Physics 614

~~o~~ Prof: John Toner (jjt@uoregon.edu)

Send me an e-mail so I can email you notes, problem sets, etc.

Course mechanics:

Grading: Problem Sets: 40%

Take-home Midterm: ~~30~~ 30%

take-home Last exam: 19.9%

Class Participation: 10.1%

Collaboration: <u>Encouraged</u> on Problem Sets

<u>Forbidden</u> (and you <u>will</u> be caught!) on midterm and last exam.

Class Participation: <u>Very</u> important; ~~and~~ worth >> 10.1% in practice (you won't get the other 89.9% without it).

TA: Xiaolu Cheng

Her office hours: 9-10 AM, Thursdays, Klamath 139

Syllabus

I) Grand Canonical ensemble

A) Review

B) Application: Classical ideal gas

C) Energy + Number fluctuations (small)

D) Bosons + Fermions - Occupation numbers

E) Bose - Einstein Condensation

F) Black Body radiation

G) Specific heat of solids

H) Fermi Systems

I) White Dwarf* stars

II) Phase Transitions

A) Clapeyron - Clausius Law

B) Supercooling, Nucleation, et al

C) Finite size effects

III) (If time permits) Magnetic systems

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* - Sorry, "Vertically Challenged Caucasian"

PS1.1

Physics 614, Problem Set #1

Due: In class, 2PM sharp! (No exceptions) Friday, April 11.

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1) For a quantum-mechanical of non-interacting particles ~~ecal~~ in the Grand Canonical ensemble, calculate the probability $p(N)$ that the system has exactly N particles. Express your answer entirely in terms of N and the mean number of particles $\bar{N}$.

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2) Do the same as (1) for a system of classical, but indistinguishable, non-interacting particles all moving in a common potential $V(\vec{r})$.

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3) What is the statistical significance of your answers to problems (1) and (2).

(PS1.2

4) Consider a system of (non-interacting) "N-yons", particles which are between Fermions and Bosons, in the following sense: For "N-yons", the largest number of particles allowed in one quantum-mechanical state is N_{max} independent of the state. ($\infty \geq N_{max} \geq 1$)

a) Find the mean occupation number $\langle n_i \rangle$ of a state with single particle energy ϵ_i.

b) Show that you recover the Fermi result for $\langle n_i \rangle$ if $N_m = 1$.

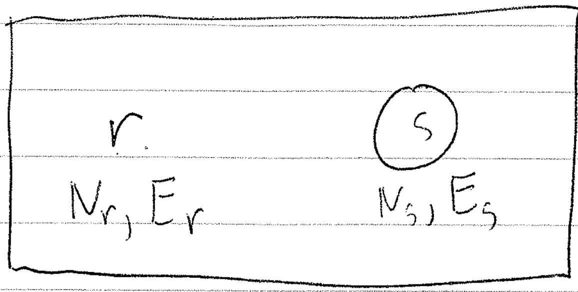
c) Show that you recover the Bose result for $N_m \to \infty$.

~~Make up class: Feb 5 (Monday), 2:47~~

Grand Canonical Ensemble review

Small system s

"reservoir" r



← Total system $(r+s)$ <u>closed</u>

$\Rightarrow$ Microcanonical

Temperature T, chemical potential μ

Can exchange Energy <u>and</u> particles

between r and s

As in canonical Ensemble, seek

P_i : Prob. that s is in <u>one</u> particular

state i with Energy E_i,

Particle # N_i

Constraints: $N_i + N_r = N$ fixed

$E_i + E_r = E$ fixed

By properties of microcanonical ensemble,

$$P_i = \frac{\Omega_r(E-E_i)}{\Omega_T(E)}$$

$$\Rightarrow \left(\frac{\partial \ln P_i}{\partial E_i}\right)_{N_i,V_i} = \left(\frac{\partial \ln \Omega_r(E-E_i)}{\partial E_i}\right)_{N_i,V_i} = -\left(\frac{\partial \ln \Omega_r(E_r)}{\partial E_r}\right)'_{N_i,V_i}\Bigg|_{E_r=E-E_i}$$

$$\underset{\uparrow}{=} -\frac{1}{k_B T_r(E-E_i)}$$

Definition of temperature

$$\underset{\uparrow}{\simeq} -\frac{1}{k_B T_r(E)} = -\frac{1}{k_B T} \quad : \text{independent of } E_s$$

reservoir much bigger than system

$$\cancel{\Rightarrow \ln P_s(E_s) = \ln P_s(E_s=0) - \beta E_s}$$

$$\Rightarrow \boxed{\ln P_i(E_i, N_i) = \ln P_i(E_i=0, N_i) - \beta E_i}$$

Same trick with N_s

$$\left(\frac{\partial \ln P_s}{\partial N_i}\right)_{E_i, V_i} = -\left(\frac{\partial \ln \Omega_r}{\partial N_i}\right)_{E_i, V_i} = \frac{\mu}{k_B T} \equiv -\alpha$$

