eg: Cu $\rho \approx 9\,g/cm^3$.

$$T_F \sim \left(\frac{1}{3\times10^{-6}}\times 3\times\frac{9}{64}\times 6\times10^{23}\right)^{\frac{2}{3}}\frac{(6.6\times10^{-34})^2}{8\times9\times10^{-31}\times1.38\times10^{-23}}$$

$$= 8\times10^4 K.$$

$^3He \quad T_F \sim 5k$

$$\langle E\rangle_0 = \int_0^{\mu_0}\varepsilon\rho(\varepsilon)d\varepsilon = \int_0^{\mu_0}d\varepsilon\cdot\frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{3}{2}}$$

$$= \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\cdot\frac{2}{5}\mu_0^{\frac{5}{2}} = \frac{3}{5}N\mu_0 = \frac{3}{5}Nk_BT_F.$$

一般的经典理想气体 $\langle E\rangle \sim \frac{3}{2}NkT$.

而费米气体 $\langle E\rangle_0 \sim \frac{3}{5}NkT_F \quad T_F \gg T$.

但$\langle E\rangle_0$不贡献热容.

2、非零温下的自由电子气.

为了利用 $F'(\varepsilon)$ 的性质，需要分部积分.

定义 $\Phi(\varepsilon) = 2\int_0^{\varepsilon}d\varepsilon'\rho(\varepsilon')\cdot\varepsilon'$

δ函数.

$$\langle E\rangle = \int_0^{\infty}F(\varepsilon)\cdot d\Phi(\varepsilon) = \Phi(\varepsilon)F(\varepsilon)\Big|_0^{\infty} - \int_0^{\infty}\Phi(\varepsilon)\underbrace{F'(\varepsilon)d\varepsilon}.$$

考察 $\Phi(\varepsilon)F(\varepsilon)\Big|_0^{\infty} \quad \Phi(\varepsilon)\sim\varepsilon^{\frac{5}{2}} \quad F(\varepsilon)\sim e^{-\varepsilon}$.

则 $\Phi(\varepsilon)F(\varepsilon)\Big|_0^{\infty} = 0$

则 $\langle E\rangle = -\int_0^{\infty}\Phi(\varepsilon)F'(\varepsilon)d\varepsilon.$ 由于$F'(\varepsilon)$在 $\varepsilon<\mu$ 时迅速下降到0.

$= -\int_{-\infty}^{+\infty}\Phi(\varepsilon)F'(\varepsilon)d\varepsilon.$ 改积分范围为$(-\infty, +\infty)$.

展开 $\Phi(\varepsilon) = \sum_{m=0}^{\infty}\frac{\Phi^{(m)}(\varepsilon)}{m!}\Big|_{\varepsilon=\mu}(\varepsilon-\mu)^m$ 由于$F'(\varepsilon)$为偶函数，所以m取偶数.

则 $\langle E\rangle = \sum_{m=0}^{\infty}\frac{\Phi^{(m)}(\varepsilon)}{m!}\Big|_{\varepsilon=\mu}\underbrace{\int_{-\infty}^{+\infty}[-F'(\varepsilon)](\varepsilon-\mu)^m d\varepsilon}$.

定义此积分为 I_m.

$$-F'(\varepsilon) = \frac{e^{\beta(\varepsilon-\mu)}\beta}{[e^{\beta(\varepsilon-\mu)}+1]^2}$$ 令 $\beta(\varepsilon-\mu)=x$.

则 $$L_m = \beta^{-m}\int_{-\infty}^{+\infty} \frac{e^x}{(e^x+1)^2}x^m dx.$$

$$L_0 = \int_{-\infty}^{+\infty} dx \frac{e^x}{(e^x+1)^2} = -\frac{1}{e^x+1}\Big|_{-\infty}^{+\infty} = 1$$

$$L_2 = (kT)^2\int_{-\infty}^{+\infty} dx \frac{x^2e^x}{(e^x+1)^2} = (kT)^2\cdot\frac{\pi^2}{3}$$

$L_4 \propto (kT)^4$ ← 高阶的最低贡献

之后我们再通过 N 求 μ.（方法仍是分部积分＋展开）

定义 $\Theta(\varepsilon) = 2\int_0^{\varepsilon} d\varepsilon' \rho(\varepsilon')$. 之后的过程类似.

