G25.2651: Statistical Mechanics

Notes for Lecture 6

I. THE IDEAL GAS

The ideal gas is simplest thermodynamic system that lends itself to analytical solution in all the ensembles we have studied thus far. It's importance lies in the fact that, for many "real" systems, the ideal gas behavior is the zeroth order approximation to these systems. Thus, deviations from ideal behavior become manifestly clear. It is therefore important that we establish what this ideal behaviour is. We will begin with the microcanonical ensemble treatment.

A. Microcanonical ensemble treatment

Consider a system of N particles in a cubic box of volume $V = L^3$.

The particles are assumed not to interact with each other. Thus, the Hamiltonian in Cartesian coordinates may be taken to be

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}$$

where we are assuming that all particles are of the same type.

The microcanonical partition function is

$$\Omega(N, V, E) = \frac{E_0}{N! h^{3N}} \int d^N \mathbf{p} \; d^N \mathbf{r} \; \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right)$$

Since the Hamiltonian is independent of the coordinates, the $3N$ coordinate integrations can be done straightforwardly. The range of each one is 0 to L. Thus, these integrations give an overall factor $L^{3N} = V^N$:

$$\Omega(N, V, E) = \frac{E_0}{N! h^{3N}} V^N \int d^N \mathbf{p} \;\; \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right)$$

To do the momentum integrals, we first change variables to

$$\mathbf{p}_i' = \frac{\mathbf{p}_i}{\sqrt{2m}}$$
$$d^N p = (2m)^{3N/2} d^N \mathbf{p}'$$

Substitution into the partition function gives

$$\Omega(N, V, E) = \frac{E_0}{N! h^{3N}} V^N (2m)^{3N/2} \int d^N \mathbf{p}' \;\; \delta\left(\sum_{i=1}^{N} \mathbf{p}_i'^2 - E\right)$$

The $3N$ dimensional integral can now be seen to an integration over the surface of a sphere defined by the equation

$$\sum_{i=1}^{N} \mathbf{p}_i'^2 = E$$

Therefore, it proves useful to transform to $3N$ dimensional spherical coordinates, $R, \theta_1, ..., \theta_{3N-1}$, where

$$R^2 = \sum_{i=1}^{N} \mathbf{p}_i'^2$$

Then

$$d^N \mathbf{p}' = d^{3N-1}\omega \ dR \ R^{3N-1}$$

where $d^{3N-1}\omega$ is the $3N-1$ solid angle integral over the $3N-1$ angles. The partition function now becomes:

$$\Omega(N,V,E) = \frac{E_0}{N!h^{3N}} V^N (2m)^{3N/2} \int d^{3N-1}\omega \ dR \ R^{3N-1} \quad \delta\left(R^2 - E\right)$$

At this point, we use an identity of δ-functions:

$$\delta\left(x^2 - a^2\right) = \frac{1}{2|a|}\left[\delta(x-a) + \delta(x+a)\right]$$

to write

$$\begin{aligned}
\Omega(N,V,E) &= \frac{E_0}{N!h^{3N}} V^N (2m)^{3N/2} \int d^{3N-1}\omega \ dR \ R^{3N-1} \quad \frac{1}{2\sqrt{E}}\left[\delta\left(R - \sqrt{E}\right) + \delta\left(R + \sqrt{E}\right)\right] \\
&= \frac{E_0}{N!h^{3N}} V^N (2m)^{3N/2} \frac{1}{2} E^{3N/2-1} \int d^{3N-1}\omega
\end{aligned}$$

We will also make use of the fact that N is large, so that we may take $3N \pm 1 \approx 3N$. Using the general formula for an n dimensional solid angle integral:

$$\int d^n\omega = \frac{2\pi^{(n+1)/2}}{\Gamma\left(\frac{n+1}{2}\right)}$$

where $\Gamma(x)$ is the Gamma function:

$$\Gamma(x) = \int_0^\infty dt t^{x-1} e^{-t}$$

which satisfies

$$\begin{aligned}
\Gamma(n) &= (n-1)! \\
\Gamma\left(\frac{1}{2} + n\right) &= \frac{(2n-1)!!}{2^n}\pi^{1/2}
\end{aligned}$$

