0.1 Phase Transition

A system containing many degrees of freedom $\to$ exhibits collective behavior.

[Example] 1. condensation of water vapor; 2. critical behavior; 3. magnetic system. ferromagnetism(自发磁化). 加热后化为 paramagnetism $M \propto H$. 这些相变存在着共性. 4. fluid-superfulid phase transition(He-3 fermion, $T_c = 2.491$ mK; He-4 boson, $T_c = 2172$ K) fermion pair 才可以产生凝聚, 而产生 fermion pair 需要极低温; 5. social/crowd behavior, market price...

$\mathrm{d}\mu = v\mathrm{d}P - s\mathrm{d}T$, 化学势的一阶导数突变为一级相变(水结冰), 二阶导数突变为二级相变.

0.1.1 Van der Waals Theory

motivation: to find the universal law for gas-liquid phase transition.

分子间相互作用势: 近程排斥, 远程吸引. 临界点 r_0. 修正 ideal gas: $P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$. b: hard-core repulsion(硬球排斥); a: attraction, $\dfrac{a}{v^2} \sim n^2 = \left(\dfrac{N}{V}\right)^2$. 1. $T \gg |\varepsilon_0|$, 可忽略相互作用; 2. $T\downarrow$, interaction $\uparrow$, condensed state(liquid state); 3. $T \to 0$, crystal state/amorphous state (mechanical in equilibrium).

0.1.1.1 Derivation of Van der Waals Equation

$$Q_N(T,V) = \frac{1}{N!h^{3N}} \int \prod_{i=1}^{N} \mathrm{d}^3\vec{q}_i \mathrm{d}^3\vec{p}_i \exp\left\{-\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i<j} V(\vec{q}_i - \vec{q}_j)\right\} = \frac{1}{N! \underbrace{\lambda_T^{3N}}_{\int \mathrm{d}^3\vec{p}}} \underbrace{\left(V - \frac{N\omega}{2}\right)^N}_{\text{hard-core repulsion}} e^{-\beta\overline{U}}$$

$$\overline{U} = \frac{1}{2}\sum_{i,j} V_{\text{attract}}(\vec{q}_i - \vec{q}_j) = \frac{1}{2}\int \mathrm{d}^3\vec{r}_1 \mathrm{d}^3\vec{r}_2 n(\vec{r}_1)n(\vec{r}_2)V_{\text{attract}}(\vec{r}_1 - \vec{r}_2) = \frac{1}{2}n^2 V \underbrace{\int V_{\text{attract}}(\vec{r})\mathrm{d}^3\vec{r}}_{u} = \frac{1}{2}\frac{N^2}{V}u$$

$$F = -k_BT\ln Q_N(V,T) = -Nk_BT\ln\left(V - \frac{N\omega}{2}\right) + Nk_BT\ln\left(\frac{N}{e}\right) + 3Nk_BT\ln\lambda_T - u\frac{N^2}{2V}$$

$$\Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V - \underbrace{\frac{N\omega}{2}}_{b}} - \underbrace{\frac{u}{2}}_{a}\frac{N^2}{V^2}$$

使用 cluster expansion 对 $V(\vec{q}_i - \vec{q}_j)$ 进行处理.

[Example] $U(r) = \begin{cases} \infty, & r \le r_0 \\ -U_0\left(\dfrac{r_0}{r}\right)^6, & r > r_0 \end{cases}$. $B(T) = -2\pi\displaystyle\int_0^\infty [e^{-U(r)/k_BT} - 1]r^2\mathrm{d}r = \frac{2\pi r_0^2}{3}\left(1 - \frac{U_0}{k_BT}\right)$,

$a = \dfrac{2\pi r_0^3 U_0}{3}, \quad b = \dfrac{2\pi r_0^3}{3}$

0.1.1.1.1 Simpler Argument

Statistical independence of particles $\to$ consider a single particle. Accessible volume(repulsion): $V - V_0, \quad V_0 \propto N \Rightarrow V_0 = bN$; potential energy(attraction): $u \propto \dfrac{N}{V} = n \Rightarrow u = -a\dfrac{N}{V}$.

$$Q_1(V,T) = f(T)\int_{V-V_0} e^{aN/VT}\mathrm{d}^3\vec{r} = f(T)(V - bN)e^{aN/VT},$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_BT\frac{\partial \ln Q_N}{\partial V}\bigg|_{T,N} = k_BT\frac{\partial}{\partial V}\left(\ln\frac{Q_1^N}{N!}\right)_{T,N} \overset{\frac{\partial N}{\partial V}=0}{=} k_BTN\frac{\partial \ln Q_1}{\partial V}$$

0.1.2 Phase Diagram

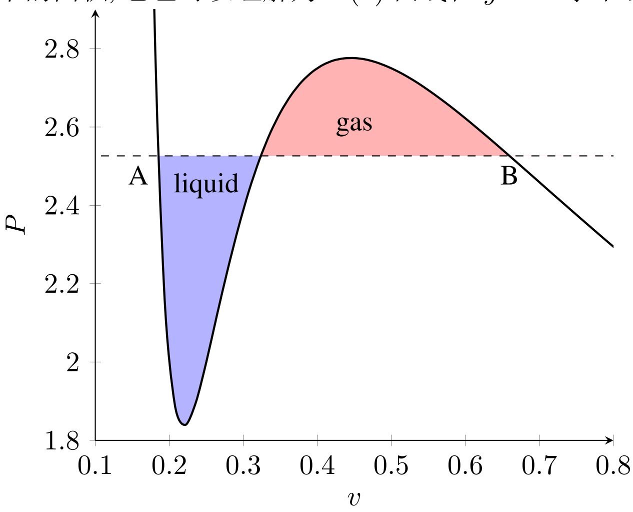
Van der Waals equation: real gas.