积分可得: $\Phi(\varepsilon) = \frac{8\pi V}{5h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{5}{2}}$ $\quad$ $\Theta(\varepsilon) = \frac{8\pi V}{3h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{3}{2}}$

则 $\Phi^{(2)}(\varepsilon) = \frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}$ $\quad$ $\Theta^{(2)}(\varepsilon) = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\varepsilon^{-\frac{1}{2}}$

$\Phi^{(4)}(\varepsilon) \sim \varepsilon^{-\frac{3}{2}}$ $\quad$ $\Theta^{(4)}(\varepsilon) \sim \varepsilon^{-\frac{5}{2}}$

$$\Rightarrow \langle N\rangle = \frac{8\pi V}{3h^3}(2m)^{\frac{3}{2}}\mu^{\frac{3}{2}} + \frac{\pi V}{h^3}(2m)^{\frac{3}{2}}\mu^{-\frac{1}{2}}\frac{\pi^2}{3}(kT)^2 + O\left[\frac{(kT)^4}{\mu^{\frac{5}{2}}}\right]$$

$$\Rightarrow \langle N\rangle = \frac{8\pi V}{3h^3}(2m)^{\frac{3}{2}}\mu^{\frac{3}{2}}\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2 + O\left(\frac{kT}{\mu}\right)^4\right] = \frac{8\pi V}{3h^3}(2m)^{\frac{3}{2}}\mu_0^{\frac{3}{2}}$$

$\langle N\rangle$ 不随温度变化；因此有 $\langle N\rangle = \langle N\rangle_0$

即 $$\mu = \mu_0\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2 + O\left(\frac{kT}{\mu}\right)^4\right]^{-\frac{2}{3}}$$

$$\approx \mu_0\left[1-\frac{\pi^2}{12}\left(\frac{kT}{\mu_0}\right)^2 + O\left(\frac{kT}{\mu_0}\right)^4\right]$$

可以通过迭代，将 μ 的表达式代入右式后用 $(1+x)^\alpha = 1+\alpha x$.

之后再考察 $\langle E\rangle$

$$\langle E\rangle = \frac{8\pi V}{5h^3}(2m)^{\frac{3}{2}}\mu^{\frac{5}{2}} + \frac{3\pi V}{h^3}(2m)^{\frac{3}{2}}\mu^{\frac{1}{2}}\cdot\frac{\pi^2}{3}(kT)^2 + O\left[\frac{(kT)^4}{\mu^{\frac{3}{2}}}\right]$$

$$= \frac{8\pi V}{5h^3}(2m)^{\frac{3}{2}}\mu^{\frac{5}{2}}\left[1+\frac{5\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+O\left[\left(\frac{kT}{\mu}\right)^4\right]\right]$$ 将 μ 的表达式代入

$\langle E\rangle_0$

$$= \frac{8\pi V}{5h^3}(2m)^{\frac{3}{2}}\mu_0^{\frac{5}{2}}\left[1-\frac{5}{24}\pi^2\left(\frac{kT}{\mu_0}\right)^2+O^4\right]\left[1+\frac{5}{8}\pi^2\left(\frac{kT}{\mu_0}\right)^2+O^4\right]$$

$$= \langle E\rangle_0\left[1+\left(-\frac{5}{24}+\frac{5}{8}\right)\pi^2\left(\frac{kT}{\mu_0}\right)^2+O^4\right]$$

$$= \langle E\rangle_0\left[1+\frac{5}{12}\pi^2\left(\frac{T}{T_F}\right)^2+O^4\right]$$

$$= \frac{3}{5}NkT_F\left[1+\frac{5}{12}\pi^2\left(\frac{T}{T_F}\right)^2+O^4\right]$$

$$C_V = \frac{\pi^2}{2}Nk\frac{T}{T_F}.$$

温度比较高时，自由电子气的热容与金属正离子晶格振动热容 $(3Nk)$ 相比，可以忽略不计.

温度比较低时(趋向于零温)，金属正离子晶格振动热容量 $\propto T^3$，则自由电子气的热容量贡献 $(\propto T)$ 占主要地位。

作业、4.26.

