

**Physics 112**  
**The “Classical” Ideal Gas**

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We will obtain the equation of state and other properties, such as energy and entropy, of the classical ideal gas. We will start with quantum statistical mechanics, and take the classical limit, since this avoids certain ambiguities. Furthermore, our result for the entropy will involve  $\hbar$  and so what we are doing is not entirely a classical theory.

A state of an ideal gas is identified by the “occupation numbers”,  $n_k$ , of the single particle states  $k$  with energy  $\epsilon_k$ . In particular, the total number of particles  $N$  and energy  $E$  are given by

$$N = \sum_k n_k, \tag{1}$$

$$E = \sum_k n_k \epsilon_k. \tag{2}$$

**We will use the Gibbs distribution, in which the number of particles is allowed to vary and, the results are expressed in terms of the chemical potential  $\mu$  rather than the mean number of particles  $N$ .**

The reason for this choice is that, as we shall now show, for non-interacting, identical particles, the grand partition of the whole system,  $\mathcal{Z}$ , *factorizes* into a product of grand partition functions for the single-particle states. The grand partition function is given by

$$\mathcal{Z} = \sum_{\{n_k\}} \exp[\beta(N\mu - E)] = \sum_{\{n_k\}} \exp\left[\beta \sum_k (\mu - \epsilon_k) n_k\right] = \sum_{\{n_k\}} \prod_k \left[e^{\beta(\mu - \epsilon_k)n_k}\right] = \prod_k \left[\sum_{n_k} e^{\beta(\mu - \epsilon_k)n_k}\right], \tag{3}$$

where  $\mu$  is the chemical potential, and  $\{n_k\}$  refers to the *set* of all allowed values of the occupation numbers  $n_k$ . To get the third expression we used that the exponential of a sum is the product of exponentials, and to get the fourth expression we used that each exponential only depends on *one* of the  $n_k$ . The summations over the different  $n_k$  can be done *independently* because there is no constraint on the total number  $N = \sum_k n_k$  in the Gibbs distribution. Hence, as stated above, the grand partition of the whole system,  $\mathcal{Z}$ , *factorizes* into a product of grand partition functions for the single-particle states, i.e.

$$\boxed{\mathcal{Z} = \prod_k \mathcal{Z}_k}, \tag{4}$$

where

$$z_k = \sum_{n_k} e^{n_k \beta (\mu - \epsilon_k)}. \quad (5)$$

The factorization of the grand partition function for non-interacting particles is the reason why we use the Gibbs distribution (also known as the “grand canonical ensemble”) for quantum, indistinguishable particles.

For fermions,  $n_k$  in the sum in Eq. (5) only takes values 0 and 1, while for bosons  $n_k$  takes values from 0 to  $\infty$  and Eq. (5) gives a geometric series which is easy to sum. The result is

$$z_k = \begin{cases} 1 + \lambda e^{-\beta \epsilon_k}, & \text{fermions,} \\ (1 - \lambda e^{-\beta \epsilon_k})^{-1}, & \text{bosons,} \end{cases} \quad (6)$$

where

$$\lambda = e^{\beta \mu} \quad (7)$$

is called the “activity” (sometimes the word “fugacity” is also used).

As discussed in class, the classical limit is when the occupancy of any single-particle state is very much less than unity. This means that the statistical weight (i.e. the exponential factor in Eq. (5)) for  $n_k = 1$ , is much less than the statistical weight for  $n_k = 0$ , i.e.

$$\lambda e^{-\beta \epsilon_k} \ll 1. \quad (8)$$

In this case, we work to first order in  $\lambda e^{-\beta \epsilon_k}$ , so the difference between bosons and fermions disappears and for both we get

$$z_k = 1 + \lambda e^{-\beta \epsilon_k}, \quad (9)$$

$$\ln z_k = \lambda e^{-\beta \epsilon_k}. \quad (10)$$

where we used  $\ln(1+x) = x + \dots$  for small  $x$ . Taking the log of Eq. (4), and using Eq. (10), gives

$$\ln \mathcal{Z} = \sum_k \ln z_k = \lambda \sum_k e^{-\beta \epsilon_k}. \quad (11)$$