Other ways to describe: $PV = RT\left(1 + \dfrac{A_2}{V} + \dfrac{A_3}{V^2} + \cdots\right)$, or $\dfrac{Pv}{k_BT} = 1 + \dfrac{B(T)}{v} + \dfrac{C(T)}{v^2} + \cdots$

$P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$ 数学上是一个 v 的三次方程. 存在三个解代表的是 gas-liquid coexistence. $v_1 = v_l, v_3 = v_g$. 特殊情况: $v_1, v_2, v_3 \to v_c$, 即 critical point.

0.1.2.1 Maxwell Construction

$G = \mu N$. 在等温曲线上, $\mathrm{d}G = \cancel{-S\mathrm{d}T} + V\mathrm{d}P$. 设 $y = P$ 水平线与 $P(v)$ 交点左右分别为 A, B. 那么从 A 到 B 的自由能变化量为 $\Delta G = \int_A^B V\mathrm{d}P = \int_A^B [\mathrm{d}(PV) - P\mathrm{d}V] = P(V_B - V_A) - \int_{V_A}^{V_B} P\mathrm{d}V = 0$, 前后分别是 $y = P$ 直线下矩形面积和 $P(v)$ 曲线下的面积, 它也可以理解为 $P(v)$ 曲线在 $y = P$ 水平线上下两面积相等. 也就是说, 在这条水平线上 liquid-gas coexistence.



计算气液两相所占体积: $v_0 = xv_l + (1-x)v_g \Rightarrow x = \dfrac{v_g - v_0}{v_g - v_l}$, 即 lever rule. $\dfrac{\partial P}{\partial v} > 0$ 是热力学不稳定的.

0.1.2.2 Critical Behavior

Critical point: $\left.\dfrac{\partial P}{\partial v}\right|_c = 0, \quad \left.\dfrac{\partial^2 P}{\partial v^2}\right|_c = 0 \Rightarrow P_c = \dfrac{a}{27b^2}, \quad T_c = \dfrac{8a}{27bR}, \quad v_c = 3b$, material dependent; $\dfrac{RT_c}{P_c v_c} = \dfrac{8}{3}$, material independent.

$P_r = \dfrac{P}{P_c}, \quad v_r = \dfrac{v}{v_c}, \quad T_r = \dfrac{T}{T_c} \Rightarrow \left(P_r + \dfrac{3}{v_r^2}\right)(3v_r - 1) = 8T_r$. 所以即使是不同类的 Van der Waals gas, 也可以通过判断 (P_r, v_r) 相等而判断其处于 **corresponding state**.

进一步使用小量: $P_r = 1 + \pi, \quad v_r = 1 + \Psi, \quad T_r = 1 + t$, 从而使用 (π, Ψ, t) 描述临界点附近状态.

0.1.2.2.1 Along the isothermal curve at $t = 0 (T = T_c)$

$\pi = -\dfrac{3}{2}\Psi^3$, 3: critical exponent.

0.1.2.2.2 Ψ_l 和 Ψ_g 对 critical point 的逼近行为

$\pi = 4t - 6t\Psi + \dfrac{3}{2}\Psi^3 \Rightarrow \begin{cases} \pi = 4t - 6t\Psi_l + \dfrac{3}{2}\Psi_l^3 \\ \pi = 4t - 6t\Psi_g + \dfrac{3}{2}\Psi_g^3 \end{cases}$. 原始的 v_l 和 v_g 是通过 Maxwell construction $\int \mathrm{d}G = 0 \Rightarrow P(V_B - V_A) - \int_{V_A}^{V_B} P\mathrm{d}V = 0$ 得到的. 使用 (π, Ψ, t) 重构:

$\int_{\Psi_l}^{\Psi_g} \pi(\Psi; t)\mathrm{d}\Psi = \pi(\Psi_g - \Psi_l) \Rightarrow 4t - 3t(\Psi_g + \Psi_l) - \dfrac{3}{8}(\Psi_g + \Psi_l)(\Psi_g^2 + \Psi_l^2) = \pi.$

联立方程组得到 $2\pi = 8t - 6t(\Psi_l + \Psi_g) - \dfrac{3}{2}\left(\Psi_l^2 + \Psi_g^2\right) \Rightarrow (\Psi_g + \Psi_l)(\Psi_g - \Psi_l) = 0 \Rightarrow \Psi_g = -\Psi_l$.

因此在临界点附近, Ψ_l 和 Ψ_g 对称地分布在临界点两侧.

0.1.2.2.3 Isothermal Compressibility Near the Critical State

$-\left(\dfrac{\partial \Psi}{\partial \pi}\right)_t = \begin{cases} \dfrac{1}{6}t^{-1}, & t > 0 \\ \dfrac{1}{12}|t|^{-1}, & t < 0 \end{cases}$, -1: critical exponent.

[Example] First observation of critical phenomenon. Water: $T_c = 373.946°\mathrm{C}$, $P_c = 217.7$ atom.

