

CC - 14: Statistical Mechanics

B.Sc Physics (Semester-6)

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Macrostate and Microstate

A system is characterized by macroscopic parameters such as total no of molecules inside it, total energy or total volume etc. These parameters are called macroscopic parameters of the system. The macroscopic state or macrostate of a system is specified by quoting the macroscopic parameters and energy of the system.

Macrostate and Microstate

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The microscopic state or the microstate of a system of particles is specified by writing the state such as position, momentum, orientation of individual particles.

Macrostate and Microstate

4 Heads	HHHH
3 Heads & 1 Tail	HHHT
	HHTH
	HTHH
	THHH
2 Heads & 2 Tails	HHTT
	HTHT
	THTH
	HTTH
	THHT
	TTHH
1 Head & 3 Tails	TTTH
	TTHT
	THTT
	HTTT
4 Tails	TTTT

Figure: Left column is macrostates and right side is microstates

Ensemble

Large Collection of identical non-interacting systems satisfying same microscopic conditions are called ensemble or statistical ensemble. Macroscopically we may not distinguish two gases existing in different states, but those gases may be microscopically different.

Micro Canonical Ensemble

Consider, completely isolated system. Microcanonical ensemble is a collection of identical systems which has fixed volume, fixed total energy and fixed total number of particles. Exchange of energy is not possible. Exchange of number of particle is not possible. We define microcanonical ensemble as

$$\begin{aligned}\rho(p, q) &= \text{constant, for } E < E_q < E + \Delta E \\ &= 0, \text{ otherwise}\end{aligned}\tag{1}$$

Ensemble

Canonical Ensemble

Only exchange of energy is possible from the system to surroundings. But number of particle in each system is fixed. The probability that from such collection of systems, a system is in i th state, is

$$P_i = \frac{e^{-\beta E_i}}{\sum_n e^{-\beta E_n}} \quad (2)$$

here $\beta = \frac{1}{k_B T}$

Ensemble

Grand Canonical Ensemble

In an ensemble where walls of the subsystems are such that, both energy and no of particles are exchanged between subsystems to bring the subsystem in equilibrium condition or most favourable condition. This ensemble is called Grand Canonical Distribution.

The probability that n_1 systems are in state 1 with energy E_1 , n_2 systems are in state 2 with energy E_2 , etc is

$$W = \frac{1}{C} \frac{N!}{n_1! n_2! \dots} \quad (3)$$

here N is total number of systems in the ensemble. N_1 be the number of particles in each of n_1 systems. N_2 be the number of particles in each n_2 systems.. etc

Ensemble

Grand Canonical Ensemble

Constraint equations

$$\sum_i n_i = N; \quad \frac{\sum_i n_i \langle E_i \rangle}{N} = \langle E \rangle; \quad \frac{\sum_i n_i \langle N_i \rangle}{N} = \langle N \rangle \quad (4)$$

Number of particles in s^{th} system:

$$n_s = N \frac{e^{-\beta E_s - \alpha N_s}}{\sum_k e^{-\beta E_k - \alpha N_k}} \quad (5)$$

The quantity Partition function for grand canonical distribution is defined as

$$Z = \sum_k e^{-\beta E_k - \alpha N_k} \quad (6)$$

Ensemble

Grand Canonical Ensemble

The quantity Partition function for grand canonical distribution is defined as

$$Z = \sum_k e^{-\beta E_k - \alpha N_k} \quad (7)$$

The quantity fugacity (in chemistry it is absolute fugacity) is defined as

$$z = e^{-\beta\mu} \quad (8)$$

Maxwell Boltzmann Distribution law

Consider a system composed of N distinguishable particles (thus classical particles!) in a volume V , n_1 of which are with energy state ϵ_1 , n_2 with ϵ_2 etc. We have k such groups. If the particles are non interacting, there are two constraints, namely total energy and total number of particles

$$E = \sum_i^k n_i \epsilon_i \quad N = \sum_i^k n_i \quad (9)$$

N particles can be arranged in $N!$ ways. Let us consider again that n_1 particles can be distributed in g_1 levels in many different ways among themselves, all having energy ϵ_1 . How many ways? First particle can be put in g_1 levels. And so the second particle can be put in g_1 levels also. etc. The arrangements among n_1 particles can be distributed in $n_1!$ ways, which does not create any new microstates Thus number of such possibilities

$$W_1 = \frac{g_1^{n_1}}{n_1!} \quad (10)$$

Maxwell Boltzmann Distribution law

For k such groups total number of microstates are

$$\Omega(g_i, n_i) = N! \times W_1 \times W_2 \cdots W_k = N! \prod_{i=1}^k \frac{(g_i)^{n_i}}{n_i!} \quad (11)$$

Now for most probable distribution we have to maximize Ω with respect to n_i . For this we take

$$\log \Omega = N \log N - N + \sum n_i \log g_i - \sum n_i \log n_i + \sum n_i \quad (12)$$

Variation of $\log \Omega$ must be zero. Thus

$$\delta(\log \Omega) = \sum (\log g_i - \log n_i) \delta n_i = 0 \quad (13)$$

Maxwell Boltzmann Distribution law

To include the two constraints mentioned above we introduce Lagrange undetermined multiplier α and β we

$$\sum [\log g_i - \log n_i - (\alpha + \beta\epsilon_i)] \delta n_i = 0 \quad (14)$$

$$n_i = g_i e^{-(\alpha + \beta\epsilon_i)} \quad (15)$$

Therefore the number of particles per state or average occupation number

$$f(\epsilon_i) = \frac{n_i}{g_i} = e^{-(\alpha + \beta\epsilon_i)} \quad (16)$$

This is Maxwell-Boltzmann Probability distribution function.