Thus, the solid angle integral is

$$\int d^{3N-1}\omega = \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}$$

and the partition function finally becomes

$$\Omega(N,V,E) = \frac{1}{N!}\frac{E_0}{E}\left[\frac{V}{h^3}(2\pi m E)^{3/2}\right]^N \frac{1}{\Gamma\left(\frac{3N}{2}\right)}$$

The entropy $S(N,V,E)$ is given by

$$S(N,V,E) = k\ln\Omega(N,V,E) = Nk\ln\left[\frac{V}{h^3}(2\pi m E)^{3/2}\right] - k\ln N! - k\ln\Gamma(3N/2) - k\ln\frac{E}{E_0}$$

Note that the term $k\ln(E/E_0) \sim \ln N$ since $E \sim N$, which is negligibly small compared to the term proportional to N and $\ln N!$. Thus, we can neglect it. Now, we can simplify $\ln N!$ using Stirling's approximation

$$\ln N! \approx N\ln N - N$$

which is valid for N very large. Also, note that

$$\Gamma(3N/2) = (\frac{3N}{2} - 1)! \approx (3N/2)!$$

so that

$$\ln \Gamma(3N/2) \approx (3N/2) \ln(3N/2) - (3N/2)$$

Substituting these approximations into the expression for the entropy, we obtain

$$S(N, V, E) = k \ln \Omega(N, V, E) = Nk \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} Nk - k \ln N!$$

We could also simplify the $\ln N!$ using Stirling's approximation, however, let us keep it as it is for now, since, as we remember from our past treatment of the microcanonical ensemble, this factor was included in the partition function in an *ad hoc* manner, in order to account for the indistinguishability of the particles. We will want to explore the effect of removing this term. Without it, the entropy is the purely *classical* entropy

$$S_{\rm cl}(N, V, E) = k \ln \Omega(N, V, E) = Nk \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} Nk$$

Other thermodynamic quantities can be easily obtained. For example, the temperature is

$$\frac{1}{kT} = \left(\frac{\partial \ln \Omega}{\partial E} \right) = \frac{3N}{2E}$$

or

$$E = \frac{3}{2} NkT$$

which is the result we obtained from our analysis of the classical virial theorem. The pressure is given by

$$P = kT \left(\frac{\partial \ln \Omega}{\partial V} \right) = \frac{N}{V}$$

or

$$PV = NkT$$

which is the famous *ideal gas law*. This is actually the equation of state of the ideal gas, as it expresses the pressure as a function of the volume and temperature. It can also be written as

$$\frac{P}{kT} = \frac{N}{V} = \rho$$

where ρ is the constant density of the gas.

One often expresses the equation of state graphically. For the ideal gas, if we plot P vs. V, for different values of T, we obtain the following plot:

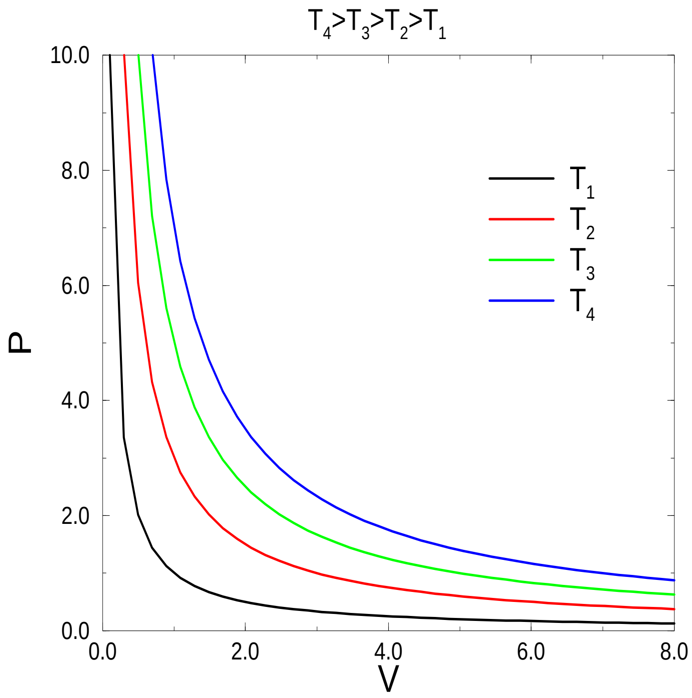


FIG. 1.

