Phys 359

STATISTICAL MECHANICS

University of Waterloo

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1 Introduction

1.1 What is Statistical Mechanics

Statistical Mechanics is thearea of Physics interested in systems with a large number of degress of freedon n. Note that these variables can be interacting or not.

There are two distinct class of Statistical Mechanics: equilibrium and non-equilibrium.

The Statistical part of Statistical Mechanics implies that it is inherently a study of probabilities and probability distributions. These laws must still remain fully consistent with physical laws.

Typically, systems are analyzed on a microscopic level. For a system of particles with charges $\{q_i\}$ and their positions $\{\vec{r}_i\}$, the dynamics are governed by the forces acting on each particle,

$$\vec{F}_i = m_i \vec{a}_i = \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0} \frac{1}{|\vec{r}_{ij}|^2}$$

But does labelling the particles really matter? For the case of $N \to \infty$, the global phenomenology is of interest.

1.2 History

1738 Daniel Bernoulli

- molecules moving in container, they collide with one another
- collisions with walls explains pressure

1850 Gay Lussac, Joule, Thomson (Lord Kelvin), Carnot

1859 James Clerk Maxwell

- $D(\nu) \sim e^{-\frac{\nu^2}{2k_B T}}$

1884 Josiash Willard Gibbs

- ensemble averaging

1900 Planck, Einstein, Bose, Pauli, Fermi, Dirac

Today Frontier is in non-equilibrium Statistical Mechanics

- cold atoms
- biology
- quantum information

2 Foundations

2.1 Essence of Statistical Mechanics

Laws of Thermodynamics:

Pros	Cons
• great because they are totally general • relationship's (Maxwell's realtions) between c_p, c_v, α, κ	• does not tell us how to compute anything • does not tell us what entropy is

The 2$^{\text{nd}}$ law of Thermodynamics reveals $\mathrm{d}U = đQ - đW$ where $đQ = T\mathrm{d}S$.

But what is S and what does it **physically** mean? Boltzman reveals the relation:

$$S = k_B \ln(\Omega)$$

Which we will come back to.

2.2 Postulate of Statistical Mechanics

There is only one postulate of Statistical Mechanics:

> *For an isolated system in equlibrium, all microstates accessible to the system are equally probable.*

In order to digest this postulate, we will require some definitions.

Definitions:

- system
  - part of the universe we care about
  - only weakly coupled to the rest of the universe
  - the dynamics/mechanics are dominated by the internal degrees of freedom and forces
- isolated
  - idealization
  - eliminates all external influences; no force, no energy/heat flux and no particle flux
  - equantities such as the energy, number of particles and colume assumed constant forever $\mathrm{d}U, \mathrm{d}N, \mathrm{d}V = 0$
- equilibrium
  - everything is no-longer changing
- microstate
  - a complete/total description of everything at the microscopic level $\{\vec{r}_i, \vec{p}_i\}$ for each i
- macrostate
  - a decription at the macroscopic level in accordance with the external constraints
  - $U, P, T, \bar{M}$
- equally probable
  - we are dealing with probabilities and statistics
  - microstates are somehow describing probabilistically the properties at the macroscopic level
- accessible
  - consistancy with the macroscopic constaints imposed by the conservation laws (fixed energy, fixed number of particles)

Posulate Follow-up:

> *We assume that the observed/realized macrostate is the one with the most microstates.*

2.3 Perspective from Coin Tossing

Consider 4 coins toassed many, many times. What are the microstates describing this system?

Macrostate Label	Macrostate		Microstate				Thermo Probability	True Probability
	N_H	N_T	A	B	C	D		
1	4	0	H	H	H	H	1	1/16
2	3	1	H	H	H	T	4	4/16
			H	H	T	H		
			H	T	H	H		
			T	H	H	H		
3	2	2	H	H	T	T	6	6/16
			H	T	T	H		
			T	T	H	H		
			T	H	H	T		
			H	T	H	T		
			T	H	T	H		
4	1	3	T	T	T	H	4	4/16
			T	T	H	T		
			T	H	T	T		
			H	T	T	T		
5	0	4	T	T	T	T	1	1/16

We note that the most probable macrostate 3 is the one with the most microstates 6.

How do we deal with very large N, N_H, N_T in order to locate the most likely macrostate? First likes get a general expression for Ω were Ω is the number of microstates. Since $N = N_H + N_T$ and N is considered fixed, there is only one free parameter N_H (taken by choice). Thus Ω can be considered a function of N_H and nothing else.

