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Statistical Mechanics

CH. 6 CLASSICAL STATISTICAL MECHANICS LECTURE NOTES

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Statistical Mechanics:

- Properties of systems in equilibrium

Hamiltonian H

$H = H(\vec{p}, \vec{q}) = T + V$

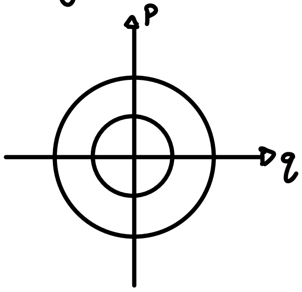
$\vec{p}$ → Generalized momenta

$\vec{q}$ → Generalized co-ordinate

Solve for Hamilton's Equations: $\dot{q}_i = \dfrac{\partial H(\vec{p}, \vec{q})}{\partial p_i}$, $\dot{p}_i = \dfrac{\partial H(\vec{p}, \vec{q})}{\partial q_i}$

We want to characterize our system energy $H(p, q) = E$

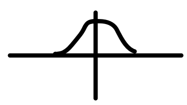
Single Particle (HO)



We call $H(\vec{p}, \vec{q})$ the energy surface of energy

Let's measure $f(\vec{p}, \vec{q})$: Ensemble average : $\langle f \rangle = \dfrac{\int F(p,q)\,\rho(p,q)\, d^{3V}p\, d^{3V}q}{\int \rho(\vec{p}, \vec{q})\, d^{3V}p\, d^{3V}q}$

Fluctuations are calculated by : $\dfrac{\langle f^2 \rangle - \langle f \rangle^2}{\langle f \rangle^2} \ll 1$



Micro Canonical Ensemble

(a) Entropy is an extensive quantity

$\Gamma(E) = \int d^{3N}\vec{p}\; d^{3N}\vec{q}$

We then say our entropy is : $S = S(E, N, V) = K \log(\Gamma(E))$

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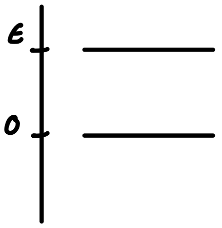
The relationship between stat mech and thermodynamics is

$S(E, V, N) = K \log \Gamma(E, V, N)$; $\dfrac{\partial S(E, V, N)}{\partial E} = T^{-1}$

S → Entropy, Γ: # of microstates

Example : 2 Distinguishable Particles



# of microstates for this system

$E = 0 \;:\; \Gamma = 1 \;,\; E = \epsilon \;:\; \Gamma = 2 \;,\; E = 2\epsilon \;:\; \Gamma = 1$

we can take our temperature and do

$$T^{-1} = k\left(\frac{\partial \log \Gamma(E)}{\partial E}\right)_{V,N} = k\left(\frac{\partial \Gamma(E)/\partial E}{\Gamma(E)}\right)_{V,N} = k\,\frac{\Delta\Gamma(E)/\Delta E}{\Gamma(E)}$$

Therefore this will then tell us that

$$T^{-1} = k\,\frac{\Delta\Gamma(E)}{\Gamma(E)}\,\frac{1}{\Delta E}$$

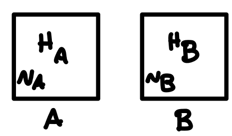
The total number of microstates is calculated by :

$$\Gamma(E) = \int d^{3N}\vec{p}\, d^{3N}\vec{q} \;,\; \Sigma(E) = \int d^{3N}\vec{p}\, d^{3N}\vec{q}$$

we now expand the energy and we see that

$$\Sigma(E') = \Sigma(E) + \left.\frac{\partial \Sigma(E')}{\partial E'}\right|_{E'=E} \cdot (E'-E)$$

we now look at a two Hamiltonian system



we use the assumption :

$$H = H_A + H_B$$

If we have the total number of microstates :

$$\Gamma(E) = \sum_{i=1}^{E/\Delta E} \Gamma_A(\epsilon_i)\,\Gamma_B(E-\epsilon_i)$$

we then move on to calculating the entropy :

$$S = k \log \Gamma(E) = k \log\left(\sum_{i=1}^{E/\Delta E} \Gamma_A(\epsilon_i)\,\Gamma_B(E-\epsilon_i)\right)$$

we now go back to E_A and E_B

$\bar{E}_A, \bar{E}_B$ for which $\Gamma_A(\epsilon_i)\Gamma_B(E-\epsilon_i)$: $\Gamma(\bar{E}_A)\Gamma(\bar{E}_B) \leq \Gamma(E) \leq \frac{E}{\Delta E}\Gamma_A(\bar{E}_A)\Gamma_B(\bar{E}_B)$

