Thermodynamics in Microcanonical Ensemble

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Abstract

In this article we find the thermodynamics of some large N particles systems and some small N particles classical systems using micro canonical ensemble. Small N particle systems are seldom done in textbooks, since statistical mechanics(SM) systems work for large N systems. We show that small N systems will help the students to get an insight about the phase space and also the computation of microstates.

Keywords: Micro canonical ensemble, phase space, entropy.

INTRODUCTION

In statistical mechanics we use ensemble method to find thermodynamic properties of a system (Huang, 2009; Pathria, 2016). Three types of ensembles- micro canonical(MCE), canonical(CE) and grand canonical ensemble (GCE) are used. Examples of finding thermodynamics of classical systems using MCE is very rare because of its inherent difficulties (Gross, 2001; Hill, 1986; Palma & Riveros, 2021; Park, Kim, & Yi, 2022; Rugh, 1997; Tobolsky, 1964). We in this article give some examples for finding the thermodynamics for large number(N) of particles and also for some small number of particle systems. MCE is a collection of systems with constant energy, constant number of particles and constant volume. For finding thermodynamics in MCE, we calculate the number of available states, Ω,in phase space for the particles to occupy in the system. From Ω,using the Boltzmann relation:

$$S = k ln\Omega$$

entropy 'S' is calculated and from entropy all other thermodynamic quantities are obtained, where 'k' is the Boltzmann's constant. Here we give three examples for large N and five examples for small N.

Microstates In Phase Space

Boltzmann imagined phase space as a 6-dimensional space with N particles which will have N trajectories. But according to Gibbs, if there are N particles, we must imagine it as a 6N dimensional space which have only one trajectory. This Gibbsian model is followed in statistical mechanics. So for N particles moving in

1. 1 D Cartesian space, the phase space is 2N dimensional
2. 2 D Cartesian space, the phase space is 4N dimensional
3. 3 D Cartesian space, the phase space is 6N dimensional

Sometimes we will have a doubt, why we use momentum as a coordinate. Momentum tells us more about the behavior of the system than velocity alone. Since mass is presumed constant, differentiate momentum with respect to time and you have force. From this you can derive work done, and from this you can derive potential energy. You can also express kinetic energy in terms of momentum. In short momentum and position are the directly observable properties of an object.

Number of States in Cartesian Space

We told you that finding Ω is the target in MCE. Before going to phase space let us imagine, how we will find Ω if it is Cartesian space.

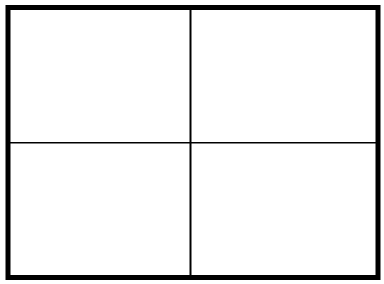

Figure 1. *Method to Find Number of States in Cartesian Space for Regular Shaped Object*

Consider an area as given in Figure 1. It consists of 4 rectangles of equal area A. Total area is 4A. Then the number of areas or in the language of statistical mechanics ``states" to occupy will be given by

$$\Omega = \frac{4A}{A} = 4$$

where A is the minimum area required by an individual state. Here we get the number of states as 4. Suppose our area is having an irregular shape, then we have to find a small area dA and take the sum of all areas or mathematically we have to integrate and get

$$A = \int dA$$

Then the number of states, $\Omega = \frac{\int dA}{\delta}$ where 'δ' is the minimum area.If the Cartesian space is 3D, $\Omega = \frac{\int d^3x}{\Delta}$ where 'Δ' is the minimum volume.

Number of States in Phase Space

After understanding the method to find Ω in Cartesian space, let us move to phase space. In phase space the total number of microstates

$$\Omega = \frac{Volume_{ph}}{h^{3N}}$$

where $Volume_{ph}$ is the phase space volume given by the product of spatial volume and momentum volume (Pathria, 2016). If the energy doesn't contain position coordinate, both volumes are separable and then we can write

$$\Omega = \frac{V^N V_{3N}}{h^{3N}}$$

where V^N is the spatial volume available for N particle, $h^{3N}$is the minimum volume andV_{3N} is the volume of 3N dimensional momentum sphere. Now we will apply this to three large N systems.The first example is given in many textbooks, but for continuity we repeat the same (Pathria, 2016).

Systems with Large N

Nonrelativistic Free Particles

We have (Pathria, 2016)

$$V_{3N} = \frac{\pi^{\frac{3N}{2}} R^{3N}}{\left(\frac{3N}{2}\right)!}$$

For free particles, energy , $\varepsilon_i = \frac{{p_i}^2}{2m}$. So the radius of the momentum sphere, $R = p = \sqrt{2mE} = R$

Then,

$$V_{3N} = \frac{\pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

The total number of microstates,

$$\Omega = \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

By Boltzmann equation

$$S = k ln\Omega$$

$$S = kln\left[\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}\right]$$

To avoid Gibb’s paradox (Pathria, 2016) we will divide Ω by $N!$. Then

$$S = kln\left[\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!\,N!}\right]$$

Using the Stirling's approximation for large N values and using

$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$, $\quad E = \frac{3}{2}NkT$

Using $\quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E}$, $PV = NkT$

Relativistic Massless Particle

For a relativistic mass less particle, the single particle energy is given by

$$\varepsilon_i = p_i c$$

The radius of the momentum sphere

$$R = \frac{E}{c}$$

The number of micro states is (Pathria, 2016)

$$\Omega = \frac{V^N}{(3N)!}\left(\frac{8\pi E^3}{c^3}\right)^N \frac{1}{h^{3N}}$$