[Discussion] $Q(Z, V, T) = \sum_{N=0}^{N_{\max}} Z^N Q_N(V, T), \quad P = \dfrac{k_B T}{V} \ln Q$. 级数各项表达式均为解析的. 若要产生奇点(singularity), 应要求 Thermodynamic limit(热力学极限), 即 $\lim_{N_{\max}, V \to \infty}$ 的同时 $\dfrac{N}{V} =$ finite const..

0.1.3 Ising Model: From Thermodynamic Approach to Statistical Approach

$$H(\{\sigma_i\}) = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - \mu B\sum_i \sigma_i,\quad \sigma_i = \pm 1(\text{binary variable})$$

0.1.3.1 Preliminary Analysis

设 N_+ 个自旋 $\uparrow$, N_- 个自旋 $\downarrow$; 又令 N_{++} 为相邻 $\uparrow\uparrow$ 的数, N_{--} 为相邻 $\downarrow\downarrow$ 的数, N_{+-} 为相邻 $\downarrow\uparrow$ 与 $\uparrow\downarrow$ 的数.

通过这些参数重构哈密顿量: $H_N = -J(N_{++}+N_{--}-N_{+-}) - \mu B(N_+ - N_-)$.

设 q 是各自旋的配位数(对于 Ising Model 即 2), 存在约束关系 $N = N_+ + N_-$, $qN_+ = 2N_{++}+N_{+-}$, $qN_- = 2N_{--}+N_{+-}$. 因此只有两个独立变量.

(N_+, N_{++}) 不是单个微观态, 存在着简并. 因此$H_N(N_+,N_{++}) = -J\left(\frac{1}{2}qN - 2qN_+ + 4N_{++}\right) - \mu B(N_+ - N)$,

$Q_N = \sum_{(N_+,N_{++})} e^{-\beta H_N(N_+,N_{++})} g_N(N_+,N_{++})$

0.1.3.2 Mean-Field Approximation

Order parameter(序参量): $L = \frac{1}{N}\sum_i \sigma_i = \frac{N_+ - N_-}{N} \in [-1,+1]$. 而 $M = \mu(N_+ - N_-) = \mu N L$.

[Discussion] 为了照顾到 $L=0$ 中"前半全 $\uparrow$, 后半全 $\downarrow$"的特殊情况, 可以进一步定义新的序参量 $S = \frac{N_{++}+N_{--}-N_{+-}}{\frac{1}{2}qN}$. 即相邻自旋方向相同为有序, 反之为无序. 因此序参量依赖于对 "序" 的定义.

$$\begin{aligned}H(\{\sigma_i\}) &= -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - \mu B\sum_i\sigma_i = -\frac{J}{2}\sum_i\left(\sum_{\langle j\rangle}\sigma_j\right)\sigma_i - \mu B\sum_i\sigma_i\\ &= -\frac{J}{2}\sum_i(q\overline{\sigma})\sigma_i - \mu B\sum_i\sigma_i = -\mu\left(B+\frac{1}{2}B'\right)\sum_i\sigma_i,\quad B' = \frac{qJ}{\mu}\overline{\sigma},\quad \text{Effective field}\end{aligned}$$

spin flip($\uparrow\Leftrightarrow\downarrow$) 引起能量变化 $\delta\varepsilon = \varepsilon_- - \varepsilon_+ = \left(-J\sum_{\langle j\rangle}\sigma_i - \mu B\sigma_i\right)_{\sigma_i=-1} - \left(-J\sum_{\langle j\rangle}\sigma_i - \mu B\sigma_i\right)_{\sigma_i=+1} = 2\mu(B+B')$.

记 $\overline{N}_\pm = N\frac{e^{-\beta\varepsilon_\pm}}{\sum_{+,-}e^{-\beta\varepsilon_i}}$, 则有 **self-consistency function**(自洽方程): $\frac{\overline{N}_-}{\overline{N}_+} = \frac{1-\overline{L}}{1+\overline{L}} = e^{-2\beta(\mu B + qJ\overline{L})}$, $\quad \overline{L} = \overline{\sigma} = \frac{1}{N}\sum_i\sigma_i$.

等式两边同 ln, 且引入 $\operatorname{arctanh} x = \frac{1}{2}\ln\left(\frac{1+x}{1-x}\right)$, 得到 $\beta\left(qJ\overline{L}+\mu B\right) = \operatorname{arctanh}\left(\overline{L}\right)$, 即 $\overline{L}$ 形式的 **Equation of State**.

[Example] 其它使用 Mean-Field approximation 的例子

1. 溶液中 electric potential $\phi(\vec{r})$, 粒子分布 $\rho(\vec{r}) = \sum_s e_s n_{s_0} e^{-\frac{e_s\phi(\vec{r})}{k_B T}}$, $\nabla^2\phi(\vec{r}) = -4\pi\rho(\vec{r})$.
2. 在 $\overline{L}\to 0$ 时, 即有 $\overline{L}\sim M\propto B$, 即 paramagnetism(顺磁). 非线性项 $\to$ ferromagnetism(铁磁).

0.1.3.2.1 $B=0$ 下的 $\overline{L}$

令 $L_0 = \overline{L}(B=0)$, 得到无外场条件下的状态方程 $\overline{L}_0 = \tanh\left(\beta Jq\overline{L}_0\right)$. $\overline{L}_0\to 0$ 代表可相变.

