is drawn from the microstate probability distribution. We related these ensemble averages to time averages by stipulating ergodicity, allowing us to use the statistical properties of the ensemble to make statements about a single member of the ensemble, observed over time.

We started by considering an ensemble of systems that were adiabatically and mechanically isolated from the rest of the universe, the microcanonical ensemble. We stipulated that all microstates of the same energy were equally likely to occur, and through this, determined the thermodynamic properties of systems such as two-level system ensembles and the ideal gas. In principle, we can use the microcanonical ensemble to make predictions about any classical statistical mechanical system.

It turns out that these calculations can be made easier by considering alternative ensembles. In the thermodynamic limit, the results in any ensemble turn out to be identical. Outside of the thermodynamic limit, we get that in some ensembles, certain observable quantities fluctuate, while in others, the quantities are exactly known. Let us introduce and derive in detail two alternative ensembles, the canonical ensemble and the grand canonical ensemble, which are used heavily in the remainder of the course. We will briefly state the so-called Gibbs ensemble, which typically does not offer much simplification of the statistical mechanics problems we consider in this course.

A. Canonical ensemble

Let us consider an ensemble of systems (S) which can exchange heat with a reservoir (R) at temperature T. The system and reservoir are adiabatically and mechanically isolated from the rest of the Universe, defining a microcanonical ensemble for the joint system $S + R$. However, what we are actually interested in is the probability distribution of microstates of the system μ_S, which is found by taking the probability distribution for joint microstates, and summing over reservoir states. Since the joint system defines a microcanonical ensemble of energy E, we may write that the probability of joint microstates, $p(\mu_S, \mu_R)$, is given by:

$$p(\mu_S, \mu_R) = \frac{1}{\Omega_{SR}(E; \Delta E)} \delta_{H(\mu_S, \mu_R) = E \pm \Delta E/2}, \tag{52}$$

where $\Omega_{SR}(E; \Delta E)$ is the total number of joint microstates consistent with energy E, and $H(\mu_S, \mu_R)$ is the Hamiltonian of the system and reservoir $H(\mu_S, \mu_R) \approx H(\mu_S) + H(\mu_R)$ in the case where their interaction represents a weak perturbation, as we have assumed previously when discussing the thermalization of two systems and the zeroth law of thermodynamics. The unconditional probability distribution for a system microstate μ_S is

$$p(\mu_S) = \frac{1}{\Omega_{SR}(E; \Delta E)} \sum_{\mu_R} \delta_{H(\mu_S, \mu_R) = E \pm \Delta E/2}, \tag{53}$$

which may be evaluated by inserting 1 as:

$$p(\mu_S) = \frac{1}{\Omega_{SR}(E; \Delta E)} \sum_{\mu_R} \delta_{H(\mu_S, \mu_R) = E \pm \Delta E/2} \sum_{E'} \delta_{H(\mu_S) = E'} = \frac{1}{\Omega_{SR}(E; \Delta E)} \sum_{E'} \sum_{\mu_R} \delta_{H(\mu_R) = E - E' \pm \Delta E/2} \delta_{H(\mu_S) = E'}, \tag{54}$$

which can be written as

$$p(\mu_S) = \frac{\Omega_R(E - H(\mu_S); \Delta E)}{\Omega_{SR}(E; \Delta E)}. \tag{55}$$

We now wish to express this result in terms of entropies, resulting in:

$$p(\mu_S) = \exp\left[\frac{1}{k_B}(S_R(E - H(\mu_S); \Delta E)) - S(E; \Delta E)\right]. \tag{56}$$