Avoiding Gibb’s paradox $\quad S = Nk\left[ln\left(\frac{8\pi VE^3}{h^3c^3}\right) - 3ln3N - lnN + 4\right]$

Using the standard expressions, we get

$$E = 3NkT$$

$$PV = \frac{NkT}{V}$$

Harmonic oscillator

$$\Omega = \frac{1}{3N!}\left(\frac{E}{\hbar\omega}\right)^{3N}$$

$$S = 3Nkln\frac{E}{3n\hbar\omega} + 3Nk$$

Entropy is extensive and hence no Gibb's paradox. So there is no need to divide Ω by $N!$.

$$U = 3NkT$$

$$P = 0$$

Small N Systems

Generally, SM is applied to large N systems. So in textbooks small N systems are not dealt with. But if the system is chaotic small dimensional systems show ergodic behavior and hence we can apply statistical mechanics to study the system (Bannur, Kaw, & Parikh, 1997; Bannur & Thayyullathil, 2009). Besides the calculation of Ω for small N systems gives a visual effect for the learners of SM. In this section we will find internal energy U only, the remaining thermodynamics is left for the reader to calculate.

Free particle bounded between the limits -L to +L

For a free particle $E = \frac{p^2}{2m}$. Area in phase space will be a rectangle. We can compute the full area directly as given below.

$$\text{Area} \quad = \int_{-L}^{L}\left(\int_{-\sqrt{2mE}}^{\sqrt{2mE}} dp\right) dq$$

$$= 4L\sqrt{2mE}$$

Hence $\Omega = \frac{4L\sqrt{2mE}}{h}$

Entropy $S = kln\frac{4L\sqrt{2mE}}{h}$

So $U = \frac{kT}{2}$

Two Free Particles

For two free particles $E = \frac{{p_1}^2}{2m} + \frac{{p_2}^2}{2m}$

where p_1 and p_2 are momenta of the two particles m be the mass of the particles. This system forms an elliptical trajectory and hence we will have four equal areas in each quadrant. Let area of one quadrant of phase space = $\int\int dp_1 dp_2$. Here p_1 will vary from 0 to $\sqrt{2mE - {p_2}^2}$ and p_2 will vary from 0 to $\sqrt{2mE}$.

So the total area of the phase space = $4\int_0^{\sqrt{2mE}}\int_0^{\sqrt{2mE-{p_2}^2}} dp_1 dp_2$

$$=2\pi mE$$

The number of microstates, $\Omega = \frac{2\pi mE}{h}$ where h is the Planck constant.

The entropy, $S = kln\Omega = kln\frac{2\pi mE}{h}$

$$U = kT$$

This can be extended to any number of free particles. Thus we can conclude that for free particles the general expression for internal energy is

$$U = \frac{NkT}{2}$$

A Freely Falling Particle

For a freely falling body $E = \frac{{p_1}^2}{2m} + mgq_1$

where q_1 is the initial position. Since we are interested in finding the internal energy, which doesn't depend on parameters other than T, we take constants as unity. Then $E = p_1^2 + q_1$. The trajectory in phase space will be a parabola and hence total phase space are twice the area in first quadrant. The limiting values of q_1 is $\sqrt{E}$ and $p_1$is $E - p_1^2$. So the area

$$= 2\int_0^{\sqrt{E}}\left(\int_0^{E-p_1^2} dq_1\right) dp_1$$

$$\Omega = \frac{4}{3h}E^{\frac{3}{2}}$$

Entropy,

$$S = kln\Omega = kln\frac{4}{3h}E^{\frac{3}{2}}$$

$$U = \frac{3kT}{2}$$

A Harmonic Oscillator

For a harmonic oscillator, $E = \frac{{p_1}^2}{2m} + \frac{K{q_1}^2}{2}$

where $p_1$and q_1 are momentum and position respectively. K is the spring constant and m is the mass of the particle. Taking the constants as unity, we will get $E = p_1^2 + q_1^2$. This system forms an elliptical trajectory and hence we will have four equal areas in each quadrant. Let area of one quadrant of phase space $\int\int dp_1 dq_1$. Here p_1 will vary from 0 to $\sqrt{E - {q_1}^2}$ and q_1 will vary from 0 to $\sqrt{E}$. So the total area of the phase space,

$$A = \pi E$$

The number of microstates, $\Omega = \frac{\pi E}{h}$ and we get

$$U = kT$$

A Quartic Oscillator

For a pure quartic oscillator(Suresh, Damodaran, & Udayanandan, 2016),$E = \frac{p^2}{2m} + \frac{Kq^4}{2}$ .Considering the constants as unity, we get $E = p^2 + q^4$. Here, Area = 4 * Area of first quadrant. Solving we get

$$\Omega = CE^{\frac{3}{4}}$$

where C is a constant which includes the value of definite integral. Entropy

$$S = kln\Omega = klnCE^{\frac{3}{4}}$$

So $$U = \frac{3kT}{4}$$

CONCLUSIONS

In this article we applied the technique of MCE in finding the microstates and hence obtaining the thermodynamics. We showed that small number systems also give the exact thermodynamics, besides giving a visual picture of calculating the microstates. We hope such examples will help both the students and the teachers in teaching MCE effectively.

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