使用极限 $\lim_{x\to 0}\tanh(x)\simeq x - \frac{x^3}{3} + O(x^5)$, 展开状态方程: $(\beta qJ-1)\overline{L}_0 = \frac{1}{3}\left(\beta qJ\overline{L}_0\right)^3$. 若 $\beta qJ - 1 > 0 \Leftrightarrow T < \frac{qJ}{k_B} = T_c$, 则存在顺磁解 $\overline{L}_0 = 0$; 同时还存在着 2 个非零解, 代表系统可自发磁化.

[Discussion] 几何观点: $y=x$ 和 $y=\tanh(\beta Jqx)$ 的交点. 在高温时只有 1 个交点, 而低温时则能产生 3 个交点.

根据中值定理, 为产生交点, 应存在 $\left.\frac{\mathrm{d}\tanh\left(\beta J\overline{L}_0\right)}{\mathrm{d}\overline{L}_0}\right|_{\overline{L}_0>0} = 1 \Rightarrow \frac{qJ}{k_B T_c} = 1$.

对于 L_0-T 相图. 这是一种 continuous phase transition, 属于二阶相变. symmetry abrupt change(对称性突变).

1. 在 T_c 左邻域, 有近似 $\lim_{T\to T_c^-}\overline{L}_0 = \overline{L}_0\frac{T_c}{T} - \frac{1}{3}\overline{L}_0^3\left(\frac{T_c}{T}\right)^3 \Rightarrow \overline{L}_0 \simeq 3^{\frac{1}{2}}\left(1-\frac{T}{T_c}\right)^{\frac{1}{2}}$.
2. 在 $T\to 0$ 时, 有近似 $\lim_{T\to 0}\overline{L}_0 \simeq 1 - 2\exp\left(-\frac{2T_c}{T}\right)$, 斜率 $\frac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}\to 0$.

研究在 $B=0$ 时的 **Specific Heat(热容)**. 无外场时系统内能为 $H(\{\sigma_i\})=-\dfrac{J}{2}\sum_i(q\bar{\sigma})\sigma_i=-\dfrac{1}{2}qJN\overline{L}_0^2$;

热容为内能偏导 $c_0=\dfrac{\partial U_0}{\partial T}=-qJN\overline{L}_0\dfrac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}$. 可见其依赖于 $\dfrac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}$; 因此 1. $T>T_c$ 时, $c_0=0$;

2. $\lim\limits_{T\to T_c^-}$ 时, 对物态方程两边都 $\dfrac{\partial}{\partial T}$, 得到 $c_0=k_BN\dfrac{T_c}{T}\overline{L}_0^2\dfrac{1-\overline{L}_0^2}{\dfrac{T}{T_c}-\left(1-\overline{L}_0^2\right)}\simeq\dfrac{3}{2}Nk_B$

研究在 $B=0$ 时的熵 S_0. 1. Statistical method. 熵 $S_0(T\geq T_c)=k_B\ln\left(2^N\right)=Nk_B\ln 2$.

2. Thermodynamic method. $S_0(T\geq T_c)=\displaystyle\int_0^T\frac{c_0(T)\mathrm{d}T}{T}=\int_0^{T_c}\frac{c_0(T)\mathrm{d}T}{T}+\cancel{\int_{T_c}^{T}\frac{c_0(T)\mathrm{d}T}{T}}=-qJN\int_1^0\frac{\overline{L}_0}{T}\mathrm{d}\overline{L}_0$

$=Nk_B\displaystyle\int_0^1\operatorname{arctanh}\left(\overline{L}_0\right)\mathrm{d}\overline{L}_0=Nk_B\ln 2$

研究 $B=0$ 时的磁化率 χ_0.

$\chi_0=\left(\dfrac{\partial M}{\partial B}\right)_T\Rightarrow\lim\limits_{T\to T_c^+}\chi_0\simeq\dfrac{NM^2}{k_B}\dfrac{1}{T-T_c},\quad\lim\limits_{T\to T_c^-}\chi_0\simeq\dfrac{NM^2}{2k_B}\dfrac{1}{T_c-T},\quad\lim\limits_{T\to 0}\chi_0\simeq\dfrac{4NM^2}{k_BT}\exp\left\{-\dfrac{2T_c}{T}\right\}.$

0.1.3.2.2 Weak External Field $B\to 0$ 在 $T\geq T_c$ 时, 有 $\overline{L}\simeq\dfrac{\mu\beta}{1-\beta qJ}B=\dfrac{\mu}{k_B(T-T_c)}B\Rightarrow\overline{L}\propto B$, 即 **Curie's law**.

0.1.3.3 Lost Correlation under Mean-Field Approximation

0.1.3.3.1 概率检验 取任意两相邻格点 $\langle i,j\rangle$, 其自旋均为↑的概率 $P_{++}=\dfrac{N_{++}}{\frac{1}{2}qN}$ 是否等价于单自旋↑概率乘积 $\dfrac{N_+}{N}\times\dfrac{N_+}{N}=P_+\times P_+$? 通过 MFT 给出的 $U_0=-\dfrac{1}{2}qJN\overline{L}_0^2, N_+=\dfrac{1}{2}N(1+\overline{L}_0), H_N(N_+,N_{++})$ 进行验证($\surd$).
同理 $P_{--}=P_-^2, P_{+-}=2P_+P_-$. 如果 Random mixing(完全随机): $\dfrac{N_{++}N_{--}}{N_{+-}^2}=\dfrac{P_{++}P_{--}}{(P_{+-}+P_{-+})^2}=\dfrac{P_+^2P_-^2}{4P_+^2P_-^2}=\dfrac{1}{4}$.
因此若该值偏离 $\dfrac{1}{4}$, 则存在着某种自旋间的 correlation.