The different curves shown are called the *isotherms*, since they represent P vs. V for fixed temperature. The heat capacity of the ideal gas follows from the expression for the energy

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2}Nk$$

From our previous analysis of the virial theorem, we can conclude that each kinetic mode contributes $k/2$ to the heat capacity.

B. Relation to thermodynamic entropy

In thermodynamics, the change in entropy in a reversible process which transforms the system from state 1 to state 2 is

$$\Delta S = \int_1^2 \frac{dQ_{\rm rev}}{T}$$

where $dQ_{\rm rev}$ is the heat absorbed in the process. We can now ask if the entropy obtained starting from the microscopic description agrees with the standard thermodynamic definition. We will consider two types of processes as described below:

I. **Isothermal expansion/compression of the system from volume, V_1 to V_2.** In an isothermal process, the temperature, T, does not change. Thus, the entropy relation can be integrated immediately to yield

$$\Delta S = \frac{1}{T}\int_1^2 dQ_{\rm rev} = \frac{\Delta Q_{\rm rev}}{T}$$

where $\Delta Q_{\rm rev}$ is the heat absorbed as the state changes from 1 to 2. Now, from the first law of thermodynamics, the change in total internal energy of the system is

$$\Delta E = \Delta Q_{\rm rev} + \Delta W_{\rm rev}$$

where $\Delta W_{\rm rev}$ is the work done on the system. Since, for the ideal gas,

$$E = \frac{3}{2}NkT$$

$$\Delta E = \frac{3}{2}Nk\Delta T$$

and $\Delta T = 0$, $\Delta E = 0$ and

$$\Delta Q_{\rm rev} = -\Delta W_{\rm rev}$$

The expansion/compression of the system gives rise to a change in pressure such that $dW_{\rm rev} = -P(V)dV$, where $P(V) = NkT/V$, is given by the equation of state (ideal gas law). Thus, the total work done on the system is

$$\Delta W_{\rm rev} = -\int_{V_1}^{V_2} \frac{NkT}{V}dV = -NkT\ln\frac{V_2}{V_1}$$

Thus,

$$\Delta Q_{\rm rev} = NkT\ln\frac{V_2}{V_1}$$

and

$$\Delta S = Nk\ln\frac{V_2}{V_1}$$

If we now use the statistical definition of entropy

$$S = Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3Nk}{2} - k\ln N!$$

the change in entropy is

$$\begin{aligned}\Delta S &= Nk\ln\left[\frac{V_2}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3Nk}{2} - k\ln N! \\ &\quad - Nk\ln\left[\frac{V_1}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3Nk}{2} - k\ln N! \\ &= Nk\ln(cV_2) - Nk\ln(cV_1) \\ &= Nk\ln\frac{V_2}{V_1}\end{aligned}$$

where $c = (1/h^3)(4\pi mE/3N)^{3/2}$. Thus, we see that the two agree exactly.

II. **Isochoric heating/cooling from temperature T_1 to T_2.** In an isochoric process, the volume remains constant. Hence,

$$\Delta W_{\rm rev} = 0$$

and, from the first law,

$$\Delta Q_{\rm rev} = \Delta E$$

$$dQ_{\rm rev} = dE$$

However, for the ideal gas

$$E = \frac{3}{2}NkT$$

$$dE = \frac{3}{2}NkdT$$

$$E_1 = \frac{3}{2}NkT_1$$

$$E_2 = \frac{3}{2}NkT_2$$

$$\frac{E_2}{E_1} = \frac{T_2}{T_1}$$

Thus, the change in entropy is

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ_{\rm rev}}{T} = \int_{T_1}^{T_2} \frac{3}{2}Nk\frac{dT}{T} = \frac{3}{2}Nk\ln\frac{T_2}{T_1}$$

From the statistical definition:

$$\begin{aligned}
\Delta S &= Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi m E_2}{3N}\right)^{3/2}\right] + \frac{3Nk}{2} - k\ln N! \\
&- Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi m E_1}{3N}\right)^{3/2}\right] + \frac{3Nk}{2} - k\ln N! \\
&= Nk\ln\left(aE_2^{3/2}\right) - Nk\ln\left(aE_1^{3/2}\right) \\
&= Nk\ln\left(\frac{E_2}{E_1}\right)^{3/2} \\
&= \frac{3}{2}Nk\ln\frac{E_2}{E_1} \\
&= \frac{3}{2}Nk\ln\frac{T_2}{T_1}
\end{aligned}$$

which agrees exactly with the thermodynamic entropy change.