求巨配分函数：

$$\beta pV = \ln \Theta = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\int_0^{+\infty} \underbrace{d\varepsilon\cdot\varepsilon^{\frac{1}{2}}}_{\frac{2}{3}d\varepsilon^{\frac{3}{2}}}\ln\left(1+e^{\beta\mu}e^{-\beta\varepsilon}\right)$$

(利用分部积分) $= \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\cdot \frac{2}{3}\beta\int_0^{+\infty}\varepsilon^{\frac{3}{2}}\frac{e^{\beta\mu}e^{-\beta\varepsilon}}{1+e^{\beta\mu}e^{-\beta\varepsilon}}$

能量平均值 $\langle E\rangle = 2\int_0^{\infty} d\varepsilon\, \rho(\varepsilon)\,\varepsilon F(\varepsilon)$

$$= \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\int_0^{+\infty} d\varepsilon\cdot\varepsilon^{\frac{3}{2}}\frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$

即 $\ln\Theta = \frac{2}{3}\beta\langle E\rangle = \ln\Theta(V,\beta,\beta\mu) = \beta pV \Rightarrow pV = \frac{2}{3}\langle E\rangle$

利用之前 $\langle E\rangle$ 的表达式

$$\ln\Theta = \frac{2}{3}\beta\langle E\rangle = \frac{2}{3}\beta^{-\frac{3}{2}}\frac{8\pi V}{5h^3}(2m)^{\frac{3}{2}}(\beta\mu)^{\frac{5}{2}}\left[1+\frac{5}{8}\pi^2(\beta\mu)^{-2}+O^{-4}(\beta\mu)\right]$$

则 $-\frac{\partial \ln \Theta}{\partial \beta}\Big|_{V,\beta\mu} = \langle E\rangle = -\frac{\partial}{\partial\beta}\beta^{-\frac{3}{2}}\,\Box = \frac{3}{2}kT\cdot\beta^{-\frac{3}{2}}\,\Box = \frac{3}{2}kT\ln\Theta$

(此时 $\beta\mu$ 为整体).

$$\langle N\rangle = \frac{\partial \ln\Theta}{\partial(\beta\mu)}\Big|_{V,\beta} = \frac{2}{3}\beta^{-\frac{3}{2}}\frac{8\pi V}{5h^3}(2m)^{\frac{3}{2}}\left[\frac{5}{2}(\beta\mu)^{\frac{3}{2}} + \frac{5}{8}\pi^2\cdot\frac{1}{2}(\beta\mu)^{-\frac{1}{2}} + O(\beta\mu)^{-\frac{5}{2}}\right]$$

$$= \beta^{-\frac{3}{2}}\frac{8\pi V}{3h^3}(2m)^{\frac{3}{2}}(\beta\mu)^{\frac{3}{2}}\left[1+\frac{\pi^2}{8}(\beta\mu)^{-\frac{1}{2}} + O(\beta\mu)^{-4}\right]$$

与之前的结论相同.

4.18. (a) 证明对于无结构费米子理想气体, 其压强由下式给出

$$\beta p = \frac{1}{\lambda^3}f_{5/2}(z),$$

其中 $z=\exp(\beta\mu)$,

$$\lambda = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2},$$

m 是粒子的质量,

$$f_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty \mathrm{d}x x^2\ln(1+z\mathrm{e}^{-x^2}) = \sum_{l=1}^{\infty}(-1)^{l+1}\frac{z^l}{l^{5/2}},$$

而且化学势和平均密度 $\rho = \langle N\rangle/V$ 之间有关系

$$\rho\lambda^3 = f_{3/2}(z) = \sum_{l=1}^{\infty}(-1)^{l+1}\frac{z^l}{l^{3/2}}.$$

下面推导一般的无结构、无内禀简并度的玻色子/费米子的巨配分函数及基本热力学性质.

