Statistical Thermodynamics

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October 11, 2010

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1 Introduction

- Syllabus http://www.tcd.ie/Physics/undergraduate/mod_physics/
- Summaries, diagrams, tables, etc. http://www.tcd.ie/Physics/local/undergraduate/JS/
- Recommended books Thermal Physics by Kittel and Kroemer, Freeman Statistical Physics by Mandl, Wiley

1.1 Syllabus and Objectives

- Counting States in classical and quantum systems.
- Fundamental assumption of statistical physics; ensembles
- Model system of 2-state components.
- Twos systems in equilibrium: entropy, temperatures and chemical potential.
- Partition functions and their relation to thermodynamic quantities.
- Third Law of Thermodynamics.
- Fermi-Dirac and Bose-Einstein Statistics.
- Quasi-classical statistics: equipartition of energy
- Application of quantum statistics to photons, gases, and solids.

The main objective is to show how a simple assumption of equal statistical weights allows the properties of individual quantum particles to be combined together properly to calculate macroscopic thermodynamic quantities, to compare with experiment.

1.2 Classical Thermodynamics

Classical Thermodynamics:

- Mathematical development of experimentally based laws
- Consequences may be tested experimentally
- Power lies in making wide-ranging deductions of great generality

Limits:

- Origins of laws?
- Macroscopic events only.
- No *a priori* calculations of the properties of a system.

Example:

Equation of state of system which relates macroscopic variables and distinguishes one system from another.

f(P, V, T) = 0 (derived from experiment)

Ideal gas law: PV = nRT (where N = number of moles)

 $R = 8.314 J K^{-1} mol^{-1}$ (determined from experiment)

Virial: $PV = A + \frac{B}{V} + \frac{C}{V^2} + \dots$

Where A, B, C... are (temperature dependant) virial coefficients determined by experiment.

1.3 Statistical Thermodynamics

- Assumes atomic nature of matter.
- Deduces macroscopic properties from atomic properties.
- ~ 10^{23} particles > Statistical Methods.
- The behaviour of collections of particles can be predicted accurately without knowing the detailed behaviour of any one particle.
- Quantum systems conceptually easier. Postulate of quantum mechanics and one extra postulate about probability ≻ Function with the same properties as entropy.

Main Problem: Computationally Complex

2 Foundations

2.1 Concepts and terminology.

Macrostate

- Defined when we know the contraining parameters (P, V, T...) of a system.
- Time independant when the system is in thermal equilibrium.

Microstate

- Quantum Microstate
 - Each quantum state is a seperate and distinct microstate of the system.
- Classical Microstate
 - Conceptually more difficult, but may be easier to calculate using classical mechanics
 - Uses phase space of position q, and momentum p, coordinates.
 - Microstate is Volume element in 6N-dimensional phase space of N particles.
 - As particles move, Hamilton's equations describe motions:

$$\dot{q}_i = \frac{\delta H}{\delta p_i}$$
 $\dot{p}_i = \frac{\delta H}{\delta q_i}$ $H = T + V$

T = Kinetic Energy, V = Potential Energy

• Liouville's Theorem: Phase volume of particles is constant

We use the quantum approach in this course

Counting States

- Statistical thermodynamics needs to know the number of microstates in the macrostate.
- Quantum microstates are discrete (e.g. particle in a box) and easy to count.

Weakly Coupled Systems

(Solving the quantum mechanics problem)

• In an isolated system (total energy, volume, number of particles are constant) Weak coupling ≻ Energy levels of single particles are effectively unchanged by weak interactions between particles, BUT, the interactions is large enough for the system as a whole to come to a common temperature.

• This allows the quantum mechanical (QM) problem to be solved.

Example:

Gas of hydrogen molecules: QM can be used to calculate the electronic, vibrational, rotational, and translational eigenvalues of the isolated hydrogen molecule - the single particle states.

(Kittel calls these orbitals)

2.2 Counting the number of microstates in a macrostate

- Specify constraining parameters of macrostate.
- Determine single particle states.
- Determine whether particles are localised:

Localised ≻ Distinguishable e.g. Magnetic nuclei of atoms in solid Weakly coupled (nuc-nuc ≪ nuc-ext B) Distinguishable (lattice sites can be labelled)

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Non-localised ≻ Indistinguishable
e.g. Gas molecules
Wavefunction of system then depends on whether particles are
Bosons or Fermions
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2.3 Bosons and Fermions

- Two indistinguishable particles, 1 and 2, and two single particle states, a and b: we have, say, ϕ a(1) and ϕ b(2).
- The system is weakly coupled, so the system wavefunction can be written as :

$\psi(1,2) = \phi_a(1)\phi_b(2)$	(independent events)
1 ()) 1 () () ()	(1)

OR

$$\psi(1,2) = \phi_a(2)\phi_b(1)$$
 (indistinguishable)

