Statistical Thermodynamics

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General Terminology

<u>KEY</u>

- E or U = internal energy
- Q = heat added
- W = work (done by the system)
- S = entropy
- m = mass
- c = specific heat
- Omega = number of micro states

Specific Heat

$$\mathbf{Cv} = \left(\frac{\mathbf{dQ}}{\mathbf{dT}}\right)_{\mathbf{v}} = \frac{\mathbf{3}}{\mathbf{2}} \mathbf{k}_{\mathbf{b}}$$
 $\mathbf{Cp} = \left(\frac{\mathbf{dQ}}{\mathbf{dT}}\right)_{\mathbf{p}} = \frac{\mathbf{5}}{\mathbf{2}} \mathbf{k}_{\mathbf{b}}$

Conservation of Energy	dU = dQ - d W
<u>Work</u>	$\mathbf{dW} = \mathbf{P} \star \mathbf{dV}$
<u>Heat</u>	$Q = \mathbf{mC} \Delta \mathbf{T}$ $dQ = dS \star \mathbf{T}$
Entropy	$dS = \frac{dQ}{T}$
	$\mathbf{s} = \mathbf{k}_{\mathbf{b}} \mathbf{ln} (\mathbf{\Omega})$

Definitions

Ideal gases

Symbol	Name	Units
Р	Pressure	P = F/A ,atm,
V	Volume	L , m^3
n	# of Mole	1/Na
R	Gas Constant	8.3145 J/(mol*K)
N	# of molecules	1+
К	Boltzmann constant	1.38065*10^-23 J/K
Т	Temperature	Kelvin

Equation of state for ideal gas

$$PV = nRT = N k_b T$$

Internal energy of monoatomic molecule

$$\mathbf{E} = \frac{3}{2} \mathbf{N} \mathbf{k}_{\mathbf{b}} \mathbf{T}$$

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Ideal gases

To find Vrms, Set kinetic energy = internal energy

$$\frac{1}{2} \mathbf{M} \mathbf{v}^{2} = \frac{3}{2} \mathbf{N} \mathbf{k}_{b} \mathbf{T}$$
$$\mathbf{v}^{2} = \frac{3}{M} \mathbf{N} \mathbf{k}_{b} \mathbf{T}$$
$$\mathbf{v} = \sqrt{\frac{3}{M} \mathbf{N} \mathbf{k}_{b} \mathbf{T}}$$

Important Thermodynamic Processes

- Isobaric
 - Constant pressure dP=0 [barometer]
- Isothermal
 - constant T, dT=0
- <u>Isochoric</u>
 - constant V, dV=0 [choros = space]
- <u>Adiabatic (isolated process)</u> dQ=0, no exchange between the system and its surroundings.

For Adiabatic Expansion, the expressions to the right are equal to a constant



 $\frac{\text{Adiabatic constant}}{\alpha = \frac{Cp}{Cv} = \frac{5}{3}}$

Important Thermodynamic Processes

<u>(cont.)</u>

- <u>Reversible</u>
 - proceeds in infinitesimal step such that each step can be reversed.
 - I.E. adding an infinitesimal amount of heat
- <u>Quasistatic</u>
 - process that happens infinitely slow such that the system is always at equilibrium
 - All Reversible processes are Quasistatic, but some quasistatic processes can be non-reversible
- Isentropic aka revisable adiabatic
 - All Adiabatic processes that are reversible must have a dS=0
 - Warning, the GRE is known to simply say "adiabatic" and mean reversible adiabatic



• Free Expansion

- This is an adiabatic process and NOT reversible in which the gas does no work
- PV=P'V' dU=0, dQ=0
- Therefore NkT=Constant

Statistical Mechanics

Methodology

- 1. Specify the macrostate and accessible microstates of the system
- 2. Choose the ensemble
- 3. Calculate the mean values and other statistical values

Macrostate

3 non interacting spins in magnetic field B

$$f$$
 $Etotal = -\mu B$, N = 3

Microstates

 $E = -\mu B$, $\Omega = 3$, $P_s = 1/\Omega$

 $E = -\mu B$ $E = \mu B$

Statistical properties

$$< Q > = \sum_{i=1}^{3} P_i Q_i$$
 $< S_1 > = \sum_{i=1}^{3} P_i S_{1,i} = (1/3) [2 (+1)+1 (-1)] = \frac{1}{3}$ (Average value of spin 1)

