

## Lecture 11

**Objectives**

1. Be able to derive the thermodynamic total energy from the partition function.
2. Be able to derive the classical partition function.
  - (a) Identify when energy levels can be treated classically.
  - (b) List the assumptions involved in the classical partition function.
  - (c) Account for indistinguishability.
  - (d) Incorporate the Heisenberg uncertainty principle.
3. Be able to derive the semi-classical partition function.
  - (a) List the assumptions.
  - (b) Differentiate between internal and center of mass degrees of freedom.
  - (c) Formulate the configuration integral.

**Thermodynamic Properties**

1. Canonical Ensemble.

Recall that the probability of observing some state  $i$  with energy  $E_i$  is given by

$$\mathcal{P}_i = \frac{\exp(-\beta E_i)}{Q(N, V, T)}$$

where  $Q(N, V, T)$  is the statistical mechanical partition function for the canonical ensemble is given by

$$Q(N, V, T) = \sum_{i=1}^{\infty} e^{-\beta E_i}$$

where  $E_i$  is the energy of the  $i$ th quantum state. Recall that the definition of a probability means that we can calculate average, or expectation values from

$$\langle J \rangle = \sum_j \mathcal{P}_j J_j = \frac{\sum_j \exp(-\beta E_j) J_j}{Q}$$

Our goal is to find an expression for  $\langle E \rangle$  in terms of  $Q$  and its derivatives. We know that

$$\langle E \rangle = \frac{\sum_j E_j \exp(-\beta E_j)}{Q}.$$

How can we get

$$\sum_j E_j \exp(-\beta E_j)$$

in terms of a derivative of  $Q$ ? Any ideas?

$$\left(\frac{\partial Q}{\partial \beta}\right) = - \sum_j E_j \exp(-\beta E_j)$$

Then the full expression for  $\langle E \rangle$  is

$$\langle E \rangle = \frac{-\left(\frac{\partial Q}{\partial \beta}\right)}{Q} = - \left(\frac{\partial \ln Q}{\partial \beta}\right) = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

Recall from the text that the primary connection formula is

$$A = -kT \ln Q$$

You can use the thermodynamic identities to obtain the other thermodynamic variables as shown in Table 2.1 of the text.

## 2. Grand Canonical Ensemble

$$\Xi(\mu, V, T) = \sum_N \sum_j \exp(-\beta E_j) \exp(\beta \mu N)$$

The primary connection formula is

$$P = \frac{kT}{V} \ln \Xi$$

Other properties are given in Table 2.2 of the text.

## Classical and Semi-Classical Partition Functions

### 1. The Classical Partition Function:

Recall that

$$\mathcal{P}_i = \frac{\exp(-\beta E_i)}{Q(N, V, T)}$$

where  $Q(N, V, T)$  is the statistical mechanical partition function for the canonical ensemble is given by

$$Q(N, V, T) = \sum_{i=1}^{\infty} e^{-\beta E_i}$$

where  $E_i$  is the energy of the  $i$ th quantum level. This is an exceedingly difficult problem to solve because we would need to find all the energy eigenvalues for a system of Avogadro's number of molecules.

We want to replace the sum over quantum states by an integral over all possible classical states. In general, when can we replace a sum with an integral?

If the energy levels are very close together, i.e., if  $E_{i+1} - E_i \gg kT$  then the system no longer looks like a quantum system, but appears classical. That means that there is a continuous distribution of energies. This is usually true for translational energies, i.e., kinetic energy.

Let us derive the classical partition function for a monatomic ideal gas. For an ideal gas there are no forces or potential energy between the particles, so we write the Hamiltonian as the kinetic energy of  $N$  particles, each with mass  $m$ .

$$H = \frac{\vec{p}^2}{2m} = \sum_{i=1}^N \frac{p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2}{2m} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

If we just replace the sum by integrals over the momenta and coordinates then we get

$$Q_{\text{cl}} = \int \dots \int e^{-\beta H} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}.$$

There are two things wrong with the above equation.

- (a) The atoms are indistinguishable.
- (b) We cannot specify the momentum and position without violating the Heisenberg uncertainty principle.

We account for indistinguishability by dividing by  $N!$ . Why? There are  $N!$  ways of arranging  $N$  atoms at  $N$  sites. If we count each one of those configurations as distinct then we would over-count the partition function by a factor of  $N!$ .