• Quantum theory gives linear combination:

$$\psi(1,2) = \phi_a(1)\phi_b(2) \pm \phi_a(2)\phi_b(1)$$

Thus we have two situations:

 $\frac{\text{For }+}{\text{Symmetric with respect to particle exchange}}$ $\psi_{BE}(1,2) = \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1) = \psi_{BE}(2,1)$ Bose-Einstein statistics > Bosons

For -Antisymmetric with respect to particle exchange $\psi_{FD}(1,2) = \phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1) = -\psi_{FD}(1,2)$ Fermi-Dirac statistics > Fermions

- All particles are either Bosons or Fermions
- Any number of bosons, but only one fermion can occupy a sing particle state. (Pauli exclusion principle)
- Total spin determines whither particles are bosons or fermions:
 - Photon spin
 - Electron spin
 - Proton spin
 - Neutron spin
- Bosons have integral spin:

⁴He atoms $\succ \sum$ spins = 3

• Fermions have half-integral spin: ³He atoms $\succ \sum \text{ spins} = 2\frac{1}{2}$

2.4 Time averages and ensemble averages

Slide 3 (Some formatting problems here)

The large number of microstates accessible to the system are dealt with statistically:

 $t_1, t_2, t_3, \ldots, t_r$ are times of r successive observations of which microstate the system is in; n(l) is number of times the system is found in state l. The probability of finding the system in state l is:

 $P(l) = \frac{n(l)}{r} (r \succ \infty) (\succ \sum_{l} P(l) = 1 because \sum_{l} n(l) = r)$

The average of some physical parameter of the system, $\langle A \rangle$, is

(1)

To get this properly, observations must be on a time scale long in comparison with the time the system takes to randomize, the Relaxation Time of the system (which varies with A).

- The ensemble or thermal average, is the average over the large number of replicas of the system
- A replica is a microstate of the system
- One replica is required for each microstate
- The collection of replicas is an ensemble
- The ensemble is used to determine P(l) easier than the time method, but apparently equivalent

Ensemble averages produce results which agree with experiment

2.5 Fundamental assumption of Statistical Thermodynamics

A system in thermal equilibrium is equally liekly to be in any of the microstates accessible to it: Equal *a priori* probabilities. (Each microstate has the same statistical weight)

2.6 Summary

- A macrostate is defined when we know the constraining parameters p, V, T, \ldots of the system
- A (quantum) microstate is a quantum state of the system
- Statistical mechanics is based on counting the microstates that make up a macrostate
- Each microstate is given the same statistical weight (equal *a priori* probabilities)
- An ensemble is the collection of microstates (replicas) of the system
- Ensembles enable microstates to be counted
- Ensembles averages are equivalent to time averages

3 A simple model system

- Set of distinct elementary magnets: spin ¹/₂ particle, spin angular momentum ^ħ/₂, at N fixed points on a line ≻ localised, distinguishable.
- Magnetic moment μ' , where $\mu' = \frac{e\hbar}{2m}$, the Bohr magneton.
- No interaction between spins, no external magnetic field.

• Each spin has two distinct possible vaules, $\pm \frac{1}{2}$, giving magnetic moment $+\mu'$ or $-\mu'$ (spin up or spin down)

$$\begin{array}{l} \underline{\text{Example}}\\ \overline{N=3}\succ2^3=8 \text{ possible arrangements of spin (microstates)}\\ & \text{M} \quad (\text{total magnetic moment, macrostate.})\\ & \text{uuu} \quad +3\mu'\\ \text{duu} \quad \text{udu} \quad \text{uud} \quad +\mu' \quad (3+1)=4 \text{ distinct values of M}\\ & \text{udd} \quad \text{dud} \quad -\mu'\\ & \text{ddd} \quad -3\mu' \end{array}$$

- As Particles are localised, duu = /= udu, etc.
- Each arrangement is a separate and distinct microstate of the system
- From the fundamental assumption, the probability of finding a given microstate is $\frac{1}{8}$
- We can define a generating function by $(u+d)^3 = uuu+...+ddd$.

Generalising:

– N Spins

- -2^N distinct microstates
- Probability of finding any single state $\frac{1}{2^N}$
- Generating function $(u+d)^N$
- Total Magnetic moment of system, M, goes from $+N\mu'$ to $-N\mu'$ in steps of $2\mu'$ by reversing a spin.
- M does not depend on arrangement on line \succ M has (N+1) distinct values.
- The macrostate of the system is described by the value of M, which is a macroscopic parameter.
- Note that the magnetisation, which is more genereally used in describing macroscopic magnetic systems, is just the total magnetic moment per unit volume, $\frac{M}{V}$

3.1 Finding the number of microstates in the macrostate

Slide 5 from handout

- With no applied magnetic feild, all microstates have the same energy \succ degenerate (QM)
- If a field B is applied, the total potential energy of the system, $U(m) = -MB = -2m\mu'B$ (so the system is more stable if spins are aligned parallel to the field, "spin up".)