 $P_{1,\uparrow} = \frac{2}{3} \qquad P(2,\uparrow|1,\uparrow) = \frac{1}{2} \qquad (\text{Probability that if spin 1 is} \\ \text{up then spin 2 is also up}) \qquad P(2\uparrow\text{and }1\uparrow) = P_{1,\uparrow} * P_{2,\uparrow} = \frac{2}{3} * \frac{2}{3} = \frac{4}{9}$

Canonical Ensemble (fixed T, V, and N)

The system of interest is in contact with heat bath, which is sufficiently large that it's not affected by the smaller system

 $E_{\text{total}} = E_b + E_s$ where $E_s << E$

Macrostate:E, V, NMicrostates:For a given microstate of the system the heat bath can be in any of
the large number of microstates such that the total energy is E
Number of microstates of heat bath = $\Omega(E - E_s)$

<u>Statistical properties</u>: Probability that the system is in microstate s with energy E_s is given by

 $P_{s} = \frac{1 * \Omega(E - E_{s})}{\sum_{s} \Omega(E - E_{s})} \quad P_{s} \text{ is decreasing function because the larger the value of } E_{s}, \text{ the less the } E_{b} \text{ is}$ $P_{s} = \frac{1}{Z} e^{-\beta E_{s}} \text{ (Boltzmann distribution), } \qquad \text{where } \beta = \frac{1}{KT} \quad \text{and} \quad Z = \text{sum over states or partition function}$

$$\sum_{S} P_{S} = 1 \quad \text{so} \quad Z = \sum_{S} e^{-\beta E_{S}} \quad \text{and} \quad P_{S} = \frac{e^{-\beta E_{S}}}{\sum_{S} e^{-\beta E_{S}}}$$

Now since we have the probability distribution, we can find mean values and other stats

$$=\sum_{s} P_{s}E_{s} = \frac{1}{Z}\sum_{s} E_{s}e^{-\beta E_{s}} = -\frac{\partial}{\partial\beta}\ln Z \quad \text{similarly} \quad =\frac{1}{Z}\frac{\partial^{2}Z}{\partial\beta^{2}}, \quad C_{\nu}=\frac{\partial }{\partial T} = \quad [-^{2}]$$

Free energy = $F = -KT \ln Z$ $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$

Aside: $S = k \ln \Omega$

Partition Function Example

Consider a system consisting of two distinguishable particles. Each particle can be in one of the two microstates with single particle energies 0 and Δ . The system is in equilibrium with a heat bath at temperature T. What are the thermodynamic properties of the system?

Microstates: (0,0), (0, Δ), (Δ , 0), (Δ , Δ) $Z_{2} = \sum_{s=1}^{4} e^{-\beta E_{s}} = 1 + e^{-\beta \Delta} + e^{-\beta \Delta} + e^{-2\beta \Delta} = (1 + e^{-\beta \Delta})^{2} \quad \text{(Partition function for two particles)}$ $Z_{1} = \sum_{s=1}^{2} e^{-\beta * 0} + e^{-\beta \Delta} = 1 + e^{-\beta \Delta} \quad \text{(Partition function for one particle)}$ $Z_{2} = Z_{1}^{2} \quad \text{and in general} \quad Z_{n} = Z_{1}^{n} \quad \text{for distinguishable particles}$

So since Z_2 is related to Z_1 so we can consider the statistical properties of the system consisting of one particle with Z_1

$$P_1 = \frac{e^{-\beta * 0}}{Z_1} = \frac{1}{1 + e^{-\beta \Delta}} \quad (\text{probability that a particle has energy 0}) \qquad , \qquad P_2 = \frac{e^{-\beta \Delta}}{Z_2} = \frac{e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}$$

 $\langle e \rangle = \sum_{s=1}^{2} P_s \epsilon_s = \frac{\Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}$ and $\langle E \rangle = 2 \langle e \rangle$ and in general for *N* distinguishable particles $\langle E \rangle = N \langle e \rangle$