0.1.3.3.2 涨落检验 将 σ_i 视为 continuous variable $\sigma=\langle\sigma_i\rangle+\delta\sigma_i=m+\delta\sigma_i$, 则
$H=-J\sum\limits_{\langle i,j\rangle}\sigma_i\sigma_j=-J\sum\limits_{\langle i,j\rangle}(m+\delta\sigma_i)(m+\delta\sigma_j)=-Jmq\sum\limits_i\delta\sigma_i=-Jmq\sum\limits_i(\sigma_i-m)=-Jmq\sum\limits_i\sigma_i+\text{const.}$
在处理时运用了 $\delta\sigma_i\delta\sigma_j\to 0$ 的技巧, 这也意味着 lost of correlation of fluctuation.

0.1.3.4 Derivation of Equation of State in Terms of Order Parameter L

Also as an [Exercise]:

$$\frac{N_+}{N}=\frac{1}{2}(1+L),\quad \frac{N_-}{N}=\frac{1}{2}(1-L),\quad L=\frac{N_+-N_-}{N}$$

$$\frac{N_{++}}{\frac{1}{2}qN}=\left(\frac{N_+}{N}\right)^2\to\frac{N_{++}}{N}=\frac{q}{8}(1+L)^2,\quad \text{similarly }\frac{N_{--}}{N}=\frac{q}{8}(1-L)^2,\quad \frac{N_{+-}}{N}=\frac{q}{4}(1-L^2)$$

$$U(L)=-\frac{1}{2}qJNL^2-\mu BNL$$

$$S=k_B\ln\left(\frac{N!}{N_+!N_-!}\right)\overset{N\to\infty}{=}-k_BN\left[\frac{1+L}{2}\ln\left(\frac{1+L}{2}\right)+\frac{1-L}{2}\ln\left(\frac{1-L}{2}\right)\right]$$

$$F(L)=U-TS=-\frac{1}{2}qJNL^2-\mu BNL+k_BTN\left[\frac{1+L}{2}\ln\left(\frac{1+L}{2}\right)+\frac{1-L}{2}\ln\left(\frac{1-L}{2}\right)\right]$$

$$\frac{\partial F}{\partial L}=0\Rightarrow -qJNL-\mu BN+\frac{1}{2}k_BTN\left[\ln\left(\frac{1+L}{2}\right)+1-\ln\left(\frac{1-L}{2}\right)-1\right]=0$$

$$\Rightarrow -qJNL-\mu BN+\frac{1}{2}k_BTN\ln\left(\frac{1+L}{1-L}\right)=0\Rightarrow\frac{1}{2}\ln\left(\frac{1+L}{1-L}\right)=\frac{qJL+\mu B}{k_BT}$$

$$\Rightarrow \operatorname{arctanh}L=\beta(qJL+\mu B),\quad \beta=\frac{1}{k_BT}$$

0.1.3.5 1st-Order Approximation-Bethe's Method @ 1935

$(q+1)$ system. σ_0 感受到 q 个 σ_i 的作用. $H_{q+1}=-\mu B\sigma_0-\mu\left(B+B'\right)\sum_{j=1}^{q}\sigma_j-J\sum_{j=1}^{q}\sigma_0\sigma_j$. Requirement: $\overline{\sigma}_0=\overline{\sigma}_j,\quad\forall j$.

$Z=\sum_{\sigma_0=\pm1}\sum_{\sigma_j=\pm1}e^{-\beta H_{q+1}}\overset{\sigma_0=+1}{=}Z_+ + \overset{\sigma_0=-1}{Z_-},\quad Z_\pm=e^{\pm\alpha}\left[2\cosh\left(\alpha+\alpha'\pm\gamma\right)\right]^q,\quad \alpha=\frac{\mu B}{k_BT},\quad \alpha'=\frac{\mu B'}{k_BT},\quad \gamma=\frac{J}{k_BT}.$

$\overline{\sigma}_0=(+1)\frac{Z_+}{Z}+(-1)\frac{Z_-}{Z},\quad \overline{\sigma}_j=\langle\frac{1}{q}\sum_j\sigma_j\rangle=\frac{1}{q}\frac{1}{Z}\frac{\partial Z}{\partial\alpha'}$ (类比巨正则系综 $Z=\sum_{r,s}e^{-\alpha N_r-\beta E_s},\quad \langle N\rangle=-\frac{\partial\ln Z}{\partial\alpha}$).

要求 $\overline{\sigma}_0=\overline{\sigma}_j\Rightarrow e^{2\alpha'}=\left[\frac{\cosh\left(\alpha+\alpha'+\gamma\right)}{\cosh\left(\alpha+\alpha'-\gamma\right)}\right]^{q-1}$. $\alpha'=\alpha'(\alpha,\gamma)$.

若 $\alpha=0$ (no external field), 此时 $\alpha'=0$ 解存在(顺磁). 非零解: $\alpha'=(q-1)\tanh\gamma\left(\alpha'-\operatorname{sech}^2\gamma\frac{\alpha'^2}{3}\right)$. 根据中值定理, 有解即要求斜率$\left(\frac{\partial}{\partial\alpha'}\right)$ 满足 $(q-1)\tanh\gamma>1$. 解得 $\gamma_c=\frac{1}{2}\ln\left(\frac{q}{q-2}\right),\quad T_c=\frac{2J}{k_B}\frac{1}{\ln\left(\frac{q}{q-2}\right)}$.