Recall from probability that the form for Ω is given by,

$$\Omega = \frac{N!}{N_H!\,(N - N_H)!}$$

The most likely macrostate is given when Ω (the number of microstates) is maximized. This means that we are interested in finding values of N_H, namely N_H^* where,

$$\left(\left.\frac{\mathrm{d}\Omega}{\mathrm{d}N_H}\right|_{N_H=N_H^*} = 0 \qquad \left(\left.\frac{\mathrm{d}^2\Omega}{\mathrm{d}N_H^2}\right|_{N_H=N_H^*} > 0$$

In order to do this, we will need to explore some mathematics ideas.

2.4 Stirlings Formula and Gaussian Integrals

Consider the integral,

$$I = \int_0^\infty x^N e^{-x}\mathrm{d}x$$

This can be evaluated using integration by parts,

$$I = N\int_0^\infty x^{N-1}e^{-x}\mathrm{d}x = \cdots = N! \tag{2.1}$$

2.4.1 Differentiation Trick

However, integration by parts N times on (2.1) is annoying. There is a nice trick. Notice that,

$$\int_0^\infty e^{-ax}\mathrm{d}x = \left(-\frac{1}{a}e^{-ax}\right|_0^\infty = \frac{1}{a} \tag{2.2}$$

One can treat a as a *dummy* variable, and examine (2.2)'s derivative with respect to a,

$$\frac{\partial}{\partial a}\int_0^\infty e^{-ax}\mathrm{d}x = \int_0^\infty \frac{\partial}{\partial a}e^{-ax}\mathrm{d}x = \int_0^\infty -xe^{-ax}\mathrm{d}x = \frac{\partial}{\partial a}\left(\frac{1}{a}\right) = -\frac{1}{a^2}$$

The reason for doing this is to simplify the process of (2.1).

If one explores the n^{th} derivative of (2.2) with respect to a, you will derive the expression,

$$\left[(-1)^N \frac{\partial^n}{\partial a^n}\int_0^\infty e^{-ax}\mathrm{d}x\right]_{a=1} = N! \tag{2.3}$$

The $(-1)^N$ term is a result of the alternating sign induced by bringing down a $-x$ each time you take a derivative.

2.4.2 Stirling's Formula

Looking back at the integral (2.1),

$$\int_0^\infty x^N e^{-x}\mathrm{d}x = N! \tag{2.4}$$

How can we approximate $N!$ using the left had side of (2.4)? To derive Stirling's Formula, we need to make a change of variables $x = N + \sqrt{N}y$. Substituting into (2.4) gives,

$$N! = \int_0^\infty \sqrt{N}e^{-N}e^{N\ln\left(N+\sqrt{N}y\right)}e^{-\sqrt{N}y}\mathrm{d}y$$

The approimation begins by expanding the logarithm for large N,

$$\ln\left(N+\sqrt{N}y\right) = \ln\left(N\left[1+\frac{y}{\sqrt{N}}\right]\right) = \ln(N) + \ln\left(1+\frac{y}{\sqrt{N}}\right)$$

Take $\epsilon = \frac{y}{\sqrt{N}} << 1$ and apply taylor series,

$$\ln(1+\epsilon) \approx \epsilon - \frac{\epsilon^2}{2}$$

Thus,

$$N! \approx \sqrt{N}e^{-N}N^N \int_{-\sqrt{N}}^\infty e^{-\frac{y^2}{2}}\mathrm{d}y$$

The lower bound can be approximated as ∞ since N is so large,

$$N! \approx \sqrt{N}e^{-N}N^N \int_{-\infty}^\infty e^{-\frac{y^2}{2}}\mathrm{d}y$$

Notice the remaining integral term. It is called the *Gaussian Integral* and has solution (see Gaussian Integrals),

$$\int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} \mathrm{d}y = \sqrt{\frac{\pi}{a}} \tag{2.5}$$

Thus letting $a = 1/2$,

$$N! \approx \sqrt{2\pi N} e^{-N} N^N \tag{2.6}$$

Equation (2.6) is known as *Stirling's Formula*. However, there is a much more useful form of Stirling's Formula. It is obtained by taking the logarithm of both sides,

$$\ln(N!) \approx \left(N + \frac{1}{2}\right)\ln(N) - \left(N - \underbrace{\frac{1}{2}\ln(2\pi)}_{\text{small compared to large } N}\right)$$

$$\ln(N!) \approx N \ln N - N \tag{2.7}$$

Note that the remaining N is not dropped. This is because for $N \sim 10^{23}$, $N \ln N - N$ and $N \ln N$ differ by about 2%.