$k\log(\Gamma_A(\bar{E}_A)\Gamma_A(\bar{E}_B)) \leq k \log \Gamma(E)$ $\therefore$ $S \leq S_A(\bar{E}_A, V_A) + S_B(\bar{E}_B, V) + \mathcal{O}(\log N)$

This tells us entropy is consistent w/ being an extensive quantity

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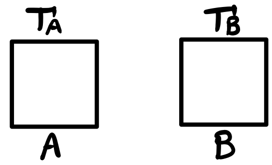
Two subsystems :



The total number of microstates is then

$$T'(E) = \sum_{i=1} T'_A(\varepsilon_i)\, T_B(E-\varepsilon_i)$$

There are many types of ensembles, the main 3 are :

- Microcanonical
- Canonical $\longrightarrow$ usually used in experimental research
- Grand Canonical

This tells us that S is extensive, $S(E,V,N) = K\log(T'(E,V,N))$

Some properties of the above relationship are

$$\left.\frac{\partial \log(T_A(E_A))}{\partial E_A}\right|_{E_A=\bar{E}_A} + \left.\frac{\partial \log(T'_B(E_B))}{\partial E_A}\right|_{E_B=\bar{E}_B} \overset{!}{=} 0$$

we get the equations for inverse temperature with,

$$\underbrace{\left.\frac{\partial S_A(E_A)}{\partial E_A}\right|_{E_A=\bar{E}_A}}_{\frac{1}{T_A}} = \underbrace{\left.\frac{\partial S_B(E_B)}{\partial E_B}\right|_{E_B=\bar{E}_B}}_{\frac{1}{T_B}}$$

The above comes from two subsystems with separate properties (E, T, V, P, N) and are then put in contact with one another.

Given two energy levels with two particles

	$N=2$		$N=3$	
ε	$E=2\varepsilon$	$T'=1$	$E=3\varepsilon$	$T'=1$
	$E=\varepsilon$	$T'=2$	$E=2\varepsilon$	$T'=3$
0	$E=0$	$T'=1$	$E=\varepsilon$	$T'=3$
			$E=0$	$T'=1$

For a two-level system we have $T'(E,N) = \dfrac{N!}{N_j!\,(N-N_j)!}$

Particle's that are <u>distinguishable</u> are said to be <u>classical</u>

Looking at the micro canonical ensemble we know E and N are fixed. we know the entropy then comes out to be

$$S = k\left[\log(N!) - \log(N_j!) - \log((N-N_j)!)\right] \quad w/ \quad \log(N!) = N\log(N) - N$$

The entropy will then become

$$S = k\left[N\log(N) - N_j\log(N_j) - (N-N_j)\log(N-N_j)\right]$$

The Final entropy comes out to be

$$S(E,N) = -Nk\left[\frac{E}{\varepsilon N}\log\left(\frac{E}{\varepsilon N}\right) + \left(1-\frac{E}{\varepsilon N}\right)\log\left(1-\frac{E}{\varepsilon N}\right)\right]$$

If we wanted to find the temperature we would do

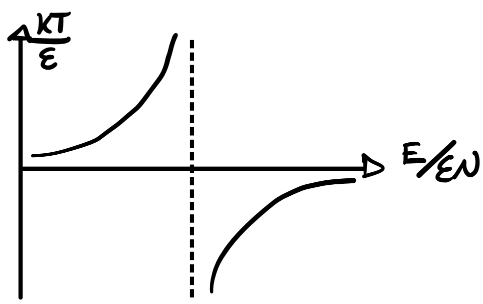
$$T^{-1} = \left(\frac{\partial S}{\partial E}\right)_N = -\frac{k}{\varepsilon}\log\left(\frac{E}{\varepsilon N - E}\right) = \frac{k}{\varepsilon}\log\left(\frac{N-N_j}{N_j}\right)$$