α independent of N_s, E_s if reservoir "big"

$$\Rightarrow \boxed{\ln P_i(E_i = 0, N_i) = \ln P_s(E_i = 0, N_i = 0) - \alpha N_i}$$

$$\Rightarrow \ln\left(P_i(E_i, N_i)\right) = \ln P_i(0,0) - \alpha N_i - \beta E_i$$

$$\Rightarrow P_i(E_i, N_i) = P_i(0,0)\, e^{-\alpha N_i - \beta E_i}$$

Normalize:

$$\boxed{P_i(E_i, N_i) = \frac{e^{-\alpha N_i - \beta E_i}}{\sum_i e^{-\alpha N_i - \beta E_i}}}$$

Define Grand Canonical Partition function

$$\boxed{\mathcal{Q} = \sum_i e^{-\alpha N_i - \beta E_i}}$$

$$q \equiv \ln\left(\mathcal{Q}(\alpha, \beta, V)\right)$$

As in canonical ensemble, all thermodynamic properties follow from $\mathcal{Q}$; or, equivalently, q.

Aside: Note change of variables between different ensembles:

Microcanonical: $\Omega(E, N, V)$

Canonical: $Z(T, N, V)$

Grand Canonical: $\mathcal{Q}(T, \mu, V)$ $\left(\alpha = \frac{\mu}{k_B T}, \beta = \frac{1}{k_B T}\right)$

Advantages: 1) Easier to control T, μ than E, N

2) Calculational: e.g.: $\cancel{P = \frac{\partial E}{\partial}}$

Microcanonical: $dE = TdS - PdV + \mu dN \Rightarrow P = -\left(\frac{\partial E}{\partial V}\right)_S$ ← hard

Canonical: $F(T, N, V) \Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$: easy

Deriving thermodynamic quantities from $\mathcal{Q}$ or q:

$\bar{N}$ = average # of particles

$$= \sum_i N_i P_i = \frac{\sum_i N_i e^{-\alpha N_i - BE_i}}{\mathcal{Q}}$$

$$= -\left(\frac{\partial}{\partial \alpha} q\right)_{B,V} = -\left(\frac{\partial}{\partial \alpha}\left(\ln\left(\sum_i e^{-\alpha N_i - BE_i}\right)\right)\right)_{B,V}$$

$\bar{E}$ = average energy = $-\left(\frac{\partial q}{\partial B}\right)_{\alpha, V} = \dfrac{\sum_i E_i e^{-\alpha N_i - BE_i}}{\mathcal{Q}}$

Does q directly (without derivatives) give us anything? Yes:

6.6

$$dq = \underbrace{\left(\frac{\partial q}{\partial \alpha}\right)_{\beta, V}}_{= -\bar{N}} d\alpha + \underbrace{\left(\frac{\partial q}{\partial \beta}\right)_{\alpha, V}}_{= -\bar{E}} d\beta - \beta \left[\frac{\sum_i \frac{\partial E_i}{\partial V} e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}} \right] dV$$

$$= \left(\frac{\partial \bar{E}}{\partial V}\right)_{\alpha, \beta} = -P$$

$$\Rightarrow \boxed{dq = -\bar{N}\, d\alpha - \bar{E}\, d\beta + \beta P\, dV}$$

~~Consider~~

$$\Rightarrow d(q + \alpha \bar{N} + \beta \bar{E}) = \alpha\, d\bar{N} + \beta\, d\bar{E} + \beta P\, dV$$

$$= \beta(-\mu\, d\bar{N} + d\bar{E} + P\, dV)$$

$$= \beta(-\mu\, d\bar{N} + T\, dS - P\, dV + \mu\, d\bar{N} + P\, dV)$$

$$= \frac{dS}{k_B}$$

$$\Rightarrow \boxed{q = -\alpha \bar{N} - \beta \bar{E} + \frac{S}{k_B} + \text{constant}}$$

Now, Seemingly irrelevant aside:

Gibbs Free Energy:

$$G \equiv \bar{E} - TS + PV = G(\bar{N}, T, P)$$

$$dG = d\bar{E} - TdS - SdT + PdV + VdP$$

$$= \cancel{TdS} - \cancel{PdV} + \mu d\bar{N} - \cancel{TdS} - SdT + \cancel{PdV} + VdP$$

$$= -SdT + VdP + \mu d\bar{N}$$

$$\Rightarrow \left(\frac{\partial G}{\partial \bar{N}}\right)_{T,P} = \mu$$

Extensivity $\Rightarrow$ $G(\bar{N}, T, P) = \bar{N} f(T,P)$

$$\Rightarrow \left(\frac{\partial G}{\partial \bar{N}}\right)_{T,P} = f(T,P) = \mu$$

$$\Rightarrow \boxed{G = \bar{N}\mu}$$

$$\cancel{\Rightarrow q = BG - B\bar{E} + BTS = B(G - \bar{E} + TS) =}$$

$$\cancel{\Rightarrow q = BG - B\bar{E} + BTS = B(G - \bar{E} + TS)}$$

$$\Rightarrow q = BG - B\bar{E} + \frac{S}{k_B} + \text{constant}$$

$$= B(G - \bar{E} + TS) + \text{constant} = BPV + \text{Constant}$$

$$\Rightarrow \boxed{q = \frac{PV}{k_B T} + \text{Constant}} \quad \boxed{*}$$

Evaluating constant : let $\alpha \to \infty$

$$q = \ln\left(\sum_i e^{-\alpha N_i - BE_i}\right) \to \ln\left(e^{-BE(N_i=0)}\right) = \ln(e^{-0}) = 0$$

$$\bar{N} \to 0 \Rightarrow \frac{PV}{k_B T} \to 0$$

$$\Rightarrow * \Rightarrow 0 = 0 + \text{Constant} \Rightarrow \boxed{\text{Constant} = 0}$$

$$\Rightarrow \boxed{q = \frac{PV}{k_B T}}$$

~~Other thermodynamic quantities~~

$$\cancel{F = G - PV = \bar{N}\mu - PV = \bar{N}\mu - k_B T q}$$

$$\cancel{\bar{E} = -\left(\frac{\partial q}{\partial B}\right)_{\alpha,V} = -\left(\frac{\partial q}{\partial T}\right)_{\alpha,V}\frac{dT}{dB} = k_B T^2\left(\frac{\partial q}{\partial T}\right)_{\alpha,V}}$$

~~Useful quantity:~~

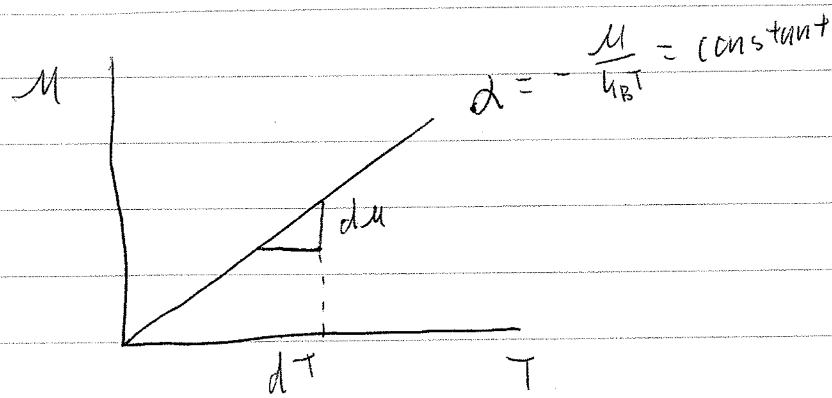
Other thermodynamic Quantities

$$F = G - PV = \bar{N}\mu - k_B T q = -k_B T(\alpha \bar{N} + q)$$

$$\bar{E} = -\left(\frac{\partial q}{\partial \beta}\right)_{\alpha,V} = -\left(\frac{\partial q}{\partial T}\right)_{\alpha,V} \frac{dT}{d\beta} = k_B T^2 \left(\frac{\partial q}{\partial T}\right)_{\alpha,V}$$

$$S = \frac{E-F}{T} = k_B \left[T\left(\frac{\partial q}{\partial T}\right)_{\alpha, V} - \frac{\bar{N}\mu}{k_B T} + q \right]$$

$$\left(\frac{\partial q}{\partial T}\right)_{\alpha, V} = \left(\frac{\partial q}{\partial T}\right)_{\mu, V} + \left(\frac{\partial q}{\partial \mu}\right)_{T, V}\left(\frac{\partial \mu}{\partial T}\right)_{\alpha, V}$$



$$\left(\frac{\partial q}{\partial \mu}\right)_{T, V} = \left(\frac{\partial q}{\partial \alpha}\right)_{T, V}\left(\frac{\partial \alpha}{\partial \mu}\right)_{T, V} = \frac{1}{k_B T}\left(-\left(\frac{\partial q}{\partial \alpha}\right)_{T, V}\right) = \frac{\bar{N}}{k_B T}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_{\alpha, V} = -k_B \alpha = \frac{\mu}{T}$$

$$\Rightarrow \left(\frac{\partial q}{\partial T}\right)_{\alpha, V} = \left(\frac{\partial q}{\partial T}\right)_{\mu, V} + \frac{\mu \bar{N}}{k_B T^2}$$