<u>Partition function of simple harmonic oscillator</u>: $\epsilon_n = \left(n + \frac{1}{2}\right)h\omega$

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta h \omega (n+1/2)} = \frac{e^{-\beta h \omega/2}}{1 - e^{-\beta h \omega}}$$

Law of Thermodynamics

- <u>Zeroth</u>: If two systems are each in thermal, mechanical, and/or diffusive equilibrium with a third system, then they are all in equilibrium with each other.
- <u>First:</u> Conservation of Energy
 - $dE = dQ dW + \mu dN = SdT pdV + \mu dN$
- <u>Second</u>: $dS \ge 0$ i.e. Entropy is always increases

$$-\Delta S \ge \int \frac{\delta Q}{T}$$

• <u>Third:</u> S(0 K) = 0

Heat Capacity

• Isochoric
$$\rightarrow C_p = \frac{1}{n} \left(\frac{dQ}{dT} \right)_p$$

$$-C_p = \frac{5}{2}Nk_B$$

• Isobaric
$$\rightarrow C_V = \left(\frac{1}{n}\frac{\delta Q}{\delta T}\right)_V$$

 $-C_V = \frac{3}{2}Nk_B$

•
$$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$$

Einstein and Debye

- Einstein
 - Each particle is a simple harmonic oscillator
 - Used for low temperature systems
- Debeye
 - Considered the density of states instead of assuming atoms have same E
 - Found correct behavior as $T \rightarrow 0$
 - where

Practical Use of Specific Heat

$$\Delta Q = nC_V \Delta T$$
$$nC_V \Delta T$$
$$\int nC_V \partial T = \int \partial Q$$

P-V Diagrams

- Isothermal Constant temperature
- Isobaric Constant pressure
- Adiabatic No energy transferred as heat $- PV^{\gamma} = const$
- Isochoric Constant volume
- Isentropic Both adiabatic and reversible
 - $-\Delta S = 0$
 - Some past GREs assume adiabatic is reversible.



More Terminology for P-V

• Free Expansion – Gas suddenly expands

- pV = p'V'

- Quasistatic Process Happens infinitely slowly
 - Always in thermodynamic equilibrium
 - Reversible processes are always quasistatic
- Reversible Process
 - System is at equilibrium at each step of process
 - Process can be reversed by changing the state of system
 - $\ \partial W = P dV$

$$-\Delta S = \int \frac{dQ}{T}$$

- Note: If dQ < 0, dS is negative

Carnot Engine

- Ideal engine
 - Reversible
- Cycle:
 - Isothermal Expansion
 - Adiabatic Expansion
 - Isothermal Compression
 - Adiabatic Compression

•
$$W = Q = \int T dS = (T_H - T_C)(S_2 - S_1)$$

Work is area inside T-S or P-V diagram



Efficiency

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

Helmholtz Free Energy

Thermodynamic potential that measures maximum reversible work obtainable from a closed system at a constant temperature

U= Internal Energy S=Entropy

For the isothermal change from one state to another:

We can then describe the system as spontaneous (F<0), at equilibrium (F=0), and Nonspontaneous (F>0)

Gibbs Free Energy and Enthalpy

Thermodynamic potential calculates maximum reversible work from a closed system at a constant temperature and pressure

$$G = U - TS + pV$$

The same concepts in Helmholtz energy apply here

 $G = \Delta U - T\Delta S + p\Delta V$

Enthalpy is the measurement of the total energy of a thermodynamic system

H = U + pV

Blackbodies

Total power emitted by a blackbody:

 $P = \sigma \epsilon A T^4$



Using Wein's displacement Law:

$$\lambda_{max} = \frac{2.9 * 10^{-3} m * K}{T}$$

Planck distribution for intensity of light emitted by a blackbody.

$$I(f,T) = \frac{2hf^{3}}{c^{2}} * \frac{1}{\frac{hf}{e^{kT} - 1}}$$

Phase Diagram



Triple Point: Point at which the T and p of a substance cause a thermodynamic equilibrium in which all three phases coexist.

Critical point: Point at which liquid and vapor phases coexist, past which a supercritical fluid exists.