$\left[\text{回忆之前通过 MFT 得到的 }T_c=\frac{qJ}{k_B}\right]\lim_{q\to\infty}T_c=\lim_{q\to\infty}\frac{2J}{k_B}\frac{1}{\ln\left(\frac{1}{1-2/q}\right)}\simeq\frac{qJ}{k_B}$, 即 MFT.

检验发现对于 1-dim Ising Model, $q=2\Rightarrow T_c=0$.

$\alpha'(T\le T_c)=\left[3(q-1)\frac{J}{k_BT_c}\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}},\quad \overline{\sigma}_0=\frac{(+1)\cdot Z_++(-1)\cdot Z_-}{Z_++Z_-}=\frac{\frac{Z_+}{Z_-}-1}{\frac{Z_+}{Z_-}+1}=\frac{\sinh\left(2\alpha+2\alpha'\right)}{\cosh\left(2\alpha+2\alpha'\right)+e^{-2\gamma}}.$

若 $\alpha=0$, 则 $\lim_{\alpha'\to0}\overline{\sigma}_0=\frac{2\alpha'}{1+e^{-2\gamma_c}}=\left[\frac{q^2}{q-1}\frac{J}{k_BT_c}3\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}$. 无论是否存在关联 q, 都存在于 $T=T_c$ 附近的发散斜率.

0.1.3.5.1 Correlation of Spin

对于 no correlation 体系, $\frac{N_{++}N_{--}}{N_{+-}^2}=\frac{1}{4}$.

将求和形式写作 $Z=\sum_{\sigma_0=\pm1}\sum_{\sigma_1\pm1}\left(\sum_{\sigma_2,\sigma_3,\cdots,\sigma_q=\pm1}\right)=Z_{++}+Z_{+-}+Z_{--}$. 存在键数约束 $N_{++}+N_{--}+N_{+-}=\frac{1}{2}qN$.

可解得 $(N_{++},N_{--},N_{+-})=\frac{qN}{4[e^{\gamma}\cosh\left(2\alpha+2\alpha'\right)+e^{-\gamma}]}\left(e^{2\alpha+2\alpha'+\gamma},e^{-2\alpha-2\alpha'+\gamma},2e^{-\gamma}\right)$.

代入检验自旋关联 $\frac{N_{++}N_{--}}{N_{+-}^2} = \frac{1}{4}\overset{\text{correlation}}{e^{4\gamma}}, \quad \gamma = \frac{J}{k_B T}$

0.1.3.5.2 Specific Heat

无外场内能为 $U_0 = -\frac{1}{2}qJN\frac{\cosh(2\alpha') - e^{-2\gamma}}{\cosh(2\alpha') + e^{-2\gamma}}$. 在 $T > T_c$ 时, 等效平均场为 $\alpha' = 0$. 此时热容为 $\frac{c_0}{Nk_B} = \frac{1}{2}q\gamma^2 \operatorname{sech}^2\gamma > 0$ $\left[\text{回忆 MFT 给出的 } c_0 \propto \overline{L}_0\frac{\mathrm{d}\overline{L}_0}{\mathrm{d}T} = 0 \text{ 和此处结果相悖, 显然是忽略了涨落关联造成的}\right]$

0.1.3.6 Exact Solution of 1-D Ising Model

考虑周期性条件 $(\sigma_{N+1} = \sigma_1)$, 哈密顿量 $H_N(\{\sigma_i\}) = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - \mu B\sum_{i=1}^{N}\sigma_i = -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - \frac{1}{2}\mu B\sum_{i=1}^{N}(\sigma_i + \sigma_{i+1})$

1. **矩阵法推导**: $Q_N = \sum_{\{\sigma_i\}}\exp\left\{\beta\sum_i\left[J\sigma_i\sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\} = \sum_{\{\sigma_i\}}\prod_i\exp\left\{\beta\left[J\sigma_i\sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\}$,

观察到可将其写作矩阵元形式: $Q_N = \sum_{\{\sigma_i\}}\prod_i\langle\sigma_i|P|\sigma_{i+1}\rangle = \sum_{\{\sigma_i\}}\langle\sigma_1|P\,\underline{\overset{\mathbb{I}}{|\sigma_2\rangle\langle\sigma_2|}}\,P|\sigma_3\rangle\cdots\langle\sigma_{N-1}|P\,\underline{\overset{\mathbb{I}}{|\sigma_N\rangle\langle\sigma_N|}}\,P|\sigma_{N+1}\rangle$

$= \sum_{\sigma_1=\pm1}\langle\sigma_1|P^N|\sigma_1\rangle = \operatorname{Tr}P^N = \lambda_+^N + \lambda_-^N \overset{\lambda_+\gg\lambda_-}{\approx} \lambda_+^N$. 其中 $\lambda_\pm$ 是矩阵 P 的特征值.

定义基矢 $|\sigma = +1\rangle = \begin{bmatrix}1\\0\end{bmatrix}, \quad |\sigma = -1\rangle = \begin{bmatrix}0\\1\end{bmatrix} \Rightarrow P = \begin{bmatrix}P_{++} & P_{+-}\\ P_{-+} & P_{--}\end{bmatrix} = \begin{bmatrix}e^{\beta(J+\mu B)} & e^{-\beta J}\\ e^{-\beta J} & e^{\beta(J-\mu B)}\end{bmatrix}$.

