بسم الله الرحمن الرحیم

جلسه ۱۴۰۰/۹/۳۰

$$\mathcal{Z} = \sum_{N=0}^{\infty} \left(e^{\beta\mu}\right)^N Z(T,V,N) \quad , \quad \underbrace{z \equiv e^{\beta\mu}}_{}$$

میل به ذره خواهی

μ کوچکتر ← ورود ذرات به آن سیستم

Grand Canonical Partition function

{ One can calculate all desired thermodynamical properties. }

☆ Ex 1: Ideal Gas in Grand Canonical Ensemble

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

$$Z(T,V,N) = \frac{\left[Z(T,V,1)\right]^N}{N!}$$

$N!$ ← due to indistinguishability of Particles. (class.)

کلاسیک ← تمیزپذیر بودن

Gibbs Correction

$\boxed{\text{adding by Hand}}$

نقص مدل کلاسیک

$\boxed{\text{Quantum statistics}}$

$$Z(T,V,1) = \frac{V}{\lambda^3}$$

$$\lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \equiv f(T)$$

$$Z(T,V,N) = \left(\frac{V}{\lambda^3}\right)^N \Big/ N!$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{[Z(T,V,1)]^N}{N!} = \sum_{N=0}^{\infty} \frac{[zZ(T,V,1)]^N}{N!}$$

$N=0$ → # of particles

$$\boxed{\mathcal{Z} = \exp(zZ(T,V,1))}$$

Grand Potential

$$\Phi = -K_B T \ln \mathcal{Z} = -PV$$

$$\left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu} = -S$$

$$\frac{\partial \Phi}{\partial V} = -P \Rightarrow K_B T \frac{\partial}{\partial V} \ln \mathcal{Z} = P \Rightarrow \boxed{K_B T \frac{\frac{\partial \mathcal{Z}}{\partial V}}{\mathcal{Z}} = P}$$

Grand Canonic

$$\left.\frac{\partial \Phi}{\partial V}\right|_{T,N} = -P \Longrightarrow \boxed{PV = K_B T \ln \mathcal{Z} = N K_B T}$$

همان چیزی که انتظار داشتیم.

$$\left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V} = -N$$

① $PV = K_B T \ln \mathcal{Z}$

② $\langle N \rangle = N = K_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z}$

③ $E = U = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}$

تا اینجا، یک نتیجه با پیش‌فرض‌های بسیار ساده‌تر
خواص گاز ایده‌آل به دست آمد.

Ex 2: A modification on Grand Canonical Ensemble

Lagrange multiplyer

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} \underbrace{e^{-\alpha\mu N}}_{\text{Particle-exchange}} \underbrace{Z(T,V,N)}_{\text{Energy-Exchange}}$$

ضریب لاگرانژ

$$\mathcal{Z}'(T,P,N) = \sum_{V} \underbrace{e^{-\gamma P V}}_{\text{Volume-Exch}} \underbrace{Z(T,V,N)}_{\text{Energy-Exchan}}$$

$$\rho'_{gc} = \frac{e^{-\beta \mathcal{H} - \gamma P V}}{\mathcal{Z}'}$$

$\gamma = ?$ — $S = \langle -K_B \ln \rho'_{gc} \rangle \longrightarrow \boxed{\gamma = \beta}$

$$\boxed{-K_B T \ln \mathcal{Z}' = G} = \langle \mathcal{H} \rangle + PV - TS$$

New Grand Canonical Partition function

accordingly we achieve Gibbs potential

قبلی $\quad \boxed{-K_B T \ln \mathcal{Z} = \Phi}$

(T,V,N)
(S,P,μ) $\rightarrow$ $\boxed{\text{Gibbs-Duhem Relation}}$

Ex 3 Solid-vapor Equilibrium → تعادل جامد-بخار / تصعید

(a typical statistical model)

Vapor phase

solid

P_g = Vapor pressure at Equilibrium
در وضعیت تعادل ترمودینامیکی فشار بخار بدست آید.

(A)

☆ Vapor Phase ⟶ Ideal Gas ⟶ (کلیه خواص مربوط به گاز ایده‌آل)

(B)

☆ Solid Phase ⟶ Harmonic oscillator

Classic regime

Discrete Regime

static → $P_s = 0$

$P_{os} = 0$

(Gas)

(A) Vapor phase

ذرات آزاد هستند که هموژنی

$$Z(T,V,N) = \frac{[Z(T,V,1)]^N}{N!} \quad , \quad Z(T,V,1) = \frac{V}{\lambda^3} = V f(T)$$

با این کمیت مشکل را حل کنم → $N!$

$\frac{1}{\lambda^3}$

$\to f(T) \sim T^{+3/2}$

General funtionlity to temperature

$T^{3/2}$ م

$$Z_g(T,V,N) = \frac{(V f(T))^N}{N!}$$ ← که مدل نوعی برای گاز بخار

$$\boxed{\mathcal{Z}_g(T,V,\mu) = e^{zVf(T)}}$$ ← برای توصیف گاز بخار

① $P = \frac{k_B T}{V} \ln \mathcal{Z} \to P = z k_B T f(T)$ $PV = N k_B T$

② $N = k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} \to N = zV f(T) \longrightarrow \boxed{z_g = \frac{N_g}{V_g f(T)}}$