首先: $\ln(1+x) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{x^n}{n}$ (要求 $-1<x\leq 1$)

$$\beta PV = \ln\Theta$$

$$= \int_0^{+\infty} d\varepsilon\cdot\rho(\varepsilon)\cdot\left[\pm\ln(1\pm e^{\beta\mu}e^{-\beta\varepsilon})\right]$$

$$= 2\pi V\left(\frac{2m}{h^2}\right)^{\frac{3}{2}}\int_0^{+\infty}\pm\ln(1\pm e^{\beta\mu}e^{-\beta\varepsilon})\,\varepsilon^{\frac{1}{2}}d\varepsilon. \quad 令\ z=e^{\beta\mu}$$

$$= \frac{2V}{\sqrt{\pi}}\underbrace{\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}}_{\lambda^{-3}}\int_0^{+\infty}\pm\ln(1\pm ze^{-y})\,y^{\frac{1}{2}}dy \quad 令\ y=x^2$$

$$\Rightarrow \beta P\lambda^3 = \frac{4}{\sqrt{\pi}}\int_0^{+\infty}\pm\ln(1\pm ze^{-x^2})x^2dx.$$

利用 $\ln(1+x)$ 的级数展开.

$$\beta p\lambda^3 = \frac{4}{\sqrt{\pi}}(\pm 1)\int_0^{+\infty}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{1}{n}(\pm)^n z^n e^{-nx^2}x^2 dx$$

$$= \frac{4}{\sqrt{\pi}}(\pm 1)\sum_{n=1}^{\infty}(-1)^{n+1}\frac{(\pm 1)^n}{n}z^n\int_0^{\infty}dx\cdot x^2 e^{-nx^2} \quad 令 nx^2\to x^2$$

$$= \frac{4}{\sqrt{\pi}}(\pm 1)\sum_{n=1}^{\infty}(-1)^{n+1}\frac{(\pm 1)^n}{n^2\sqrt{n}}z^n \underbrace{\int_0^{\infty}\sqrt{n}dx(nx^2)e^{-nx^2}}_{\int_0^{\infty}dx\cdot x^2e^{-x^2}=\frac{\sqrt{\pi}}{4}}$$

$$= \sum_{n=1}^{\infty}\frac{(\mp 1)^{n+1}}{n^{\frac{5}{2}}}z^n = \beta p\lambda^n$$

(Fermi子取负号. Bose子取正号).

则 $\beta pV = \ln\Theta = \frac{V}{\lambda^3}\sum_{n=1}^{\infty}(\pm 1)^{n+1}\frac{z^n}{n^{\frac{5}{2}}}$

泰勒展开合理性要求：$-1 < e^{\beta\mu}e^{-\beta\varepsilon} \le 1$.

① 对电子气不适用. 因为 μ 太大了. (费米温度 $8\times10^4 \gg$ 远温)

② Bose子化学式小于零, 可以适用.

③ 低温 Fermi子, 化学势为正, 但由于 $e^{-\beta\varepsilon}$ 可以看为一种近似, 但不是一种好的近似 (eg. ^3He 费米特征温度为5K).

④ 一般高温 Fermi子, 化学势由正转负, 可以满足条件.

(b) 类似地, 证明内能 $\langle E\rangle$ 满足关系

$$\langle E\rangle = \frac{3}{2}pV.$$

$$\langle E\rangle = -\frac{\partial\ln\Theta}{\partial\beta}\Big|_{V,z}$$

$$= \frac{3}{2}kT\ln\Theta = \frac{3}{2}kT\beta pV = \frac{3}{2}pV.$$

$$\langle N\rangle = \left(\frac{\partial\ln\Theta}{\partial z}\right)\Big|_{V,\beta}\underbrace{\frac{\partial z}{\partial(\beta\mu)}\Big|_{\beta,V}}_{=z} = \frac{V}{\lambda^3}\sum_{n=1}^{\infty}(\pm 1)^{n+1}\frac{z^n}{z^{\frac{3}{2}}}$$

对经典理想气体. $z = e^{\beta\mu} \ll 1$. 上面级数求和只取第一项 $(n=1)$

$$\beta PV = \ln \Theta = \langle N \rangle \Rightarrow PV = NKT. \quad \langle E \rangle = \frac{3}{2} NKT$$

之后对玻色—爱因斯坦凝聚作讨论.