$$\Rightarrow S = k_B \left[T\left(\frac{\partial q}{\partial T}\right)_{\mu, V} + \frac{\mu \bar{N}}{k_B T} - \frac{\bar{N}\mu}{k_B T} + q \right]$$

$$\Rightarrow \boxed{S = k_B\left(\frac{\partial}{\partial T}(Tq)\right)_{\mu, V}} = k_B\left(\frac{\partial}{\partial T}\left(\frac{PV}{k_B}\right)\right)_{\mu, V}$$

$$= V\left(\frac{\partial P}{\partial T}\right)_{\mu, V}$$

Convenient rewriting of $\mathcal{Q}$: $\left(\alpha \equiv \frac{\mu}{k_B T}\right)$

Define <u>fugacity</u> $y \equiv e^{-\alpha} = e^{\frac{\mu}{k_B T}}$

$$\mathcal{Q} = \sum_i e^{-\alpha N_i - \beta E_i} = \sum_{N=0}^{\infty} y^N \left(\sum_i{}_N e^{-\beta E_i} \right)$$

where $\sum_i{}_N$ = sum over all states with a <u>given</u> N

$\Rightarrow \sum_i{}_N e^{-\beta E_i} = Z$ = canonical partition function

$$\Rightarrow \boxed{\mathcal{Q}(y, T, V) = \sum_{N=0}^{\infty} y^N Z(N, T, V)}$$

Example: Arbitrary Classical Ideal Gas

Canonical Partition function:

$$\boxed{Z(N,V,T) = \frac{V^N f^N(T)}{N!}} \quad (1)$$

For instance: 1) Mono-atomic gas, $f(T) = \left(\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2mk_BT}}\right)^3$

$$= C\,T^{3/2}$$

(C = constant)

2) Diatomic gas, rotational degrees of freedom only,

$$f(T) = C\,T^{3/2} \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\frac{\hbar^2 \ell(\ell+1)}{2Ik_BT}}$$

$$\to C'\,T^{5/2} \quad \text{as } T \to \infty$$

(C' = another constant)

Quite frequently, $f(T) \propto T^n$

So, from (1), Grand Canonical Partition Function: $y = e^{-\alpha}$

$$\mathcal{Q} = \sum_{N=0}^{\infty} y^N Z(N,V,T) = \sum_{N=0}^{\infty} \frac{[y V f(T)]^N}{N!}$$

$$= e^{y V f(T)}$$ (Sum is just Taylor series for e^x with $x = y V f(T)$)

$$\Rightarrow q = \ln \mathcal{Q} = y V f(T)$$

$$\Rightarrow \bar{N} = -\left(\frac{\partial q}{\partial \alpha}\right)_{T,V} = -\left(\frac{\partial q}{\partial y}\right)_{T,V}\left(\frac{\partial y}{\partial \alpha}\right)_{T,V} = e^{-\alpha}\left(\frac{\partial q}{\partial y}\right)_{T,V}$$

$$= y\left(\frac{\partial q}{\partial y}\right)_{T,V} = y V f(T) = q = \frac{PV}{k_B T}$$

Fundamental result of Grand canonical Partition function

$$\Rightarrow PV = \bar{N} k_B T$$: Ideal gas law (again, damn it!)

Also $\bar{N} = q$

Other Thermodynamic Functions:

$$\bar{E} = k_B T^2 \left(\frac{\partial q}{\partial T}\right)_{\alpha, V} = k_B T^2 \left(\frac{\partial q}{\partial T}\right)_{y, V} = k_B T^2 V y f'(T)$$

$$= k_B T^2 \left(V y f(T)\right) \frac{f'(T)}{f(T)} = \bar{N} k_B T^2 \frac{f'(T)}{f(T)}$$

If $f(T) \propto T^n$ (always is in "classical" limit)

Then $\bar{E} = \bar{N} k_B T^2 \left(\frac{n}{T}\right) = n \bar{N} k_B T$

Ex: monoatomic gas: $n = \frac{3}{2}$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = n \bar{N} k_B$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}(\bar{E} + PV)\right)_p = \left(\frac{\partial}{\partial T}\left(n \bar{N} k_B T + \bar{N} k_B T\right)\right)_p$$

$$= (n+1) \bar{N} k_B$$

$$\Rightarrow \boxed{\gamma = \frac{C_p}{C_V} = 1 + \frac{1}{n}}$$

Particle Number and Energy Fluctuations in the Grand Canonical Ensemble

Hope: They're small

Result: They are.