The reservoir is assumed to be much larger than the system. Therefore, by extensivity, we expect that the typical energy of the reservoir is much larger than the typical energy of the system. If we define E^* as the most likely energy of the system, then we are stipulating that $E \gg E^*$. Therefore, we may Taylor expand the reservoir entropy as

$$p(\mu_S) = \exp\left[\frac{1}{k_B}(S_R(E; \Delta E)) - \frac{H(\mu_S)}{T} - S(E; \Delta E)\right] \equiv \frac{1}{Z}e^{-\beta H(\mu_S)}, \tag{57}$$

where we have defined $\beta = \frac{1}{k_B T}$ (as factors of β show up very frequently), and defined a normalization constant, called the *partition function* $Z^{-1} = \exp\left[k_B^{-1}(S_R(E; \Delta E) - S(E; \Delta E))\right]$. This quantity is constant with respect to variations of the system microstate μ_S. Since we know that the left-hand side of the previous equation is a probability, it must be that

$$Z = Z(T, \mathbf{x}, N) = \sum_{\mu_S} e^{-\beta H(\mu_S)}. \tag{58}$$

The partition function in and of itself is probably the most useful quantity to consider in the canonical ensemble. To see why, let us first relate Z to thermodynamic quantities by evaluating it.

$$Z = \sum_{\mu_S} \int dE'\, e^{-\beta H(\mu_S)} \delta(E' - H(\mu_S)) = \int dE'\, e^{-\beta E'} \rho(E') = \int \frac{dE'}{\Delta E}\, e^{-\beta E'} e^{S_S(E'; \Delta E)/k_B}, \tag{59}$$

with $\rho(E')$ being the density of system microstates, related to the total number of microstates in an energy shell of width ΔE by $\Omega(E', \Delta E) = \rho(E')\Delta E'$. The argument of the exponential is suggestive of a free energy, as we may write $-\beta E' + S_S(E'; \delta E)/k_B = -\beta(E' - TS(E'; \Delta E))$. The dependence on ΔE does however appear confusing, as we do not stipulate a ΔE when specifying a thermodynamic free energy. Note that the dependence of S on ΔE is logarithmic. We know that a typical form of $S \sim \ln \Omega \sim \ln \zeta^N \Delta E \sim N \ln \zeta + \ln \Delta E \approx N \ln \zeta$. In other words, the energy width is negligible in the thermodynamic limit. Therefore, the ΔE parameter is essentially irrelevant, and we identify $F(E') \equiv E' - TS(E')$, and write

$$Z = \int \frac{dE'}{\Delta E} e^{-\beta F(E')}. \tag{60}$$

Like many sums over exponential quantities, it is dominated by the extremum of the argument of the exponential E^* (at fixed temperature). The dominant contribution comes from the *minimum* of the free energy. Let us evaluate it:

$$Z \approx \frac{1}{\Delta E}\int dE' \exp\left[-\beta F(E^*) - \frac{1}{2}\beta \frac{d^2F}{dE^2}\Big|_{E=E^*}(E-E^*)^2\right] = e^{-\beta F(E^*)}\sqrt{\frac{2\pi}{\beta d^2F/dE^2|_{T,E^*}}}\frac{1}{\Delta E}. \tag{61}$$

The free energy derivative is evaluated as

$$\frac{d^2(\beta F)}{dE^2} = -\frac{1}{k_B}\frac{d^2S}{dE^2}\Big|_{E=E^*,T} = -\frac{1}{k_B}\frac{dT^{-1}}{dE}\Big|_{E=E^*,T} = \frac{1}{k_BT^2}\frac{dT}{dE}\Big|_{E=E^*,T} = \frac{1}{k_BT^2C_{\mathbf{x}}}. \tag{62}$$

The partition function then becomes

$$Z \approx (\Delta E)^{-1}\sqrt{2\pi k_BT^2C_{\mathbf{x}}}e^{-\beta F(E^*)}. \tag{63}$$

The logarithm is given as

$$\ln Z = -\beta F(E^*) + \ln(\Delta E)^{-1}\sqrt{2\pi k_BT^2C_{\mathbf{x}}} \approx -\beta F(E^*). \tag{64}$$