③ $E = U = \langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln Z = K_B T^2 \frac{\partial}{\partial T} \ln Z$

$$U = E = z V K_B T^2 f'(T)$$

④ $A = F = U - TS = N K_B T \ln z - z V K_B T f(T)$

⑤ $S = -N K_B \ln z + z V K_B \left[T f'(T) + f(T) \right]$

① ② ③ ④ ⑤ $\longrightarrow$

$$\begin{cases} PV = N K_B T \\ U = N K_B T^2 \dfrac{f'(T)}{f(T)} = \dfrac{3}{2} N K_B T \\ C_V = N K_B \dfrac{2T f(T) f'(T) + T^2 \left[f(T) f''(T) - f'(T)^2 \right]}{(f(T))^2} \end{cases}$$

$f(T) \sim T^{3/2} \rightarrow \boxed{f(T) = \frac{1}{\lambda^3}}$

گاز ایده‌آل استاندارد

$N K_B \frac{3}{2}$

$\frac{3}{2} N K_B T$

$$f(T) \sim T^{3/2} \sim T^{n} \begin{cases} n = 3/2 \\ \mathcal{H} = pc \longrightarrow n = 3 \end{cases}$$

ultra Relativistic Regime

Ⓑ Solid Phase. (localized particle $\rightarrow P_s = 0$)

$\boxed{\text{Harmonic oscillator}}$

$Z(T, V, N) = \left[Z(T, V, 1) \right]^N \longrightarrow$ $\boxed{\text{فرض تمیزپذیر}}$

Recall $Z(T, V, 1) = \begin{cases} \dfrac{1}{\beta \hbar \omega} \longrightarrow \text{class} \\ \dfrac{1}{2 \sinh\left(\frac{\beta \hbar \omega}{2} \right)} \longrightarrow \text{Discrete} \end{cases}$

تابع اجزاء

$$Z(T,V,1) = \varphi(T)$$ فقط تابعی از دماست $\rightarrow (K_B, \hbar, \omega)$

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} \big[\underbrace{z\varphi(T)}\big]^N$$

$z\varphi(T) < 1$

شرط همگرایی

$$\qquad // \quad = \big[1 - z\varphi(T)\big]^{-1}$$

$$PV = K_B T \ln \mathcal{Z} = -K_B T \ln(1 - z\varphi(T))$$

$$\rightarrow P = \frac{-K_B T}{\infty V} \underbrace{\ln(1 - z\varphi(T))}_{\text{عدد محدود}} \overset{?}{=} 0$$

in thermodynamical limit $\left\{\begin{array}{l} N \rightarrow \infty \\ V \rightarrow \infty \end{array}\right.$

$$P = \frac{\text{عدد محدود}}{V} \sim 0$$

$$\boxed{N = K_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \frac{z\varphi(T)}{1 - z\varphi(T)}}$$

$$N_s = \frac{z_s \varphi(T)}{1 - z_s \varphi(T)} \longrightarrow N_s - N_s z_s \varphi(T) = z_s \varphi(T)$$

$$N_s = z_s \varphi(T) + N_s z_s \varphi(T)$$

$$N_s = z_s \varphi(T)\,[1 + N_s]$$

حد ترمودینامیک $\quad \boxed{z_s \varphi(T) = \frac{N_s}{1 + N_s} \simeq 1}$ یک

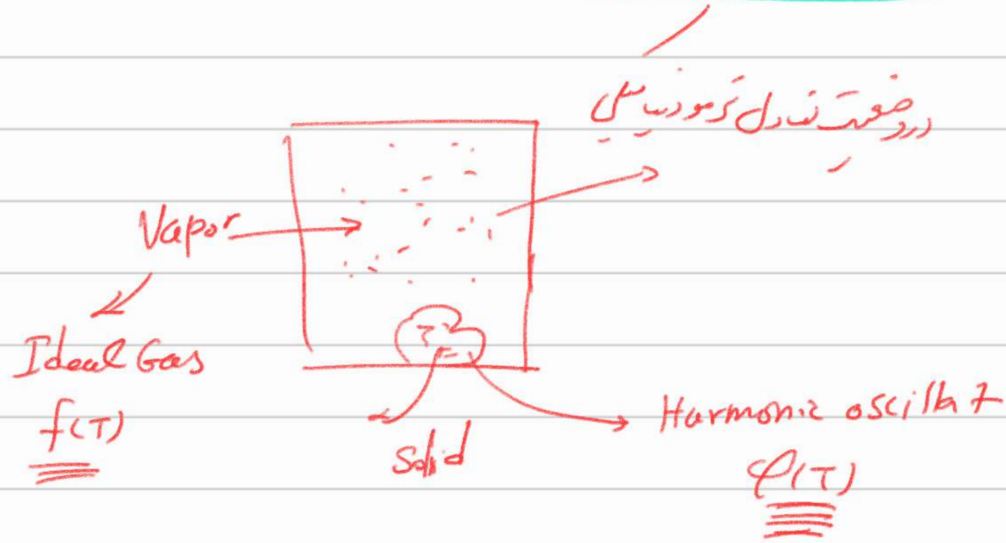
$N_s \gg 1 \rightarrow \boxed{z_s \sim \frac{1}{\varphi(T)}}$ تقریب قابل قبول