$$\text{Usually,} \quad \frac{\sqrt{\overline{(\Delta N)^2}}}{\bar{N}} \propto \frac{1}{\sqrt{\bar{N}}} \to 0 \quad \text{as } \bar{N} \to \infty$$

$$\frac{\sqrt{\overline{(\Delta E)^2}}}{\bar{E}} \propto \frac{1}{\sqrt{\bar{N}}} \to 0 \quad \text{as } \bar{N} \to \infty$$

<u>Except</u>: at phase transitions

$$\text{where} \quad \frac{\sqrt{\overline{(\Delta N)^2}}}{\bar{N}} \propto N^{-\gamma}, \quad \gamma < \frac{1}{2}.$$

(<u>But</u>: always have $\gamma > 0$; in contradiction to Pathria, page 110).

$$\bar{N} = -\left(\frac{\partial q}{\partial \alpha}\right)_{T,V} = \frac{\sum_i N_i e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}}$$

$$\overline{N^2} = \frac{\sum_i N_i^2 e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}}$$

$$\Rightarrow \overline{\Delta N^2} \equiv \overline{(N - \bar{N})^2} = \overline{N^2} - \bar{N}^2$$

$$= \frac{\sum_i N_i^2 e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}} - \left(\frac{\sum_i N_i e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}}\right)^2$$

$$\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{V,T} = -\frac{\sum_i N_i^2 e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}} - \frac{\sum_i N_i e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}^2} \frac{\partial \mathcal{Q}}{\partial \alpha}$$

$$= -\left(\frac{\sum_i N_i^2 e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}} - \left(\frac{\sum_i N_i e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}}\right)^2\right)$$

$$= -\overline{\Delta N^2} \Rightarrow$$

$$\boxed{\overline{\Delta N^2} = -\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{V,T}} \propto \bar{N} \text{ (unless at phase transition)}$$

$$\Rightarrow \frac{\sqrt{\overline{(\Delta N)^2}}}{\bar{N}} \propto \frac{\sqrt{\bar{N}}}{\bar{N}} \propto \frac{1}{\sqrt{\bar{N}}} \to 0$$

$\Rightarrow$ Canonical and Grand Canonical Ensembles Equivalent.

Evaluating $\frac{\partial \bar{N}}{\partial \alpha}$ in terms of more familiar things:

$$G = \bar{E} - TS + PV = F + PV = \mu \bar{N}$$

~~$d(PV) = dG - dF$~~

$$\Rightarrow P\cancel{dV} + VdP - SdT - P\cancel{dV} + \mu dN = \mu \cancel{dN} + N d\mu$$

$$\Rightarrow \boxed{d\mu = \frac{V}{N} dP - \frac{S}{N} dT}$$

$$\boxed{d\mu = v\, dP - s\, dT}, \quad v \equiv \frac{V}{N}, \quad s \equiv \frac{S}{N}$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial v}\right)_T = v\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial P}{\partial (\ln v)}\right)_T$$

$$\left(\frac{\partial \mu}{\partial \bar{N}}\right)_{V,T} = \left(\frac{\partial \mu}{\partial v}\right)_T \left(\frac{\partial v}{\partial \bar{N}}\right)_{V,T} = \left(\frac{\partial P}{\partial (\ln v)}\right)_T \left(-\frac{V}{\bar{N}^2}\right)$$

$$\Rightarrow \frac{\sqrt{\overline{(\Delta N)^2}}}{\bar{N}} \propto \frac{\sqrt{\bar{N}}}{\bar{N}} \propto \frac{1}{\sqrt{\bar{N}}} \to 0$$

$\Rightarrow$ Canonical and Grand Canonical Ensembles Equivalent.

Evaluating $\frac{\partial \bar{N}}{\partial \alpha}$ in terms of more familiar things:

$$G = \bar{E} - TS + PV = F + PV = \mu \bar{N}$$

~~$d(PV) = dG - dF$~~

$$\Rightarrow P\cancel{dV} + VdP - SdT - P\cancel{dV} + \cancel{\mu dN} = \cancel{\mu dN} + N d\mu$$

$$\Rightarrow \boxed{d\mu = \frac{V}{\bar{N}} dP - \frac{S}{\bar{N}} dT}$$

$$\boxed{d\mu = v\, dP - s\, dT}, \quad v \equiv \frac{V}{\bar{N}}, \quad s \equiv \frac{S}{\bar{N}}$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial v}\right)_T = v\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial P}{\partial (\ln v)}\right)_T$$

$$\left(\frac{\partial \mu}{\partial \bar{N}}\right)_{V,T} = \left(\frac{\partial \mu}{\partial v}\right)_T \left(\frac{\partial v}{\partial \bar{N}}\right)_{V,T} = \left(\frac{\partial P}{\partial (\ln v)}\right)_T \left(-\frac{V}{\bar{N}^2}\right)$$