此时最低能级的占据数不是微观量，而之前求和^时没考虑$\varepsilon=0$的点，此时要补上.

$$\beta PV = \ln \Theta = \frac{V}{\lambda^3} \sum_{n=1}^{\infty} \frac{z^n}{n^{\frac{5}{2}}} - \ln(1-z)$$

$$N = \frac{V}{\lambda^3} \sum_{n=1}^{\infty} \frac{z^n}{n^{\frac{3}{2}}} + \frac{z}{1-z}$$

可以看出，当$T\downarrow$或$V\downarrow$时，$\frac{V}{\lambda^3}$都会$\downarrow$，但N不能发生变化$\Rightarrow z\uparrow$

μ逐渐从一个绝对值很大的负数变为0. 则$z\to 1$.

$$N = \frac{V}{\lambda^3} \sum_{n=1}^{\infty} \frac{1}{n^{\frac{3}{2}}} + n_0 \uparrow$$

若$T=0$，玻色子会全部处于最低能级，可以定义一个凝聚温度，此温度时玻色子开始在最低能级凝聚(无相互作用)，凝聚温度以下，最低能级占据数逐渐增加，逐步会具有N的宏观量级.

T_c: $\frac{n_0}{N} = 0$ & $z=1$. $\quad N = V\left(\frac{2\pi m k T_c}{h^2}\right)^{\frac{3}{2}} \underbrace{\sum_{n=1}^{\infty} \frac{1}{n^{\frac{3}{2}}}}$ $\doteq 2.612$

$$\Rightarrow T_c = \left(\frac{N}{2.612V}\right)^{\frac{2}{3}} \frac{h^2}{2\pi m k}.$$

eg: ^4He: $\rho = 0.145\ g/cm^3$

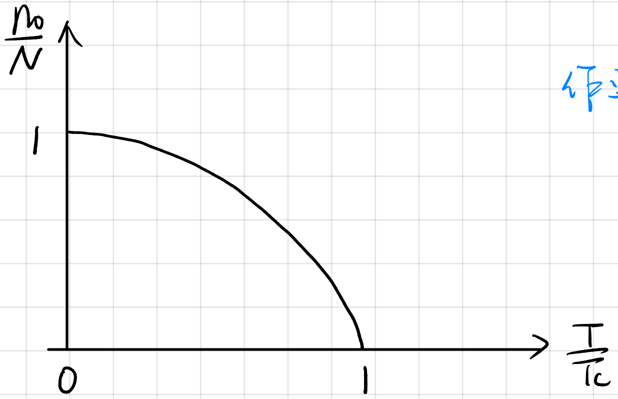
$$T_c = \left(\frac{6\times10^{23} \cdot \frac{0.145}{5}}{2.612\times10^{-6}}\right)^{\frac{2}{3}} \cdot \frac{(6.6\times10^{-34})^2}{2\times3.14\times1.38\times10^{-23}} \cdot \frac{1}{4\times1.67\times10^{-27}} \approx 3K.$$

$T \geq T_c$. $\quad \frac{n_0}{N} = 0$

$T < T_c \quad N = V\lambda^{-3}(T) \cdot 2.612 + n_0$

$$= \frac{V\lambda^{-3}(T)}{V\lambda^{-3}(T_c)} N + n_0$$

$$= \left(\frac{T}{T_c}\right)^{\frac{3}{2}} N + n_0 \Rightarrow \frac{n_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}$$



作业：T一定，V→0 也会有BCE。

求凝聚密度① $\rho_c = \frac{N}{V_c}$ ② $\frac{n_0}{N}$ 与 ρ_c 的关系。

下面考察热容。

$$T<T_c \quad \ln\Theta = \frac{V}{\lambda^3}\underbrace{\sum_{n=1}^{\infty}\frac{1}{n^{\frac{3}{2}}}}_{1.342} - \ln(1-z)$$

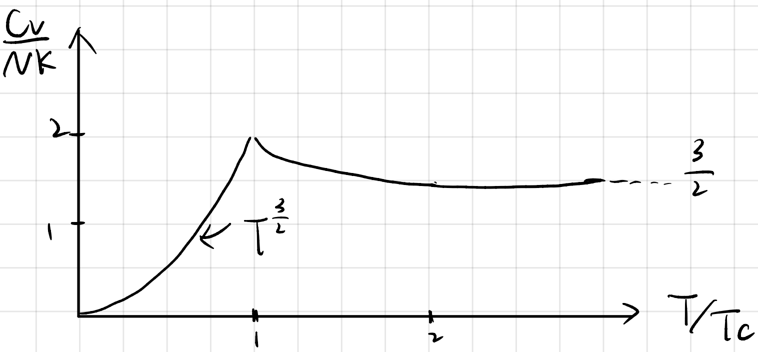
$$= 1.342\frac{V}{\lambda^3} - \ln(1-z)$$

$$\langle E\rangle = -\frac{\partial \ln\Theta}{\partial\beta}\bigg|_{V,\beta\mu} = \frac{3}{2}kT\cdot 1.342\frac{V}{\lambda^3} \propto T^{\frac{5}{2}}$$