$$U = \langle \mathcal{H} \rangle = \frac{z K_B T^2 \varphi'(T)}{1 - z\varphi(T)}$$

$$F = N K_B T \ln z + K_B T \ln(1 - z\varphi(T))$$

$$S = -N K_B \ln z - K_B \ln(1 - z\varphi(T)) + \frac{z k_B T \varphi(T)}{1 - z\varphi(T)}$$

گاز جامد
[illegible]
[illegible]
هستند



A
B
?

$$\frac{\mu_g}{T_g} = \frac{\mu_s}{T_s} \qquad \boxed{\mu_g = \mu_s}$$

$T_g = T_s$

$\mu_g < \mu_s \longrightarrow$ تصعید می‌شود
گاز جامد ← گاز بخار

$\mu_g > \mu_s \longrightarrow$ از گاز ← گاز جامد

$$z = e^{\beta\mu} \longrightarrow \mu_g = \mu_s \qquad \boxed{z_g = z_s}$$

$T_g = T_s$

$$Z_g = \frac{N_g}{V_g f(T)} \quad , \quad Z_s = \frac{1}{\varphi(T)}$$

$$Z_g = Z_s \longrightarrow \frac{N_g}{V_g f(T)} = \frac{1}{\varphi(T)} \Longrightarrow \boxed{\frac{N_g}{V_g} = \frac{f(T)}{\varphi(T)}}$$

شرط تعادل ترمودینامیکی

دمای بحرانی

Critical temperat

$$T > T_c \begin{cases} Z_g < Z_s \\ \mu_g < \mu_s \end{cases} \longrightarrow \frac{N_g}{V_g} < \frac{f(T)}{\varphi(T)}$$

وقتی به سمت فاز گاز

وقتی از فاز جامد به فاز گاز

$$T < T_c \begin{cases} Z_g > Z_s \\ \mu_g > \mu_s \end{cases} \longrightarrow \frac{N_g}{V_g} > \frac{f(T)}{\varphi(T)}$$

وقتی از سمت فاز گاز به سمت

فاز جامد.

$$\frac{N_g}{V_g} = \frac{f(T)}{\varphi(T)}$$

Phenomenological Description

فشار بخار تعادلی

(مدل گاز ایده‌آل)

$$P_g = \frac{N_g K_B T}{V_g} = \frac{f(T)}{\varphi(T)} K_B T \quad e^{-\epsilon_a / K_B T}$$

انرژی گسستگی

Δ'

Δ

Binding Energy in solid phase

$$P_g = K_B T \; e^{-\epsilon_a / K_B T} \; \frac{f(T)}{\varphi(T)}$$

$$* \quad \boxed{P_g = k_B T e^{-\epsilon_a/k_BT}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\left(2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right)^3} \quad *$$

(31) مدل اینشتین ساده اما نتایج سازگاری با آزمایش دارد برای فشار بخار تعادلی

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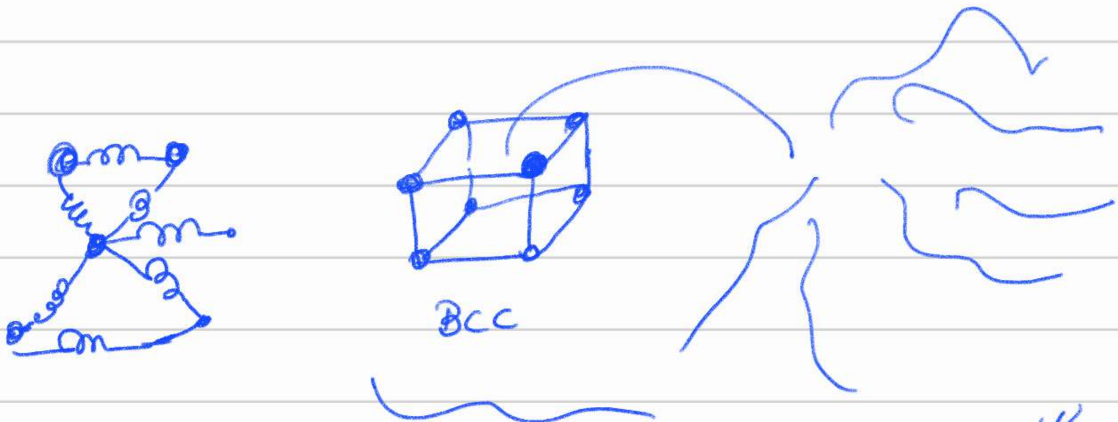
Condensed matter phys



فاز جامد ——— فاز گاز

ϵ_a = Binding Energy

$Q = MC$

↑

گرمای نهان

latent Heat

Ice $T=0$ ⟶ Liquid $T=0$