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T} = -\frac{\bar{N}^2}{V}\left(\frac{\partial \ln V}{\partial P}\right)_{T,N}$$

$$\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{V,T} = -k_B T\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = k_B T\frac{\bar{N}^2}{V}\left(\frac{\partial \ln V}{\partial P}\right)_{T,N}^{-1}$$

$$\Rightarrow \boxed{\frac{\overline{\Delta N^2}}{\bar{N}^2} = \frac{k_B T}{V}\left(\frac{\partial \ln V}{\partial P}\right)_{T,N}^{-1} = \frac{k_B T}{V}\kappa_T}$$

κ_T = isothermal compressibility

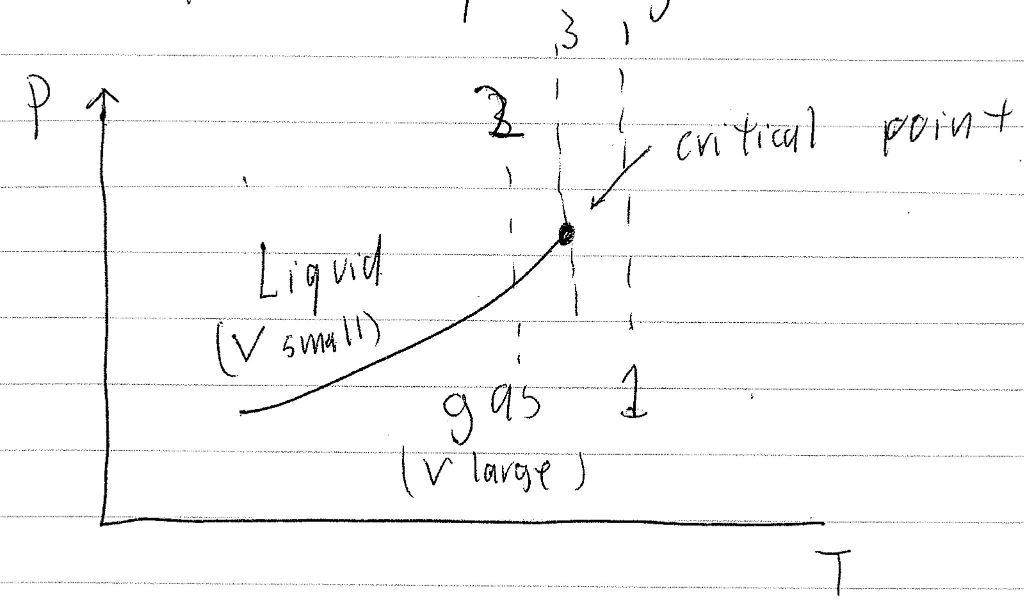
Independent of N

(i.e., intensive)

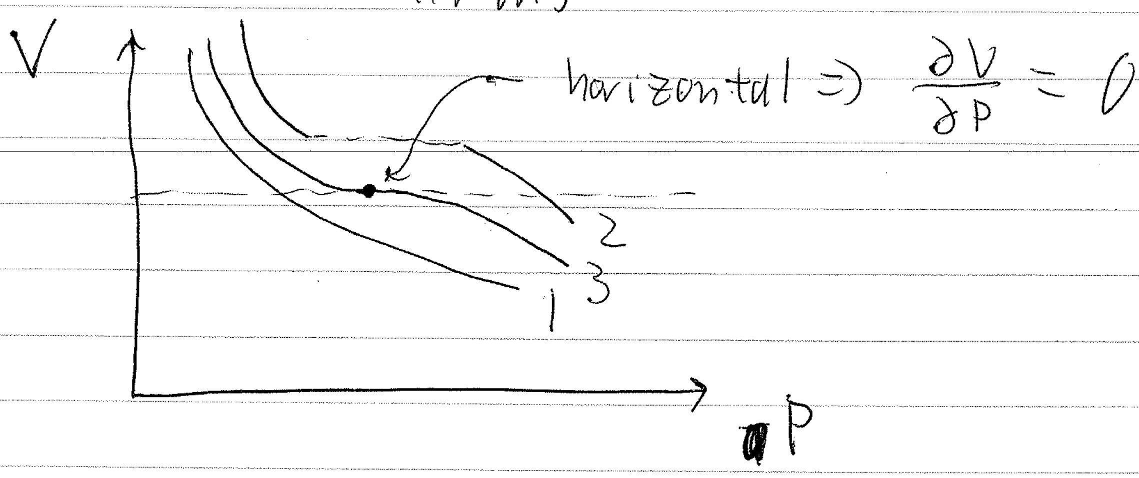
except at phase transitions

At phase transitions:

Example: Liquid-gas transition:



Isotherms:



$\Rightarrow \frac{\overline{\Delta N^2}}{\bar{N}^2} >> \frac{1}{\bar{N}}$ at critical point

