Revision

19 January 2012
11:01

Tip:

Revise in detail ALL the QM exercises done in class.

Basic concepts (part A in particular)

- 3 laws of thermodynamics
- State function
- Thermodynamic potential
- Maxwell relations (8 of them)
  (Remember minus signs!)
- Ensembles:
  - Microcanonical
  - Canonical
  - Grand Canonical
- Quantum gas - Distributions
- Equipartition theorem
- Chemical potential (μ)

QM vs Classical

1. Role of h and it's meaning
2. Gibbs paradox - Factor of $\frac{1}{N!}$
3. Third law
4. Violations of equipartition theorem

Practical level

Classical	QM
Phase-state Γ	Discrete
Hamiltonian H	Energy
$H{:}\,\Gamma$	Levels
Integrals $\leftrightarrow$	Resum series (eg. exponential,
	geometric, arithmetic)

Microcanonical

Classical

$$\Omega = \frac{1}{h^N N!}\int_{E<H<E+\Delta} d^{3N}q\, d^{3N}p$$

Careful about $N!$

Integral depends on what it is

Quantum

Ω =number of different configurations at microscopic level yielding the same macroscopic quantities (E,N,V)

Compute entropy

$S = k \ln \Omega$

When possible, invert

$S(E) \rightarrow E(S)$

Use maxwell relations

$$T = \frac{\delta E(S)}{\delta S} = \left(\frac{\delta S(E)}{\delta E}\right)^{-1}$$

$$P = -\frac{\delta E}{\delta V}$$

$$C_V = \frac{\delta E}{\delta T}$$

Canonical (partition function)

Classical

$$Z_N = \frac{1}{N!\,h^N}\int_\Gamma d^{3N}q\; d^{3N}p\; e^{-\beta H}$$

$d^{3N}q\; d^{3N}p$ must be generalized to appropriate Γ

Careful with N!

No constraint on integral

Quantum

$$Z_N = \sum_{\{\hat{m}_k\}} e^{-\beta \sum_k \hat{m}_k \hat{\epsilon}_k}$$

$\hat{\epsilon}_k$ energy levels

$\hat{m}_k$ occupation number

How many possible on this level

Σ_k sum over levels

$\{\hat{m}_k\}$ Summation over all possible choices of occupation number

Compute

$$F = -kT \ln Z_N$$

Maxwell

$$S = -\frac{\delta F}{\delta T}$$

$$P = -\frac{\delta F}{\delta V}$$

Use

$$F = U - TS$$

$$U = E$$

Grand Canonical

- Write (possibly compute) Z_N

  QM or classical determines partition function
- Define

  $$Z = \sum_N z^N Z_N$$

  Z= grand partition function

  Z_N =partition function

  z^N =Fugacity $z = C^{\beta\mu}$

  Substitute in ONLY at very end

  Σ_N = sum over all possible number of particles
- Equation of state

  $$\frac{PV}{kT} = \ln Z$$
- Average number of particles

  $$< N > \;= z\frac{\delta}{\delta z}\ln Z$$
- Internal energy

  $$E = U =< H > \;= -\frac{\delta}{\delta\beta}\ln Z$$

  $$Z = Z(\beta, z)$$

2009 past paper

A1:

1st law differential form

$dU = T\,dS - P\,dV$
$dU = \delta Q - \delta W$
δQ not a differential
Helmoltz
$F = U - TS$
$dF = d(U - TS)$
$= TdS - PdV - TdS - SdT$
$= -SdT - PdV$
Maxwell relations because <u>dF is exact</u>

$$dF = \left(\frac{\delta F}{\delta T}\right) dT + \left(\frac{\delta F}{\delta V}\right) dV$$

$$\Rightarrow \begin{cases} S = -\dfrac{\delta F}{\delta T} \\ P = -\dfrac{\delta F}{\delta V} \end{cases}$$

A2: Photon gas

$$F = -\frac{a}{3} VT^4$$

Maxwell relations

$$S = -\frac{\delta F}{\delta T} = \frac{4a}{3} VT^3$$

$$P = -\frac{\delta F}{\delta V} = \frac{1}{3} aT^4$$

$$U = E = F + TS = -\frac{a}{3} VT^4 + \frac{4}{3} aVT^4 = aVT^4$$

EQ of state: Relation between microscopic quantities
P,V,E in this case

$$PV = \frac{1}{3} aVT^4$$

$$\Rightarrow \boxed{PV = \frac{1}{3} E}$$

Adiabatic transformation: Reversible and $\delta Q = 0$
Remember that $dS = \frac{\delta Q}{T}$

$$\Rightarrow dS = 0$$

$$d\left(\frac{4}{3} aVT^3\right) = 0 \Rightarrow VT^3 = constant$$

$$P = \frac{a}{3} T^4 \Rightarrow \boxed{VP^{\frac{3}{4}} = constant}$$

A3
Chemical potential

$$\mu = \frac{\delta F}{\delta N}$$

Assume F independent of N

$$\Rightarrow \mu = 0$$

Number of particles is not fixed by physics considerations

<u>2011</u>

A1

$$< \hat{m} > \frac{1}{-1 + e^{\beta(\epsilon - \mu)}}$$

Bose-Einstein

$$< \hat{m} > \frac{1}{e^{\beta(\epsilon - \mu)}}$$

Maxwell-Boltzmann

$$< \hat{m} > \frac{1}{1 + e^{\beta(\epsilon - \mu)}}$$

Fermi-Dirac

Microscopic Fundamental difference

Bose-Einstein: Obeyed by bosons for which the wave-function is symmetric under exchange of identical particles
Fermi-Dirac: same but anti-symmetric
Maxwell-Boltzmann: Just a model, no physical realization in nature
For fixed β, μ, and large $-\epsilon$ they coincide
In this limit, classical mechanics is a very good approximation