Partition function & Thermodynamic functions of an Ideal gas

Partition function is defined by

$$Z = \sum_{\{n\}} e^{-\beta\epsilon_n} \quad (17)$$

where the sum is over all possible states. the index n is not on number of particles, but on number of microstates. Let us write Z for exercise below..

Write the Z for 2 classical particles distributed in 2 energy states ϵ_1 & ϵ_2

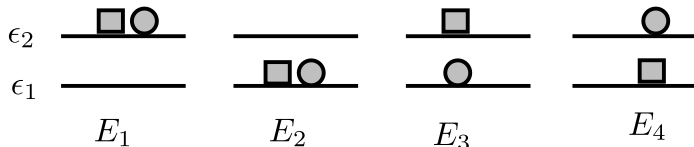


Figure: The partition function is $Z = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3} + e^{-\beta E_4}$, here each microstate has energies $E_1 = 2\epsilon_2$, $E_2 = 2\epsilon_1$, $E_3 = \epsilon_1 + \epsilon_2$ and $E_4 = \epsilon_1 + \epsilon_2$

Partition function & Thermodynamic functions of an Ideal gas

When you got your Z then

Formula we need in our daily life:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (18)$$

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \quad (19)$$

$$F = -Nk_B T \ln Z \quad (20)$$

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V,N}; \quad P = -\left(\frac{\partial F}{\partial V} \right)_{T,N}; \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad (21)$$

Chemical Potential

α is related to chemical potential (μ) as

$$\alpha = -\beta\mu \quad (22)$$

$$z = \text{fugacity} = e^{-\alpha} = e^{\mu/k_B T} \quad (23)$$

Classical Entropy Expression

$$S = k_B (\ln Z + \beta \langle E \rangle) \quad (24)$$

Partition function

$$Z = \int e^{-\beta E} \frac{dq_1 dq_2 \cdots dq_f dp_1 dp_2 \cdots dp_f}{h^f} \quad (25)$$

for N number of molecules. degree of freedom $f = 3N$. After doing the integration we get

$$Z = \frac{V^N}{h^{3N}} \left[\frac{2m\pi}{\beta} \right]^{3N/2} ; \quad \langle E \rangle = \frac{3}{2} N k_B T \quad (26)$$

$$S = N k_B \left[\ln V + \frac{3}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{2\pi m}{h^2}\right) + \frac{3}{2} \right] \quad (27)$$

Gibb's Paradox

Let us consider two same gas with volume V and number of particle N , separated by a card board. Total entropy is $S_i = Nk_B \ln V + Nk_B \ln V = 2Nk_B \ln V$. If we remove the separator, the same two gases mix and total volume $2V$ number of particle is $2N$. Thus final entropy is $S_f = 2Nk_B \ln(2V)$. So this mixing process, changes the entropy by $\Delta S = S_f - S_i = 2Nk_B \ln 2$. But mixing of same two gases by removing a separator between them is reversible process. So if we put back the separator, the entropy must not change. Change of entropy should be zero. This contradicts the formula above. This is known as Gibbs paradox.

The paradox is resolved by considering particles as indistinguishable. Thus for a classical gas, permutation of N particles in a given state cannot alter the state of gas. The correct counting is $\frac{1}{N!}$ fewer states.

Sackur Tetrode equation

$$Z = \frac{V^N}{N! h^{3N}} \left[\frac{2m\pi}{\beta} \right]^{3N/2} ; \quad \langle E \rangle = \frac{3}{2} N k_B T \quad (28)$$

$$S = N k_B \left[\ln(V/N) + \frac{3}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{2\pi m}{h^2}\right) + \frac{5}{2} \right] \quad (29)$$

This above entropy equation is called Sackur Tetrode equation. We can check for the above example,

$$\Delta S = 0$$

Law of Equipartition of Energy (with proof)

$$E = \alpha p_i^2 \quad (\text{no sum here}) \quad (30)$$

$$\langle \epsilon \rangle = \frac{\int E e^{\beta E} dq_1 dq_2 \cdots dq_f dp_1 dp_2 \cdots dp_f}{\int e^{\beta E} dq_1 dq_2 \cdots dq_f dp_1 dp_2 \cdots dp_f} = \frac{1}{2} k_B T \quad (31)$$

Solve the above integration in home work exercise / class..

Applications to Specific Heat and its Limitations

This is from Equipartition of energy theorem. The Hamiltonian can be written as

$$H = \frac{1}{2m} \sum_i p_i^2 + \frac{k}{2} \sum_i q_i^2 \quad (32)$$

Do the same integration as done before for finding average energy value and show

$$\langle E \rangle = 3k_B T \quad (33)$$

$$C_V = 3R \quad (34)$$

This is Dulong Petit law.

Thermodynamic Functions of a Two-Energy Levels System

Please attend class for this tutorial.

Find the expressions for P , $\langle E \rangle$, F , etc for two level problem. This is very important problem. Also try to solve the problem for three level problem.

Negative Temperature

Consider a two level system. And find average occupation number. Then find

$$\frac{\bar{n}_1}{\bar{n}_2} = \exp\left(\frac{\epsilon_2 - \epsilon_1}{k_B T}\right) \quad (35)$$

from above find, T and see that population inversion can cause negative temperature. This proves that for a two level system, population inversion can not happen.