In fact,

Find:

$$\frac{\overline{\Delta N^2}}{\bar{N}^2} \propto \bar{N}^{\frac{2-d-\eta}{2d}} \approx \bar{N}^{-\frac{1}{6}}, \quad d=3$$

$(\eta \approx .02)$

$$= \bar{N}^{-\frac{1}{16}}, \quad d=2$$

Non-Interacting Quantum Particles:

Bose-Einstein and Fermi-Dirac Statistics

Consider a system of N non-interacting quantum particles in a system with a set $\{i\}$ of single particle quantum-mechanical states with energies ϵ_i

Note: i labels single particle states, Not overall states of system

State of system specified by occupation numbers $\{n_i\}$

$$N = \sum_i n_i$$

$$E = \sum_i n_i \epsilon_i$$

Bose-Einstein statistics: n_i can be any integer $[0, \infty]$

Fermi-Dirac: $n_i = 0, 1$ (2 particles can't be in same state)

Grand Canonical Partition Function

$$\mathcal{Q} = \sum_{\{n_i=0\}}^{N_m} e^{-\alpha \sum_i n_i - \beta \sum_i n_i \epsilon_i}$$

$$N_m = \begin{cases} 1 & \text{Fermi-Dirac} \\ \infty & \text{Bose-Einstein} \end{cases}$$

$$\mathcal{Q} = \sum_{n_1=0}^{N_m} \sum_{n_2=0}^{N_m} \cdots \sum_{n_L=0}^{N_m} e^{-(\alpha+\beta\epsilon_1)n_1} \, e^{-(\alpha+\beta\epsilon_2)n_2} \cdots e^{-(\alpha+\beta\epsilon_L)n_L}$$

Sum of products = Product of sums

$$\Rightarrow \mathcal{Q} = \left(\sum_{n_1=0}^{N_m} e^{-(\alpha+\beta\epsilon_1)n_1}\right)\left(\sum_{n_2=0}^{N_m} e^{-(\alpha+\beta\epsilon_2)n_2}\right) \cdots \left(\sum_{n_L=0}^{N_m} e^{-(\alpha+\beta\epsilon_L)n_L}\right)$$

$$= \prod_i \left(\sum_{n_i=0}^{N_m} e^{-(\alpha+\beta\epsilon_i)n_i}\right)$$: Simple Factoring

(1)

Aside:

~~Ca~~ Much easier than Canonical Ensemble:

$$Z(N,T,V) = \sum_{\{n_i\}}{}' e^{-\beta \sum_i n_i \epsilon_i}$$

$\sum_{\{n_i\}}{}'$: Sum with constraint $\sum_i n_i = N$ fixed

$\Rightarrow$ Can't treat each sum as independent

In Grand Canonical Ensemble, you can.

That's the payoff of GCE.

Back to (1): Doing independent sums

$$\sum_{n_i=0}^{N_m} e^{-(\alpha+\beta\epsilon_i)n_i} \equiv S_i \quad , \quad \alpha = -\frac{\mu}{k_B T} = -\beta\mu$$

Fermi-Dirac: $N_m = 1$, $S_i = 1 + e^{-(\alpha+\beta\epsilon_i)} = 1 + e^{-\beta(\epsilon_i - \mu)}$

Bose-Einstein: $N_m = \infty$, $\sum_{n_i=0}^{\infty} e^{-(\alpha+\beta\epsilon_i)n_i} = \frac{1}{1-e^{-(\alpha+\beta\epsilon_i)}}$

$$= \frac{1}{1-e^{-\beta(\epsilon_i-\mu)}}$$

$$\Rightarrow \mathcal{Q} = \prod_i \left(1 + \sigma e^{-\beta(\epsilon_i - \mu)}\right)^{\sigma}$$

Single Particle states

$\sigma = +1$ Fermi-Dirac

$ = -1$ Bose-Einstein

Mean occupation numbers:

$$\langle n_i \rangle = \sum_{\{n_j\}} n_i P(\{n_j\})$$

$$= \frac{\sum_{\{n_j\}} n_i e^{-\sum_j (\alpha + \beta\epsilon_j) n_j}}{\mathcal{Q}}$$

$$= -\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Q}}{\partial \epsilon_i}\right)_{\{n_j\}, j\neq i, V, \alpha, T}$$

$$\ln \mathcal{Q} = \sum_i \sigma \ln\left(1 + \sigma e^{-\beta(\epsilon_i - \mu)}\right)$$