The Heisenberg uncertainty principle states that

$$\delta p \delta q \geq h.$$

This means that each  $dpdq$  pair in the integral contributes a factor of  $h$  to the integral which must be divided out. Since there are  $3N$   $dpdq$  pairs this gives a factor of  $h^{3N}$ . The correct expression is then

$$Q_{\text{cl}} = \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta H} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}$$

We can integrate over all the  $qs$  to get

$$Q_{\text{cl}} = \frac{1}{N! h^{3N}} \left[ \int_v dq \right]^{3N} \left[ \int \dots \int \exp\left(\frac{-\sum p_i^2}{2mkT}\right) dp_1 \dots dp_{3N} \right]$$

$$Q_{\text{cl}} = \frac{V^N}{N! h^{3N}} \left[ \int_{-\infty}^{\infty} \exp\left(\frac{-p^2}{2mkT}\right) dp \right]^{3N}$$

From Appendix 2 of the book

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

so

$$Q_{\text{cl}} = \frac{V^N}{N!h^{3N}} (2\pi mkT)^{3N/2} = \frac{V^N}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2}$$

We define the thermal de Broglie wave length as

$$\Lambda = \left( \frac{h^2}{2\pi mkT} \right)^{1/2}$$

so

$$Q_{\text{cl}} = \frac{V^N}{N!\Lambda^{3N}}$$

Now calculate the equation of state from the thermodynamic connection formula

$$P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} = kT \left( \frac{\partial \ln \left( \frac{V^N}{N!\Lambda^{3N}} \right)}{\partial V} \right)_{N,T}$$

$$P = kT \left( \frac{\partial [\ln V^N - \ln N! - \ln \Lambda^{3N}] +}{\partial V} \right)_{N,T} = kT \left( \frac{\partial \ln V^N}{\partial V} \right)_{N,T}$$

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

## 2. Semi-classical Partition Function:

The translational part of the partition function can usually always be treated classically because the energy levels are so close together. This suggests that we derive a semi-classical partition function where we treat some variables classically and some quantum mechanically. We **assume** that the Hamiltonian operator can be separated into two parts:

$$\hat{H} = \hat{H}_{\text{cm}} + \hat{H}_{\text{int}}$$

where cm stands for center of mass (translation and intermolecular interactions) and int stands for internal or intramolecular (vibrations, rotations, etc.). hence

$$Q = \sum_i \sum_j \exp \left[ -\beta(E_i^{\text{cm}} + E_j^{\text{int}}) \right] = \sum_i \exp(-\beta E_i^{\text{cm}}) \sum_j \exp(-\beta E_j^{\text{int}}) = Q_{\text{cm}} Q_{\text{int}}$$

We have implicitly assumed that the center of mass and intramolecular wave functions are independent. This is not true in general, except for the case of the ideal gas.  $H_{\text{cm}}$  is given by

$$H_{\text{cm}} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\vec{q}^N)$$

where  $\vec{q}^N$  is shorthand notation for  $\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N$ . We next assume that  $Q_{\text{cm}}$  can be evaluated classically

$$Q_{\text{cm}} = \frac{V^N}{N!h^{3N}} \left[ \int_{-\infty}^{\infty} \exp\left(\frac{-p^2}{2mkT}\right) dp \right]^{3N} \int \dots \int \exp[-\beta U(\vec{q}^N)] d\vec{q}^N$$

The first integral can be done as before. The second is called the configuration integral and we define  $Z$  as the configurational partition function. So,

$$Q = \frac{ZQ_{\text{int}}}{N!\Lambda^{3N}}$$

$$Z = \int \dots \int \exp[-\beta U(\vec{q}^N)] d\vec{q}^N$$

Note that  $Z$  contains all the intermolecular interactions, but for an ideal gas ( $U = 0$ )  $Z \neq 0$ . What is it?

Note that  $Z$  is the only density dependent part of the factored semi-classical partition function, since  $Q_{\text{int}}^{\text{ideal gas}} = f(T)$ .