P 有两个特征值 $\lambda_\pm = e^{\beta J}\cosh(\beta\mu B) \pm [e^{-2\beta J} + e^{2\beta J}\sinh^2(\beta\mu B)]^{\frac{1}{2}} = e^{\beta J}\left[\cosh(\beta\mu B) \pm \sqrt{e^{-4\beta J} + \sinh^2(\beta\mu B)}\right]$.

$$\ln Q_N \approx N\ln\lambda_+ = N\beta J + N\ln\left\{\cosh(\beta\mu B) + \left[e^{-4\beta J} + \sinh^2(\beta\mu B)\right]^{\frac{1}{2}}\right\}$$

$F(B,T) = -k_B T\ln Q_N = -NJ - Nk_B T\ln\left\{\cosh(\beta\mu B) + \left[e^{-4\beta J} + \sinh^2(\beta\mu B)\right]^{\frac{1}{2}}\right\}, \quad M = \left(\frac{\partial F}{\partial B}\right), \quad \lim_{B\to0}M = 0$

2. **递推法导出配分函数**. 将 J 写作形式 J_i, 在无外场$(B=0)$下: $Q_N = \sum_{\{\sigma_i\}}\prod_i e^{\beta J_i\sigma_i\sigma_{i+1}}$. 分离出最后一项

$\sum_{\sigma_N=\pm1}e^{\beta J_{N-1}\sigma_{N-1}\sigma_N} = e^{\beta J_{N-1}\sigma_{N-1}} + e^{-\beta J_{N-1}\sigma_{N-1}} = 2\cosh(\beta J_{N-1}\sigma_{N-1}) \overset{\text{even function}}{=} 2\cosh(\beta J_{N-1})$

于是有递推关系: $Q_N = 2\cosh(\beta J_{N-1})Q_{N-1}, \quad Q_1 = \sum_{\sigma_1=\pm1}(1) = 2 \Rightarrow Q_N = Q_1\prod_{i=1}^{N-1}2\cosh(\beta J_i)$

类比 $\langle E\rangle = -\frac{\partial\ln Q}{\partial\beta}$, 通过求偏导得到空间关联 $\langle\sigma_k\sigma_{k+1}\rangle = -\frac{1}{\beta}\frac{\partial\ln Q_N}{\partial J_k} = \tanh(\beta J_k)$,

$$\langle\sigma_k\sigma_{k+r}\rangle \overset{\sigma_i^2=1}{=} \langle\sigma_k\sigma_{k+1}\cdot\sigma_{k+1}\sigma_{k+2}\cdots\sigma_{k+r-1}\sigma_{k+r}\rangle = \frac{1}{Q_N}\frac{\partial}{\beta\partial J_k}\frac{\partial}{\beta\partial J_{k+1}}\cdots\frac{\partial}{\beta\partial J_{k+r-1}}Q_N = \prod_{i=k}^{k+r-1}\tanh(\beta J_i) = \tanh^r(\beta J)$$

$$= e^{-r/\xi}, \quad \text{correlation length: } \xi = \frac{1}{\ln[\coth(\beta)]} \Rightarrow \text{随距离增大而迅速衰减.} \quad \lim_{T\to0}\xi = \infty, \quad \lim_{T\to\infty}\xi = 0$$

0.1.3.7 Phase Transition & Space Dimension

spin flip: energetically unfavored, entropically favored. $F = 2J - k_B T\ln N < 0 \Rightarrow T > \frac{2J}{k_B\ln N}$.

1D: $(+,+,-,+,+)$ 染色 元素翻转 $+\to-$, 不会消耗能量; 2D: $\begin{pmatrix}- & - & - & - & -\\ - & - & - & - & -\\ - & + & + & + & -\\ - & - & - & - & -\end{pmatrix}$ 染色元素翻转, 需要消耗能量.

0.1.3.8 Development of Ising Model

0.1.3.8.1 Spin Glass

$H = -\sum_{\langle i,j\rangle}J_{ij}\sigma_i\sigma_j - h\sum_i\sigma_i$, metastable state.

0.1.3.8.2 Hopfield Network Learning & Computation. $V_i \to \begin{cases} 1, & \text{if} \sum_j \omega_{ij} V_j > U \\ 0, & \text{if} \sum_j \omega_{ij} V_j < U \end{cases}.$

0.1.3.8.3 Boltzmann Machine $V_i = 0 \to 1, \quad \frac{P_{V_i=0}}{P_{V_i=1}} = e^{-\Delta E_i/k_B T}.$

0.1.4 Landau's Theory (of 2nd Order Phase Transition)

Critical exponents: $\alpha, \beta, \gamma, \delta$. External field h; Order parameter: $m_0 = m(h=0)$;

Response functions: C_0 (热容), $\chi_0 \sim \frac{\partial m}{\partial h}$ (磁化率).

$$\lim_{h\to 0, T\to T_c^-} m_0 \sim (T_c - T)^{\beta}, \quad \lim_{h\to 0} \chi_0 \sim \begin{cases} (T-T_c)^{-\gamma}, & T \to T_c^+ \\ (T_c - T)^{-\gamma'}, & T \to T_c^- \end{cases},$$

$$\lim_{h\to 0} m\Big|_{T=T_c} \sim h^{1/\delta}, \quad \lim_{h\to 0} C_0 \sim \begin{cases} (T-T_c)^{-\alpha}, & T \to T_c^+ \\ (T_c - T)^{-\alpha'}, & T \to T_c^- \end{cases}$$