即 $C_V \propto T^{\frac{3}{2}}$

$$C_V = \frac{3}{2}k\cdot 1.342\cdot\frac{5}{2}\cdot T^{\frac{3}{2}}\, V\,(2\pi mk)^{\frac{3}{2}}\, h^{-3}$$

$$C_V(T_c) = \frac{15}{4}\cdot 1.342\, k\,\frac{N}{2.612} = 1.927\,Nk$$



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统计力学"三部曲"

(i) 能谱. $\{\nu \to E_\nu\} \longrightarrow \hat{H}\psi_\nu = E_\nu \psi_\nu$

(ii) 配分函数 $Q = \sum_\nu e^{-\beta E_\nu}$ (正则).

宏观　　微观

(iii) Micro → Macro. Thermodynamics　$F = -kT \ln Q$.

↘ Dynamics.

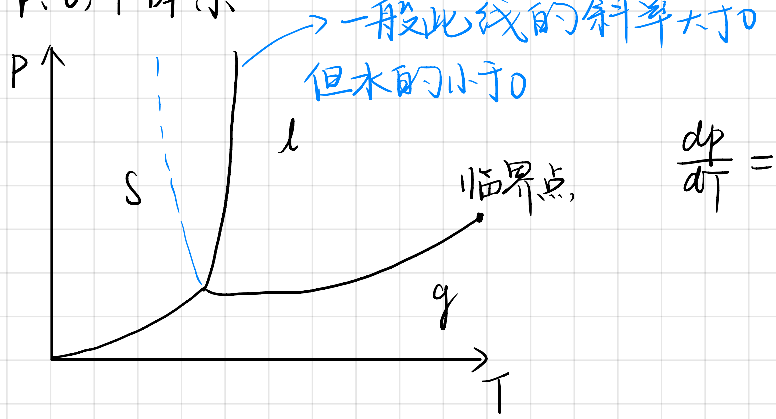
$\Rightarrow dF = -SdT - pdV + \mu dN + \cdots$

相变的统计力学 (相变由相互作用导致)

统计力学的核心问题：涨落与相变.

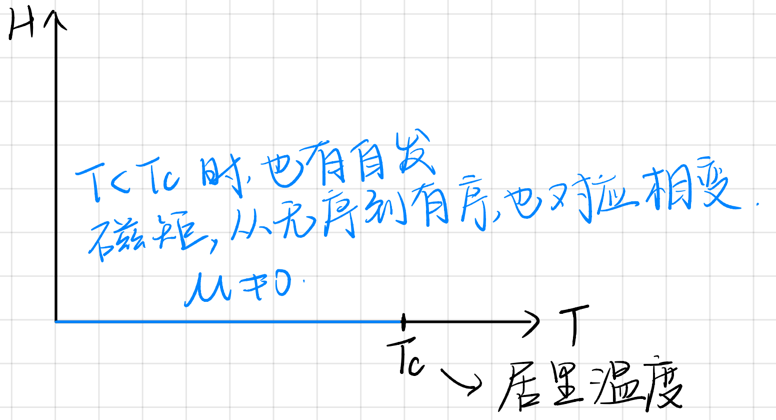
0. 引言.

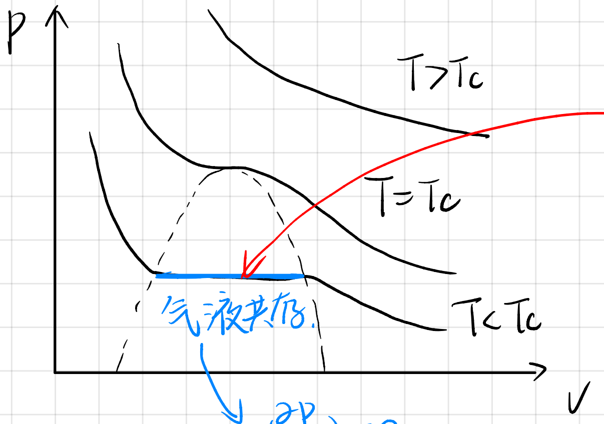
P, V, T 体系



$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

(H, M, T) 体系与 (p, V, T) 对应.