## Statistical Mechanics of Ideal Gases

1. Review the semi-classical partition function,

$$Q = \frac{ZQ_{\text{int}}}{\Lambda^{3N}N!}$$

Assumptions:

- (a)  $Q$  is separable into two independent parts, one having center of mass degrees of freedom,  $Q_{\text{cm}}$ , and one involving only the intramolecular degrees of freedom,  $Q_{\text{int}}$ .

$$H = H_{\text{cm}} + H_{\text{int}} \Rightarrow Q = Q_{\text{cm}}Q_{\text{int}}$$

- (b)  $Q_{\text{cm}}$  can be treated classically

$$H_{\text{cm}} = \sum_{i=1}^N \frac{p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2}{2m} + U(\vec{r}^N)$$

$$Q_{\text{cm}} = \frac{1}{N!h^{3N}} \int \dots \int e^{-\beta H} d\vec{p}^N d\vec{r}^N$$

$$Q_{\text{cm}} = \frac{1}{N!h^{3N}} \int \dots \int e^{-\beta U(\vec{r}^N)} d\vec{r}^N \int \dots \int \exp\left[-\frac{\sum p_i^2}{2mkT}\right] dp^{3N}$$

$$Q_{\text{cm}} = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} Z$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

$$Z = \int \dots \int e^{-\beta U(\vec{r}^N)} d\vec{r}^N$$

2. For an ideal gas  $U(r) = 0$  so,

$$Z = \left[ \int dx \right]^{3N} = V^N$$

$$Q = \frac{Q_{\text{int}} V^N}{\Lambda^{3N} N!}$$

The remainder of the class will be devoted to finding the intramolecular partition function, i.e., the partition function for internal degrees of freedom, for an ideal gas.

3. Energy level spacings. We identify five energy states: nuclear-spin states, electronic states, vibrational states, rotational states, and translational states. Let  $\Delta\epsilon$  be the spacing between energy levels in each of these states. In general, the sequence of level spacings go as:  $\Delta\epsilon_n > \Delta\epsilon_e > \Delta\epsilon_v > \Delta\epsilon_r > \Delta\epsilon_t$ . The energy level spacings are the determining factor in treating the system classically or quantally. If  $\Delta\epsilon \gg kT$  then the system can be treated classically.



4. A rigorous calculation of  $Q_{\text{int}}$  would be very difficult because the internal modes are coupled to each other. However, this coupling is often infinitesimally small. Hence, we can make reasonable approximations about the internal modes which decouple the problem and allow relatively simple calculations.
5. One such approximation is the Born-Oppenheimer approximation, which assumes that the electron movement is rapid relative to the nuclear movement. In other words, the electrons move adiabatically with respect to the nuclei. This separates the nuclear and electronic energy levels. In what we do for the rest of the term we will assume that all other internal modes are also separable. It is important to recognize that this is not always a good approximation.

In particular, the vibrational and rotational degrees of freedom can be closely coupled. The separation of rotational and vibrational modes is called the rigid rotor approximation. Any calculations we do without accounting for this coupling will be in error. Sometimes this error can be a substantial fraction of the final answer.

6. We *assume* that all internal modes are separable so that the total energy is given by a simple sum of all internal energies:

$$\epsilon_{\text{int}} = \epsilon_n + \epsilon_e + \epsilon_v + \epsilon_r$$

Hence, the total internal Hamiltonian is given by

$$H_{\text{int}} = \sum \epsilon_n + \sum \epsilon_e + \sum \epsilon_v + \sum \epsilon_r$$

Now define a *molecular* partition function

$$Q = \frac{q^N}{N!}$$

where  $q$  is the partition function for an isolated molecule. Then,

$$q_{\text{int}} = q_n q_e q_v q_r$$

This gives

$$Q = \frac{V^N}{\Lambda^{3N} N!} (q_n q_e q_v q_r)^N$$

$$\ln Q = N \ln V - 3N \ln \Lambda - \ln N! + N \ln q_n + n \ln q_e + N \ln q_v + N \ln q_r$$

This means that many thermodynamic properties can be written as

$$J = J_t + \sum_{i \in \{n, e, v, r\}} J_i$$

We get this by recalling the relationship between thermodynamic properties and  $\ln Q$ . See Table 2.1

7. Translational partition function:

It is traditional to group the  $V$  and  $N!$  terms with the translational partition function,

$$Q_t = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N$$