We can in turn express the energy in terms of temperature

$$E = N\varepsilon\,\frac{1}{1+e^{\varepsilon/kT}}$$

we now look at limiting conditions,

$T \to 0$: $E \to 0$; $T \to \infty$: $E = \frac{\varepsilon N}{2}$;



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Define Entropy, Temperature (S,T). Our variables for the microcanonical ensemble are

Macro Variables : (E, N, V)

We will look at this with two examples:

1. Example : ______ ε ______ 0 N, S, T?

2. Example : Ideal gas : $H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$

Before we do this we want to look closer at Thermodynamics. we first wish to look at a "Quasi-Static" Thermodynamic transformation: slow change of $(E, V, \ldots)$.

Examining the change of entropy, this mathematically is

$$dS(E,V,N) = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV$$

We then can say from the viewpoint of Thermodynamics

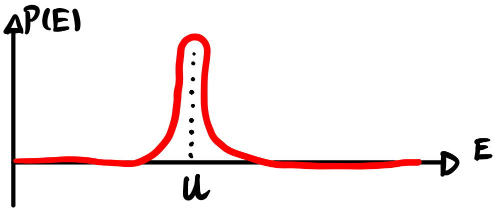
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \;,\; \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

The Recipe when using this is:

* Calculate the Entropy $S(E,V,N) = K\log(\Gamma(E,N,V)) \rightsquigarrow \equiv \Omega$
* Take $S = S(E,V,N) \rightsquigarrow$ Invert to solve for $E(S,V,N) = U(S,V,N)$

$\Rightarrow$ E - "Total Energy", U - "Internal Energy"

We can choose to look at this in the Canonical Ensemble: T, N, V. Inside this system we can calculate an internal energy U.



microcanonical
canonical
$\Big\}$ Same thermodynamics

Equipartition Theorem:

We wish to calculate the following value

$$\langle x_i , \partial H/\partial x_j \rangle = \frac{\int_{E<H<E+\Delta E} x_i \, \partial H/\partial x_j \, d^{3N}\vec{p}\, d^{3N}\vec{q}}{\int_{E<H<E+\Delta E} d^{3N}\vec{p}\, d^{3N}\vec{q}} = \delta_{ij} KT$$

$\rightsquigarrow \Omega$

In the microcanonical ensemble each state is as equally probable $\therefore \rho = 1$

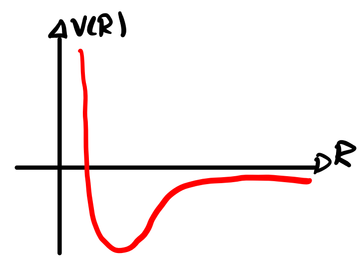
$$\frac{\partial H}{\partial q_i} = -\dot{p}_i \longrightarrow \text{One of Hamiltonian Eqn. of motion}$$

We can do the above but sum over all particles

$$\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = -3NKT \rightsquigarrow \text{For any } H!!$$

The Hamiltonian can be calculated via:

$$H = \sum_{i=1}^{3N} A_i P_i^2 + \sum_{i=1}^{3N} B_i Q_i^2$$



$P_i \rightarrow$ Generalized momentum, $Q_i \rightarrow$ Generalized co-ordinate

We can also say the following to calculate the expectation value of H:

$$\langle H \rangle = \frac{1}{2}\sum_{i=1}^{3N}\left(P_i \frac{\partial H}{\partial P_i} + Q_i \frac{\partial H}{\partial Q_i}\right) \Rightarrow \langle H \rangle = \frac{1}{2} f KT \;,\; f = 6N$$

This is a direct application of the equipartition theorem!