In the thermodynamic limit, since $F \sim N$ and $C_{\mathbf{x}} \sim N$, the logarithm is dominated by $-\beta F(E^*)$ as $N \to \infty$. Therefore, we write

$$F(T, \mathbf{x}, N) \equiv F(E^*) = -kT\ln Z. \tag{65}$$

The partition function is associated with the free energy function assuming that the system is at its most likely energy. How likely is the system to be at this energy? We need the probability density as a function of energy, rather than microstate, to answer that. It is straightforwardly found as:

$$p(E) = \sum_{\mu_S}\frac{1}{Z}e^{-\beta H(\mu_S)}\delta(H(\mu_S)-E) = \frac{1}{Z\Delta E}e^{-\beta F(E)} = \frac{1}{\sqrt{2\pi k_BT^2C_{\mathbf{x}}}}e^{-\frac{(E-E^*)^2}{2k_BT^2C_{\mathbf{x}}}}. \tag{66}$$

This probability density tells us that the mean energy $\langle E\rangle = E^*$ (so the mean is the mode), and the energy uncertainty is $\sigma_E = \sqrt{2k_BT^2C_{\mathbf{x}}}$. The relative ratio is

$$\frac{\sigma_E}{E^*} = \sqrt{2k_BT^2}\frac{\sqrt{C_{\mathbf{x}}}}{E^*} \sim N^{-1}, \tag{67}$$

which goes to zero in the thermodynamic limit. Therefore, we may say that the energy becomes sharply defined in the thermodynamic limit.

It is conceptually satisfying to explicitly construct the distribution function for the system energies. If one wants average energies, variances, and cumulants, there is a simpler way which in practice is more useful for calculations. In particular, differentiating the partition function with respect to β gives

$$\frac{1}{Z}\frac{\partial Z}{\partial \beta}\Big|_{\mathbf{x},N} = \frac{1}{Z}\sum_{\mu_S} -H(\mu_S)e^{-\beta H(\mu_S)} = -\langle E\rangle. \tag{68}$$

Taking the second derivative of Z with respect to β gives the second moment via

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}\Big|_{\mathbf{x},N} = \langle E^2\rangle. \tag{69}$$

The variance is then found as

$$\sigma_E^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}\Big|_{\mathbf{x},N} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\Big|_{\mathbf{x},N}\right)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}\Big|_{\mathbf{x},N}. \tag{70}$$

B. Grand canonical ensemble

The grand canonical ensemble expands on the idea of the canonical ensemble by allowing the particle and reservoir to not only exchange energy, but also particle number. The total energy of system and reservoir is E, and the total particle number of system and reservoir is N. The setup is otherwise the same. In what follows, we skip most of the steps of the derivation of the unconditional probability distribution, as it is similar to the derivations in the canonical ensemble. The main conceptual difference is that the microstates of the system have *variable* particle number.

The unconditional probability distribution we define is $p(\mu_S, N|N(\mu_s) = N)$ where μ_S refers to a system microstate with N particles. It immediately follows that

$$p(\mu_S, N|N(\mu_s) = N) = \frac{\Omega_R(E - H(\mu_S), N - N(\mu_S))}{\Omega_{SR}(E, N)}, \tag{71}$$

where we have omitted references to ΔE. Expressing the number of microstates in terms of entropy, and using $E^* \ll E$ and $N^* \ll N$ (in other words, that the most like energy and particle number of the system is much less than those of the reservoir), we have

$$p(\mu_S, N|N(\mu_s) = N) = \frac{1}{Q}e^{\beta\mu N - \beta H(\mu_s)}, \tag{72}$$

where we have made the identification $\frac{\partial S}{\partial N}\Big|_{E,\mathbf{x}} = -\frac{\mu}{T}$, which follows from the first law of thermodynamics (we are, and have been implicitly assuming that the correspondence between information theoretic and thermodynamic quantities is perfect). The grand canonical partition function is simply

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\mu_s;N(\mu_S)=N} e^{-\beta H(\mu_s)} \tag{73}$$

The probability that the system has N particles, and any energy, is simply given by the sum over microstates of a given number of particles N, and is

$$p(N) = e^{\beta\mu N}\frac{Z(T,\mathbf{x},N)}{Q(T,\mathbf{x},\mu)}, \tag{74}$$

allowing us to equivalently express the grand canonical partition function as:

$$Q(T,\mathbf{x},\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,\mathbf{x},N). \tag{75}$$