These two examples illustrate that the statistical approach agrees exactly with the standard thermodynamic definition of entropy.

C. Canonical ensemble treatment

The canonical partition function for the ideal gas is much easier to evaluate than the microcanonical partition function. Recall the expression for the canonical partition function $Q(N,V,T)$:

$$Q(N,V,T) = \frac{1}{N!h^{3N}}\int d^N\mathbf{p}\; d^N\mathbf{r}\; e^{-\beta\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}}$$

Note that this can be expressed as

$$Q(N,V,T) = \frac{1}{N!h^{3N}} V^N \left[\int d\mathbf{p} e^{-\beta \mathbf{p}^2/2m}\right]^N$$

since the Hamiltonian is completely separable. Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!} \left[\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]^N$$

The expressions for the energy

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$$

and pressure

$$P = kT\left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)$$

gives rise to the results $E = 3NkT/2$ and $PV = NkT$ just as for the microcanonical ensemble. Note also that the entropy $S(N,V,T)$ given by

$$S = k \ln Q(N,V,T) + \frac{E}{T}$$

becomes

$$S(N,V,T) = Nk \ln\left[\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right] + \frac{3}{2}Nk - k\ln N!$$

which reduces to the microcanonical expression exactly if we use the fact that $\beta = 3N/2E$:

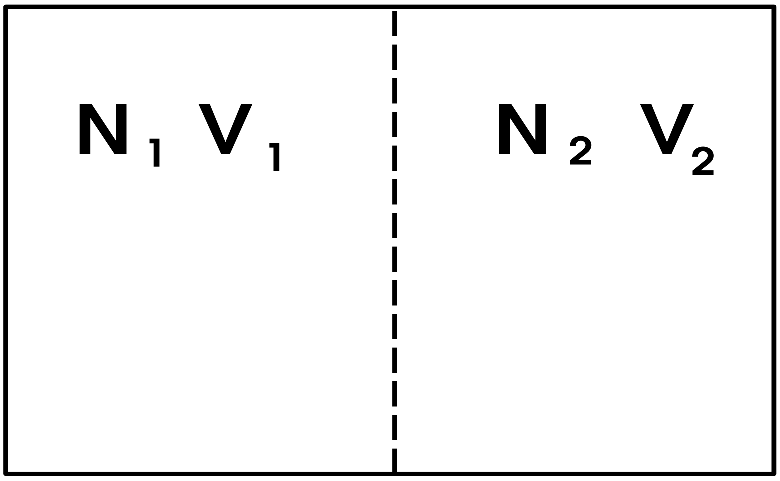
$$S(N,V,E) = k\ln \Omega(N,V,E) = Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2}Nk - k\ln N!$$

Thus, the canonical and microcanonical ensembles gives rise to exactly the same thermodynamics!! Let us now look more carefully at the expression for the entropy.

D. The Gibbs paradox

Consider an ideal gas of N particles in a container with a volume V. A partition separates the container into two sections with volumes V_1 and V_2, respectively, such that $V_1 + V_2 = V$. Also, there are N_1 particles in the volume V_1 and N_2 particles in the volume V_2. It is assumed that the number density is the same throughout the system

$$\rho = \frac{N_1}{V_1} = \frac{N_2}{V_2}$$



$$N_1 + N_2 = N$$

$$V_1 + V_2 = V$$

FIG. 2.

If the partition is now removed, what should happen to the total entropy? Since the particles are identical, the total entropy should not increase as the partition is removed because the two states cannot be differentiated due to the indistinguishability of the particles. Let us analyze this thought experiment using the classical expression entropy derived above (i.e., we leave off the $\ln N!$ term).