Application of Equipartition Theorem: 3D Ideal Gas (N particles)

$$\langle H \rangle = \frac{3}{2} NKT$$

we get "3/2" from the fact that: $H = \sum_{i=1}^{3N} A_i P_i^2 + \cancel{\sum_{i=1}^{3N} B_i Q_i^2}^{\,0} = \sum_{i=1}^{3N} A_i P_i^2$

we now choose to look at

$$\Sigma(E) = \frac{1}{h^{3N}} \int_{H<E} d^3\vec{p} \ldots d^3\vec{p}_N \ldots d^3\vec{r}_N \qquad (*)$$

where the entropy is calculated with

$$S = k\log(\Sigma(E)) \,,\ S = k\log(\Gamma(E))$$

we first introduce

$$\Theta(E-E') = \begin{cases} 1 & \text{for } E-E' \geq 0 \\ 0 & \text{for } E-E' < 0 \end{cases}$$

(*) Now becomes

$$\Sigma(E) = \frac{1}{h^{3N}} \iint \Theta(E-H)\, d^{3N}\vec{p}\, d^{3N}\vec{q} \quad , \quad \Theta \to \Theta(E - \sum_{i=1}^{N} 1/2m\, \vec{p}_i^{\,2})$$

we now make the change of co-ordinates: $\vec{u}_i = 1/\sqrt{2m}\, \vec{p}_i$. The volume element then becomes $d^3\vec{p}_i = (2m)^{3/2} d^3\vec{u}_i$. Applying this we have

$$\Sigma(E) = \frac{V^N}{h^{3N}} (2m)^{3N/2} \int \Theta(E - \sum_{i=1}^{N} \vec{u}_i^{\,2})\, d^{3N}\vec{u}. \qquad (**)$$

Given an arbitrary vector $\vec{r}$, it is true that

$$\vec{r}_1 = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \rightsquigarrow r_1^2 = x_1^2 + y_1^2 + z_1^2 \quad w/\ r = \sqrt{x_1^2 + y_1^2 + z_1^2}$$

Doing this but with a different notation

$$\vec{R}_E = \begin{pmatrix} u_1 \\ \vdots \\ u_n \end{pmatrix} \rightsquigarrow \vec{R}_E = (|\vec{R}_E|, \vec{R}_E)$$

This then will change (**) to

$$\Sigma(E) = \frac{V^N}{h^{3N}} (2m)^{3N/2} \int \Theta(E - R_E^2) R_E^{3N-1}\, dR_E\, d\Omega_{R_E}$$

we can use the following

$$\int e^{-(\vec{u}_1^2+\vec{u}_2^2+\vec{u}_3^2+\dots)/\epsilon}\, d^{3N}\vec{u} \Rightarrow \int e^{-R_E^2/\epsilon} R_E^{3N-1}\, d\Omega_{R_E}$$

we then have enough to solve for $\Sigma(E)$

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Once we have $\Sigma(E)$, we will be able to solve for our entropy.

we wish to solve the following

$$J = \int_0^\infty \Theta(E-R_E)R_E^{3N-1}\, dR_E \cdot \underbrace{\int d\hat{R}_E}_{\substack{3N-1 \\ \text{Angles}}}$$

3N-1 co-ordinates

When we solve for the radial component we get

$$\int d\hat{R}_E = 3N\frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}$$

When we work everything out we find $\Sigma(E)$ to be

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

we can then calculate the entropy, then solve for E.

$$S(E,V) = K\log(\Sigma(E)) = k\left[\log C_{3N} + N\log(V/h^3) + 3N/2\log(2mE)\right]$$

using Stirlings formula and simplifying we get

$$S(E,V) = \frac{3Nk}{2} + Nk\log\left(V\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right)$$

Doing this we find E to be

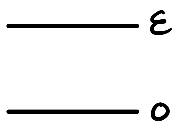
$$E = \frac{3h^2}{4\pi m}\frac{N}{V^{2/3}}\exp\left(\frac{2S}{3Nk}-1\right)$$

we can find quantities like

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{2}{3}\frac{E}{Nk} \quad \therefore \quad E = \frac{3}{2}NkT, \quad C_V = \left(\frac{\partial E}{\partial T}\right)_V, \quad P = -\left(\frac{\partial E}{\partial V}\right)_S$$

we were able to rederive the ideal gas from the microcanonical ensemble

Now lets look at a new system with two particles



$N=2$: identical bosons , $E=\varepsilon$: $\frac{1}{\sqrt{2}}\left(\varphi_0(1)\varphi_\varepsilon(2)+\varphi_\varepsilon(1)\varphi_0(2)\right)$

Our final definition for Σ is

$$\Sigma(E)=\frac{1}{N!\,h^{3N}}\int_{H<E} d^{3N}p\, d^{3N}q$$