As shown in class, the grand potential  $\Omega$  is related to  $\mathcal{Z}$  by

$$\Omega (= -PV) = -k_B T \ln \mathcal{Z}, \quad (12)$$

where  $P$  is the pressure, and combining this with Eq. (11) gives

$$\boxed{\Omega = -k_B T \lambda \mathcal{Z}^{(1)}} \quad (13)$$

where  $z^{(1)}$  is the (canonical) partition function for a single particle:

$$\boxed{z^{(1)} = \sum_k e^{-\beta\epsilon_k}.} \quad (14)$$

To carry out the sum in Eq. (14) we use the result for the single particle density of states discussed earlier in class, and convert the sum over states to an integral over  $\epsilon$ . Considering spin-0 (in the class we will discuss the trivial changes that come from a non-zero spin) the density of states is given by

$$\rho(\epsilon) = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}. \quad (15)$$

Hence  $z^{(1)}$  in Eq. (14) is given by

$$z^{(1)} = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon = \frac{V}{4\pi^2} \left( \frac{2mk_B T}{\hbar^2} \right)^{3/2} \int_0^\infty x^{1/2} e^{-x} dx. \quad (16)$$

As discussed in Math. Methods classes, the integral is  $\Gamma(3/2) = \sqrt{\pi}/2$ , and so

$$z^{(1)} = V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = \frac{V}{V_Q}, \quad (17)$$

where

$$\boxed{V_Q = \left( \frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}} \quad (18)$$

is the “quantum volume” already discussed in class. Hence, from Eqs. (11), (14) and (17)

$$\ln \mathcal{Z} = \lambda \frac{V}{V_Q}, \quad (19)$$

so

$$\boxed{\mathcal{Z} = e^{\lambda V/V_Q}.} \quad (20)$$

Using Eq. (12), then gives the desired expression for the grand potential  $\Omega$

$$\boxed{\Omega(T, V, \mu) = -k_B T \lambda \frac{V}{V_Q},} \quad (21)$$

(remember  $\lambda = e^{\beta\mu}$ ).

Since we are using the Gibbs distribution with a variable number of particles, we have calculated the grand potential, which is expressed in terms of the chemical potential rather than the number of particles. However, in practice, experiments are carried out with a given number of particles, not a given value of the chemical potential.

Hence we have to convert expressions like Eq. (21), written in terms of  $\mu$ , to ones written in terms of the mean number of particles  $N$ .

This is a general problem with the Gibbs distribution. Fortunately this conversion is very easy here for the *classical* ideal gas because we will find a *closed form* expression for  $\mu(T)$  as a function of  $n$ , Eq. (24) below. It will be less easy when we consider *quantum* ideal gases. To obtain the result for  $\mu(T)$ , recall that the *mean* number of particles is given by

$$\langle N \rangle = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V}, \quad (22)$$

which, according to Eq. (21), yields

$$\langle N \rangle = e^{\beta \mu} \frac{V}{V_Q}, \quad (23)$$

(remember that  $\lambda = e^{\beta \mu}$ ). Although fluctuations in the number of particles are allowed in the Gibbs distribution, their relative size is small (of order  $N^{1/2}$ ). Hence, for conciseness of notation, from now on, we will omit the brackets and denote the mean number of particles simply by  $N$ .

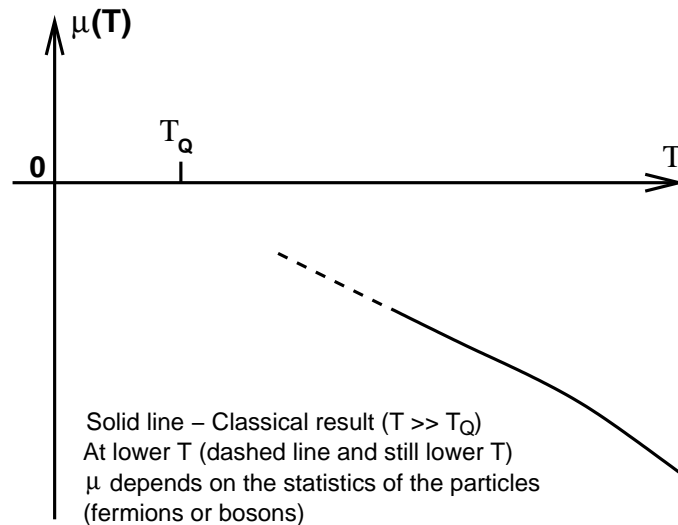
Eq. (23) gives the desired expression for the chemical potential:

$$\mu(T) = k_B T \ln(n V_Q) = -k_B T \ln \left[ \frac{1}{n} \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \right] = -\frac{3}{2} k_B T \ln \left( \frac{T}{T_Q} \right) \quad (24)$$

where  $n = N/V$  is the particle density, and

$$T_Q = \frac{2\pi \hbar^2}{m k_B} n^{2/3},$$

is a temperature below which quantum effects are important. Since the condition to be in the classical regime is  $n V_Q \ll 1$ , see Eq. (25) below, (or equivalently  $T \gg T_Q$ ), it follows that  **$\mu$  must be negative**. Furthermore, Eq. (24) shows that  **$\mu$  gets more negative with increasing  $T$** . The variation of  $\mu(T)$  with  $T$  in the classical regime is sketched in the figure below.