Now we can apply this to the problem of maximizing Ω (which is equivalent to mazimizing $\ln \Omega$) because the logarithm is monotonically increasing.

$$0 = \frac{\partial \ln \Omega}{\partial N_H} = \frac{\partial}{\partial N_H}\left[\ln\left(\frac{N!}{N_H!\,(N - N_H)!}\right)\right]$$

Through some manipulation, and applying (2.7), one obtains the expected result,

$$N_H = \frac{N}{2}$$

2.4.3 Gaussian Integrals

Before continuing, we should take a moment to explore how (2.5) is solved. Let,

$$I_x = \int_{-\infty}^{\infty} e^{-ax^2} \mathrm{d}x$$

Here comes the trick. Multiply I_x by itself and switch from rectangular coordinates to polar coordinates,

$$I_x I_y = \int_{-\infty}^{\infty} e^{-ax^2} \mathrm{d}x \int_{-\infty}^{\infty} e^{-ay^2} \mathrm{d}y$$

$$I^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-a\left(x^2+y^2\right)} \mathrm{d}x\mathrm{d}y$$

Where we take $\mathbb{R}^2(x, y) \mapsto \mathbb{R}^2(r, \phi)$

$$I^2 = \int_{0}^{2\pi}\int_{0}^{\infty} r e^{-ar^2} \mathrm{d}r\mathrm{d}\phi$$

Which reveals that $I^2 = \pi/a$. Thus,

$$I = \sqrt{\frac{\pi}{a}}$$

2.5 Connections between Thermodynamics and Statistical Mechanics

Consider a lattice of Cu^{2+} atoms. In a lattice the Cu^{2+} atoms are distinguishable because they have unique locations. Now apply an external magnetic field.

$$H_{\text{zeaman}} = -\vec{\mu} \cdot \vec{B}$$

Recall that $\vec{u} = g\mu_B \vec{s}$ has units J/T where T is tesla. Where for an electron,

$$\mu_B = \frac{e\hbar}{2m} = 9 \times 10^{-24}\,\mathrm{JT}^{-1} \qquad g \approx 2$$

For $\vec{B} = B\hat{z}$, $H_{\text{zeaman}} = 2\mu_B B s_z \equiv b s_z$. The splitting of the two spin states $s_z = \pm 1$ for $B = 1\,\mathrm{T}$ has characteristic temperature of,

$$\frac{H_{\text{zeaman}}}{k_B} = \frac{\varepsilon}{k_B} = \frac{10 \times 10^{-23}\,\mathrm{J}}{1.4 \times 10^{23}\,\mathrm{JK}^{-1}} \approx 0.6\,\mathrm{K}$$

Now consider N electrons subject to the field $\vec{B}$ where there are N_+ spins "up" and N_- spins "down". This is completely analogous to the coin flipping example. The total energy of the system is given by,

$$U = -N_-\varepsilon + N_+\varepsilon$$

Not that $N = N_+ + N_-$ and thus,

$$\frac{U}{N} = \varepsilon - 2\varepsilon\frac{N_-}{N}$$

Constraining U and using the substitution,

$$\frac{N_-}{N} = \frac{1-x}{2} \qquad \frac{N_+}{N} = \frac{1+x}{2}$$

Then the microstate measure is given by,

$$\Omega = \frac{N!}{N_+!N_-!}$$

Becomes (after some manipulation as using (2.7))

$$\ln\Omega = -N\left[\left(\frac{1+x}{2}\right)\ln\left(\frac{1+x}{2}\right) + \left(\frac{1-x}{2}\right)\ln\left(\frac{1-x}{2}\right)\right]$$

Now recall that for fixed volume $\mathrm{d}V = 0$,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$$

But since U depends only on x, we can write,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial x}\right)\left(\frac{\partial x}{\partial U}\right)$$

Thus reveals a slight connection between S the entropy and Ω through x in this example. Further analysis with motivate Boltzman's equation,

$$S = k_B \ln\Omega + S_0$$