As in the canonical ensemble, we can identify the mean number of particles and the variance of the number of particles by finding the extremum and curvature of the argument of the exponent. We proceed by expressing $p(N) \sim e^{\beta\mu N + \ln Z(N)} = e^{\beta\mu N - \beta F(N)} \sim e^{-\beta\mathcal{G}}$, where I have suppressed other dependences of Z on temperature and generalized coordinates and have introduced the grand potential $\mathcal{G}$. The maximum of the argument of the exponent with respect to N gives the mean number of particles:

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,\mathbf{x}}(N^*,T,\mathbf{x}). \tag{76}$$

Note that while in thermodynamics, μ depends on the mean number of particles, in this expression for the probabilities, it is a constant with respect to N. This is an implicit equation which determines the most likely number of particles N^* in terms of the chemical potential. The fluctuations are found in terms of the second derivative of the exponential argument, as

$$\frac{1}{\sigma_N^2} = \beta\frac{\partial^2 F}{\partial N^2}\Big|_{T,\mathbf{x}}(N^*) = \beta\frac{\partial\mu}{\partial N}\Big|_{T,\mathbf{x}}, \tag{77}$$

which may be re-arranged as

$$\sigma_N = k_B T\frac{\partial N}{\partial\mu}\Big|_{T,\mathbf{x}}(N^*). \tag{78}$$

Similarly to the case of the canonical ensemble, we may take derivatives of the grand canonical partition function in order to find the mean, variance, and higher-order cumulants of the particle number. The derivation is parallel to the case of the canonical ensemble and it is

$$\frac{1}{Q}\frac{\partial Q}{\partial(\beta\mu)}\Big|_{T,\mathbf{x}} = \langle N\rangle \tag{79}$$

The variance is then found as

$$\sigma_N^2 = \frac{\partial^2 \ln Q}{\partial(\beta\mu)^2}\Big|_{T,\mathbf{x}}. \tag{80}$$

Similarly to the case of the canonical ensemble, we may relate the grand partition function to the grand potential via

$$\mathcal{G} = -k_B T \ln Q(T, \mathbf{x}, \mu). \tag{81}$$

By extensivity, we may write $\mathcal{G} = \mathbf{J}\cdot\mathbf{x}$. Therefore $\ln Q = -\mathbf{J}\cdot\mathbf{x}/k_B T$, and so

$$\langle N\rangle = \frac{\partial \ln Q}{\partial(\beta\mu)}\Big|_{T,\mathbf{x}} = -\frac{1}{k_B T}\mathbf{x}\cdot\frac{\partial \mathbf{J}}{\partial(\beta\mu)}\Big|_{T,\mathbf{x}}, \tag{82}$$

while

$$\sigma_N^2 = -\frac{1}{k_B T}\mathbf{x}\cdot\frac{\partial^2 \mathbf{J}}{\partial^2(\beta\mu)}\Big|_{T,\mathbf{x}} = \frac{\partial\langle N\rangle}{\partial(\beta\mu)}. \tag{83}$$

Let us consider as an example, a system where the generalized coordinate is the volume. Then $\mathbf{J}\cdot\mathbf{x} = -PV$. The mean number of particles is

$$\langle N\rangle = V\frac{\partial P}{\partial\mu}, \tag{84}$$

while the variance is

$$\sigma_N^2 = k_B T\frac{\partial\langle N\rangle}{\partial\mu}. \tag{85}$$

The variance, relative to the mean, sometimes called the Fano factor, is given by

$$\frac{\sigma_N^2}{\langle N\rangle} = \frac{k_B T}{V}\frac{\partial\langle N\rangle}{\partial P}\Big|_{T,\mathbf{x}} = n k_B T \kappa_T, \tag{86}$$

where $\kappa_T = -V^{-1}\partial V/\partial P|_T$ is the isothermal compressibility. In order for the ratio of variance to mean to be positive, we require that $\kappa_T > 0$ - in analogy to the statement in the canonical ensemble that the specific heat must be positive to have a positive energy variance.

C. Examples in the canonical and grand canonical ensemble

Let us now apply the ideas we have developed in the context of a familiar system such as the ideal gas. We will compute the thermodynamic properties of the ideal gas in the canonical and grand-canonical ensemble.