**To describe a classical ideal gas with a FIXED density of particles  $n$  using the Gibbs distribution, we have to let  $\mu(T)$  vary with  $T$  according to Eq. (24).**

The condition that we are in the classical regime, i.e. the occupancy is much less than unity even for the lowest single particle level which we take to be at zero energy, is  $\lambda \ll 1$ , see Eq. (8). From Eq. (23), this is equivalent to

$$\boxed{nV_Q \ll 1 \quad (\text{condition to be in the classical regime}).} \quad (25)$$

As discussed in class this corresponds to the mean separation between particles ( $n^{-1/3}$ ) being much greater than the thermal de Broglie wavelength (the de Broglie wavelength of a particle whose energy is  $k_B T$ ). Equivalently, from Eq. (24), we can write

$$\boxed{T \gg T_Q \quad (\text{condition to be in the classical regime}),} \quad (26)$$

showing that classical regime is a *high temperature* regime.

Eq. (23) can be substituted into Eq. (21), and noting that  $\Omega = -PV$ , we get

$$\boxed{PV = Nk_B T,} \quad (27)$$

the famous ideal gas law.

The (Helmholtz) free energy is  $F = \Omega + \mu N$  which, using Eqs. (21) and (23) and recalling that  $F$  should be expressed in terms of  $N$  not  $\mu$ , is given by  $F = -k_B T N + \mu N$  or

$$\boxed{F(T, V, N) = Nk_B T [\ln(nV_Q) - 1] .} \quad (28)$$

**Now that we have determined  $F$ , it is more convenient to use it, rather than  $\Omega$ , to determine other quantities, because  $F$  is expressed in terms of  $N$ , which is specified and kept fixed, whereas  $\Omega$  is expressed in terms of  $\mu$ , which varies with  $T$  and  $V$  (in such a way as to keep  $N$  constant).**

For example, the entropy is given by

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V, N} = Nk_B \left[ 1 - \ln(nV_Q) - T \frac{\partial}{\partial T} \ln V_Q \right] . \quad (29)$$

Since  $V_Q \propto T^{-3/2}$ ,  $(\partial/\partial T) \ln V_Q = -3/(2T)$ . Hence we have

$$\boxed{S = Nk_B \left[ \frac{5}{2} - \ln(nV_Q) \right] ,} \quad (30)$$

a well known result, which is called the Sackur-Tetrode equation. The entropy is proportional to the number of particles  $N$  if the density  $n$  is kept constant, i.e. the entropy is *extensive*. Note too that although we have taken the classical limit, the expression for the entropy involves  $\hbar$ . The reason is that only in quantum mechanics can one define precisely the sum over states and hence give an *absolute* definition for the entropy (rather than just entropy *differences*). More discussion of this, along with a discussion of experimental verification of Eq. (30) will be given in class.

The energy can be obtained from

$$\begin{aligned} U &= \left( \frac{\partial(\beta F)}{\partial\beta} \right)_{N,V} \\ &= N \frac{\partial}{\partial\beta} [\ln(nVQ) - 1]_{N,V}. \end{aligned} \quad (31)$$

The only quantity which depends on  $\beta$  is  $V_Q$ , and  $V_Q \propto \beta^{3/2}$ , so

$$\boxed{U = \frac{3}{2} N k_B T.} \quad (32)$$

This is an example of a well known result of classical statistical mechanics, called the “equipartition theorem”. This states that every quadratic term in the microscopic expression for the energy contributes  $(1/2)k_B T$  to the average energy. Here we have  $N$  atoms for each of which the energy is

$$\frac{1}{2} m (v_x^2 + v_y^2 + v_z^2), \quad (33)$$

which has 3 quadratic terms. Hence the total average energy is  $(3/2)Nk_B T$ , in agreement with Eq. (32)

The specific heat at constant volume,  $C_V$ , can be obtained from  $C_V = (\partial U / \partial T)_{N,V}$  or equivalently from  $C_V = (T \partial S / \partial T)_{N,V}$ , and the result is

$$\boxed{C_V = \frac{3}{2} N k_B.} \quad (34)$$