- The overall degeneracy is lifted, but the states of the same m are still degenerate
- Negative energy systems are stable, Systems look for the least amount of energy.

Example

 $\begin{array}{ll} N{=}4 & (even) \\ \Omega(4,\pm 2) = 1 \\ \Omega(4,\pm 1) = 4 \\ \Omega(4,0) = 6 \end{array}$

Thus, with no external magnetic field, the state with m=0;

- Is the most probable macrostate
- Can be in any of 6 microstates
- Therefore is the least well defined, has least known about it, is the most random

3.2 The shape of $\Omega(N,m)$ for large N(~ 10¹⁶)

- The mathematical derivation is set out in JS3002A.
- We take the natural logarithm to convert products to sums
- We split out constant terms
- We recognise that $N\gg m\gg 1$

We obtain $ln\Omega \approx ln\Omega(N,0) - \frac{2m^2}{N}$ and $\Omega(N,m) \approx \Omega(N,0)exp(-\frac{2m^2}{N})$ (3) where $\Omega(N,0) = \frac{N!}{(\frac{N}{2})!}$

 This is a Gaussian distribution with a maximum at m=, and the most probable macrostate has an equal number of up and down spins.

– $\Omega(N,m)$ is an extremely sharply peaked function (width $\sim \sqrt{N})$

Slide 7 Handout

4 Entropy and temperature

The objective is to develope statistical expressions for entropy and temperature.

4.1 Entropy

(Diagram)

- Consider two systems of fixed volume in thermal contact \succ energy is exchanged
- Individual systems cannot exchange particles (thermally conducting wall separates systems)
- − Combined system is isolated \succ total energy of combined system is constant: $U = U_1 + U_2 = \text{constant}$.
- Every accessible state of the combined system is equally probable ≻ most probable division of energy is that fir which the combined system has the maximum number of accessible states.

Take systems (1) and (2) to be model spin systems in thermal contact in a magnetic field:

- The number of spins, N_1, N_2 is constant
- The spin excess $2m_1, 2m_2$ is variable
- The energy $U_1(m_1), U_2(m_2)$ is variable

 $[U(m) = -2m\mu'B]$

- For the combined system, we have some constraints:
 - * $N = N_1 + N_2 = \text{constant}$
 - $* U(m) = U_1(m_1) + U_2(m_2) = \text{constant}$
 - $* 2m = 2m_1 + 2m_2$
- The number of states of the combined system, for given m_1 and m_2 is:

 $\Omega_1(N_1, m_1)\Omega_2(N_2, m_2)$

- But $m_2 = m - m_1$ and so we can sum over m_1 to count all the states for a given total energy:

$$\Omega(N,m) = \sum_{m_1 = -\frac{1}{2}N_1}^{\frac{1}{2}N_1} \Omega_1(N_1,m_1)\Omega_2(N_2,m_2)$$

Where $\Omega(N, m)$ is the number of states of the combined system.

- For some value of m_1 , say $\overline{m_1}$, the product will have a maximum value. for a large system, we can show that this maximum is so large that the statistical properties are completely dominated by this most probably product.

 $\Omega(N,m) \approx \Omega_1(N_1, \bar{m_1})\Omega_2(N_2, m - \bar{m_2}) = \Omega_{max}$

- This is all we have to determine. To ensure that the combined system is large enough, we let one component be a resevoir or heat bath. (Arbitrarily large system whose total energy is effectively constant, despite energy exchange with the other component of the total system.)

In this case, the average of a macroscopic physical quantity is accurately determined by the microstates of the most probable product.

- For our model system, $\Omega_{max} \sim 2^N$ and correction term
- So if $N = 2^N \sim 10^{30}$, the correction term is 1 part in 10^{28}
- We now generalise using internal energy U, and differentiating to find the maximum.
- Let $\Omega(U, N, V) = \Omega_1(U_1, N_1, V_1)\Omega_2(U_2, N_2, V_2)$ where total volume and particle number are fixed.

For maximum:

$$\mathrm{d}\Omega = 0 = \left(\frac{\partial\Omega_1}{\partial U_1}\right) \mid_{V_1,N_1} \Omega_2 dU_1 + \left(\frac{\partial\Omega_2}{\partial U_2}\right) \mid_{V_2,N_2} \Omega_1 dU_2$$

and $dU = 0 = dU_1 + dU_2$

$$\succ \frac{1}{\Omega_1} \left(\frac{\partial \Omega_1}{\partial U_1} \right) \mid V_1, N_1 = \frac{1}{\Omega_2} \left(\frac{\partial \Omega_2}{\partial U_2} \right) \mid V_2, N_2$$

$$\succ \left(\tfrac{\partial ln\Omega_1}{\partial U_1} \right) \mid V_1, N_1 = \left(\tfrac{\partial ln\Omega_2}{\partial U_2} \right) \mid V_2, N_2$$

Now we recall the central equation of thermodynamics.