1. *Ideal gas: canonical ensemble*

The starting point is the partition function. The partition function is given by

$$Z = \frac{1}{N!}\int\left(\prod_{i=1}^{N}\frac{d^3q_i d^3p_i}{h^3}e^{-\beta\frac{p_i^2}{2m}}\right) = \frac{1}{N!}\prod_{i=1}^{N}V\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3 = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N. \qquad (87)$$

The free-energy is given by

$$F = -kT\ln Z = -k_BT\left(N\ln V/\lambda^3 - N\ln N + N\right) = -Nk_BT\left(\ln(n\lambda^3)^{-1} + 1\right), \qquad (88)$$

with $n = N/V$. The internal energy is given by

$$E = -\frac{\partial \ln Z}{\partial\beta}\Big|_{V,N} = -\frac{\partial}{\partial\beta}3N\ln\beta^{-1/2} = \frac{3N}{2\beta} = \frac{3}{2}Nk_BT. \qquad (89)$$

The entropy is given by

$$S = (E-F)/T = Nk_B\left(\ln(n\lambda^3)^{-1} + \frac{5}{2}\right). \qquad (90)$$

The chemical potential is given by

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V} = -k_BT\left(\ln(n\lambda^3)^{-1} + 1\right) + k_BT = k_BT\ln(n\lambda^3). \qquad (91)$$

The pressure may immediately be found via

$$P = -\frac{F - \mu N}{V} = Nk_BT/V. \qquad (92)$$

You may have noticed that the math associated with the calculation of the partition function (the normalization constant for the canonical ensemble microstate probability distribution) was considerably simpler than the math associated with the number of microstates (the normalization constant for the microcanonical ensemble microstate probability distribution). The origin of this is that in the microcanonical ensemble, we are counting states with a constraint that the energy is within some energy shell. Often, counting states with a constraint is harder than counting without constraints. In the canonical case, we relax that constraint, allowing the system to have any energy, integrating over all possible states, but with a weight factor $e^{-\beta H}$. The magic here is that in the thermodynamic limit, the energy in the canonical ensemble becomes sharply defined anyway giving the same result as the microcanonical ensemble.

2. *Ideal gas: grand canonical ensemble*

The case of the grand canonical ensemble is similarly simple. The grand canonical partition function is

$$\mathcal{Q}(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,T,V) = \sum_{N=0}^{\infty} e^{\beta\mu N} (V/\lambda^3)^N/N! = \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right]. \tag{93}$$

The mean number of particles is given by (I'm omitting average brackets with the implicit assumption that we are in the thermodynamic limit):

$$N = \frac{\partial \ln \mathbf{Q}}{\partial(\beta\mu)} = e^{\beta\mu}\frac{V}{\lambda^3} \implies \mu = k_B T \ln n\lambda^3. \tag{94}$$

The pressure is given by

$$\mathcal{G} = -k_B T \ln \mathcal{Q} = -PV \implies P = Nk_B T/V, \tag{95}$$

using $\ln \mathcal{Q} = e^{\beta\mu}\frac{V}{\lambda^3} = N$.

We may now work backwards to the other potentials. For example, we know that

$$F = \mathbf{G} + \mu N = -Nk_B T + Nk_B T \ln n\lambda^3 = -Nk_B T\left(\ln(n\lambda^3)^{-1} + 1\right). \tag{96}$$

and that implies an entropy of

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} = Nk_B\left(\ln(n\lambda^3)^{-1} + 1\right) + Nk_B T\frac{3}{2T} = Nk_B \ln\left(\ln(n\lambda^3)^{-1} + \frac{5}{2}\right). \tag{97}$$

And of course, the energy $E = \frac{3}{2}Nk_B T$, which follows from $E = F - TS$.

To summarize, we have computed the thermodynamic potentials and the equation of state for the ideal gas in the microcanonical, canonical, and grand canonical ensemble, with all three being in exact agreement in the thermodynamic limit of $N \to \infty$. At the same time, the different ensembles give a different picture of what is going on, and have computational advantages relative to each other.