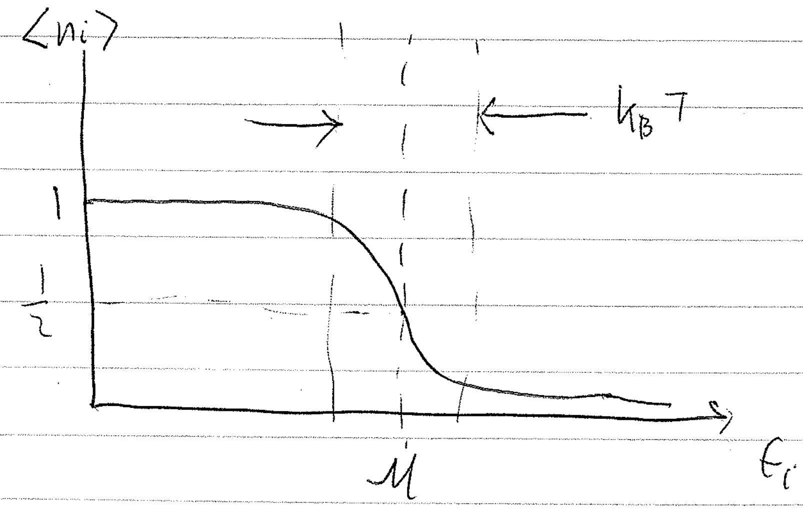
$$\Rightarrow \frac{\partial \ln \mathcal{Q}}{\partial \epsilon_i} = \frac{\sigma\left(-\beta\sigma e^{-\beta(\epsilon_i - \mu)}\right)}{1 + \sigma e^{-\beta(\epsilon_i - \mu)}} = \frac{-\beta\sigma^2}{e^{\beta(\epsilon_i - \mu)} + \sigma}$$

$\sigma = \pm 1$

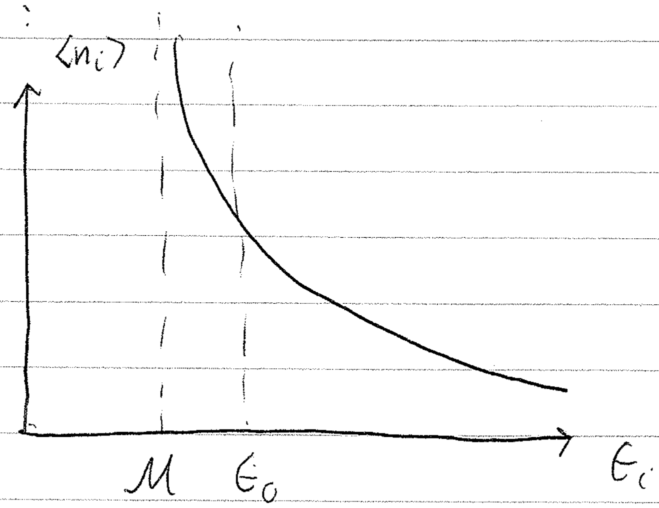
$\Rightarrow \sigma^2 = 1$

$$\Rightarrow \langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 6} = \begin{cases} \dfrac{1}{e^{\beta(\epsilon_i-\mu)}+1}, & \text{Fermi-Dirac} \\[2ex] \dfrac{1}{e^{\beta(\epsilon_i-\mu)}-1}, & \text{Bose-Einstein} \end{cases}$$

Fermi:



Bose:



In both cases, $\mu \uparrow \Rightarrow \langle n_i \rangle \uparrow$, all i

All thermodynamic quantities derivable from $\langle n_i \rangle$

E.g.,

$$\bar{N} = \sum_{\{n_i\}} n_i P(\{n_i\}) = \sum_i \langle n_i \rangle = f(\mu)$$

$$\bar{E} = \sum_{\{n_i\}} n_i \epsilon_i P(\{n_i\}) = \sum_i n_i P(\{n_i\}) \epsilon_i = \sum_i \langle n_i \rangle \epsilon_i$$

Procedure in Practice: know N

choose μ such that $\bar{N} = N$

(i.e., $\mu = f^{-1}(N)$)

Use this μ to calculate $\bar{E}$, P, etc.

Since $\mu \uparrow \Rightarrow \langle n_i \rangle \uparrow$, all i,

$\mu \uparrow \Rightarrow \bar{N} \uparrow$, $E \uparrow$

Example: Arbitrary Classical Ideal Gas

Canonical Partition function:

$$\boxed{Z(N,V,T) = \frac{V^N f^N(T)}{N!}} \quad \boxed{(1)}$$

For instance: 1) Mono-atomic gas, $f(T) = \left(\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2mk_BT}}\right)^3$

$$= C\,T^{3/2}$$

(C = constant)

2) Diatomic gas, rotational degrees of freedom only,

$$f(T) = C\,T^{3/2} \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\frac{\hbar^2 \ell(\ell+1)}{2Ik_BT}}$$

$$\to C'\,T^{5/2} \quad \text{as} \quad T \to \infty$$

(C' = another constant)

Quite frequently, $f(T) \propto T^n$