The entropies S_1 and S_2 before the partition is removed are

$$\begin{aligned} S_1 &\sim N_1 k \ln V_1 + \frac{3}{2} N_1 k \\ S_2 &\sim N_2 k \ln V_2 + \frac{3}{2} N_2 k \end{aligned}$$

and the total entropy is $S = S_1 + S_2$.

After the partition is removed, the total entropy is

$$S \sim (N_1 + N_2) k \ln(V_1 + V_2) + \frac{3}{2}(N_1 + N_2) k$$

Thus, the difference $\Delta S = S_{\text{after}} - S_{\text{before}}$ is

$$\begin{aligned} \Delta S &= (N_1 + N_2) k \ln(V_1 + V_2) - N_1 k \ln V_1 - N_2 k \ln V_2 \\ &= N_1 k \ln(V/V_1) + N_2 k \ln(V/V_2) > 0 \end{aligned}$$

This contradicts our predicted result that $\Delta S = 0$. Therefore, the classical expression must not be quite right.

Let us now restore the $\ln N!$. Using the Stirling approximation $\ln N! = N \ln N - N$, the entropy can be written as

$$S = Nk \left[\frac{V}{Nh^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right] + \frac{5}{2} Nk$$

which is known as the *Sackur-Tetrode* equation. Using this expression for the entropy, the difference now becomes

$$\Delta S = (N_1+N_2)k\ln\left(\frac{V_1+V_2}{N_1+N_2}\right) - N_1 k\ln(V_1/N_1) - N_2 k\ln(V_2/N_2)$$
$$= N_1 k\ln(V/V_1) + N_2 k\ln(V/V_2) - N_1 k\ln(N/N_1) - N_2 k\ln(N/N_2)$$
$$= N_1 k\ln\left(\frac{V}{N}\frac{N_1}{V_1}\right) + N_2 k\ln\left(\frac{V}{N}\frac{N_2}{V_2}\right)$$

However, since the density $\rho = N_1/V_1 = N_2/V_2 = N/V$ is constant, the terms appearing in the log are all 1 and, therefore, vanish. Hence, the change in entropy, $\Delta S = 0$ as expected. Thus, it seems that the $1/N!$ term is absolutely necessary to resolve the paradox. This means that only a correct quantum mechanical treatment of the ideal gas gives rise to a consistent entropy.

E. Isothermal-isobaric ensemble

Finally, let us look at the ideal gas in the isothermal-isobaric ensemble. The partition function is given by

$$\Delta(N,P,T) = \frac{1}{V_0}\int_0^\infty dV e^{-\beta PV} Q(N,V,T)$$
$$= \left[\frac{2\pi m}{\beta}\right]^{3N/2} \frac{1}{V_0 N! h^{3N}} \int_0^\infty dV e^{-\beta PV} V^N$$

We change variables to

$$v = \beta PV$$

so that

$$\Delta(N,P,T) = \left[\frac{2\pi m}{\beta}\right]^{3N/2} \frac{1}{V_0 N! h^{3N}} \frac{1}{(\beta P)^{N+1}} \int_0^\infty dv e^{-v} v^N$$
$$= \left[\frac{1}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{1}{\beta P}\right]^N \frac{1}{\beta P V_0}$$

The enthalpy is given by

$$\bar{H} = -\frac{\partial}{\partial\beta}\ln\Delta(N,P,T)$$

which, for the ideal gas, becomes

$$\bar{H} = \frac{3N}{2}kT + (N+1)kT = \frac{5N+1}{2}kT$$

But recall that the enthalpy is $\bar{H} = E + P\langle V\rangle$, where E is the average energy. Since $E = 3NkT/2$, we have

$$P\langle V\rangle = (N+1)kT$$

This result can also be derived by considering the average volume, given by

$$\langle V\rangle = -kT\left(\frac{\partial \ln\Delta}{\partial P}\right) = \frac{N+1}{P}kT$$

But recall the work virial theorem, which states that

$$P\langle V\rangle = \langle P_{\rm int} V\rangle + kT$$

where $P_{\rm int}$ is the instantaneous internal pressure obtained from $P_{\rm int} = -\partial H/\partial V$. Thus, the appropriate form of the ideal gas law is

$$\langle P_{\rm int} V\rangle = NkT$$