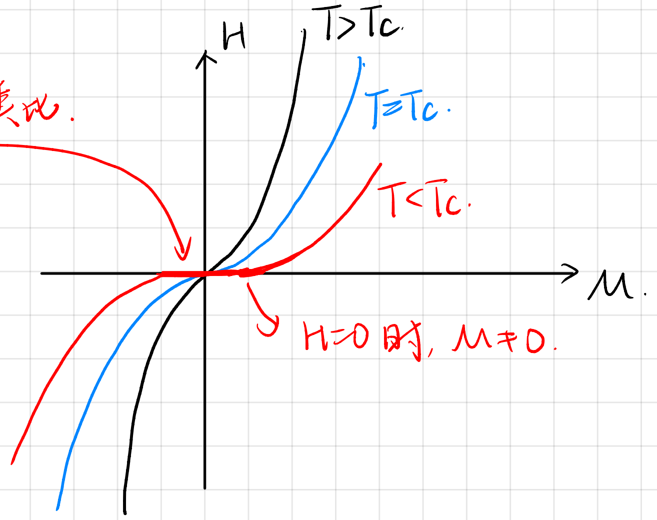


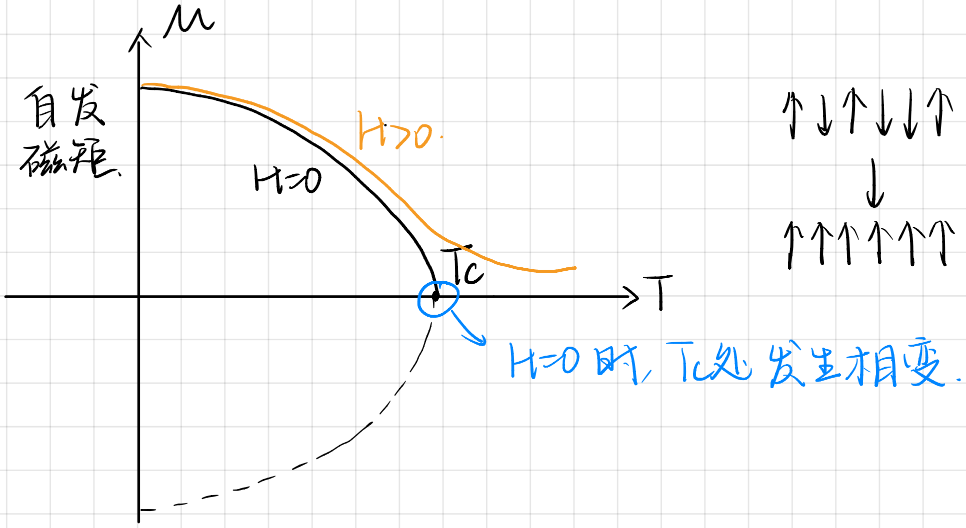


$\left(\frac{\partial P}{\partial V}\right)=0$

$\Downarrow$

$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \longrightarrow \infty$ "奇异性"





↑↓↑↓↓↑ : T>Tc

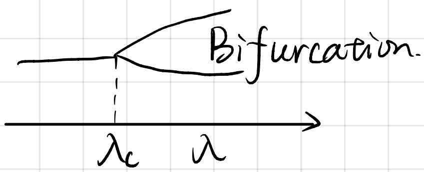
↓

↑↑↑↑↑↑ : T<Tc

为什么只在Tc发生相变？

* Basic Idea:

(1) 相变是宏观性质"突变" ⟶ "Singular Behavior".



(2) 相变由相互作用导致(例外：玻色—爱因斯坦凝聚).

由于平衡要求 $F=E-TS$ 最小：相互作用导致的熵与内能竞争.

(3). Paradox:

以正则系综为例: $\underbrace{F=-kT\ln Q}_{\text{解析}}$. $\underbrace{Q=\sum_\nu e^{-\beta E_\nu}}_{\text{解析}}$

F应当是解析的，为什么会有奇异性？"由于无穷的求和"