[Example] 1. superfluid He: $\alpha \approx -0.01294$; 2. 0th approximation of Ising Model & Van der Waals theory of gas-liquid phase transition: $\alpha = \alpha' = 0, \quad \beta = \frac{1}{2}, \gamma = \gamma' = 1, \delta = 3$; 3. CO2: $\beta = 0.34, \quad \delta = 0.42, \quad \gamma = 1.32$. N2: $\beta = 0.33, \quad \delta = 0.42, \quad \gamma = 1.35$

[Discussion] Critical exponents. 考虑稳定性条件, 导出其关系 $\alpha' + 2\beta + \gamma' \geq 2$ (Rushbrooke's inequality).

0.1.4.1 Constrained Free Energy

平衡态下, $\mathrm{d}F = -S\mathrm{d}T - M\mathrm{d}H, \quad M = -\left(\frac{\partial F}{\partial H}\right)_T \Rightarrow F(T,H,M)$, let $\frac{\partial F(T,H,M)}{\partial M}\Big|_{\text{equilibrium}} = 0$. M acts as a constraint.

Continuous variable m_0: $m_0 = 0 \xrightarrow{\text{phase transition}} m_0 \neq 0$.

Free energy (analytic function of m_0): $\lim_{t, m_0 \to 0} \psi_0(t, m_0) = q(t) + r(t) m_0^2 + s(t) m_0^4 + \cdots, t = \frac{T - T_c}{T_c}$,

其中 $q(t), r(t), s(t)$ 是 phenomenological parameters(唯象参数).

一级相变: m_0-T 相图中, m_0 出现骤降. 在 gas-liquid PT 中, $m_0 = \rho_l - \rho_g$.

[Discussion] ψ_0 是对 m_0 的偶函数, 因为要求系统具有:

1. symmetry: 能量不应依赖于磁化的方向, 即 $\psi_0(m_0) = \psi_0(-m_0)$;

2. 稳定性: 自由能需要在 $m_0 = 0$ (高温相) 取得极小值, 若有奇次项则使得 $\frac{\partial \psi_0}{\partial m_0}\Big|_{m_0=0} \neq 0$.

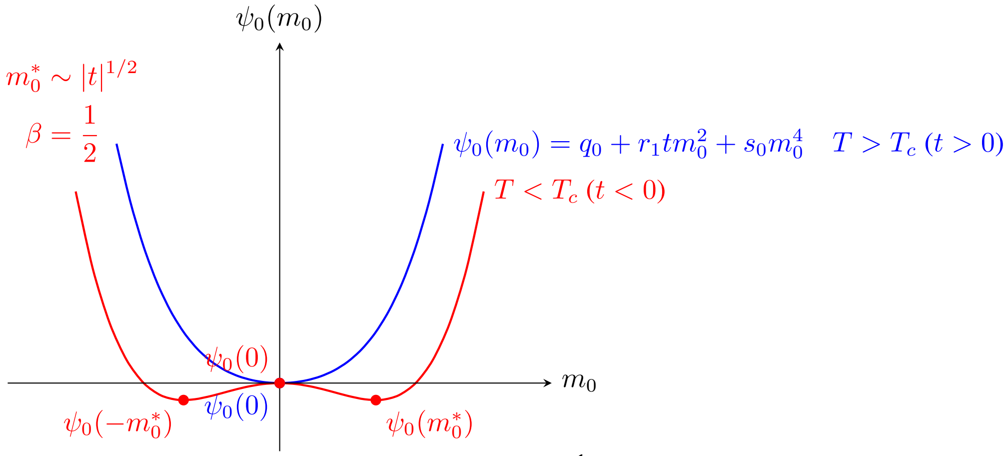
化学势 μ 全微分: $\mathrm{d}\mu(T,p,h) = -S\mathrm{d}T + v\mathrm{d}p - m\mathrm{d}h$. 加入外场 h 得到约化的化学势: $\widetilde{\mu} = \mu + mh$,

其全微分为 $\mathrm{d}\widetilde{\mu} = -S\mathrm{d}T + v\mathrm{d}p - h\mathrm{d}m$. 那么 $\mu = \widetilde{\mu} - mh = \overbrace{\underline{\widetilde{\mu}_0(T,p) + \alpha(T,p)m^2 + \beta(T,p)m^4}}^{\text{Gibbs Free Energy}} - mh$.

平衡态: $\frac{\partial \psi_0}{\partial m_0} = r(t) m_0 + 2s(t) m_0^3 = 0 \Rightarrow m_0 = 0, \pm\sqrt{\frac{-r(t)}{s(t)}}$. 将 $r(t), s(t)$ 以 t 阶数展开:

$r(t) = r_0 + \boxed{r_1 t} + r_2 t^2 + \cdots, \quad s(t) = \boxed{s_0} + s_1 t + s_2 t^2 + \cdots$. 仅取框选项, 即

$\psi_0 = q_0 + r_1 t m_0^2 + s_0 m_0^4, \quad r_1 > 0, \quad s_0 > 0$. 存在关系 $\sqrt{\frac{-r(t)}{2s(t)}} \simeq \sqrt{\frac{r_1 |t|}{2s_0}} \Rightarrow \beta = \frac{1}{2}, \quad m_0 \sim t^{\beta}$($\beta$ 的定义).



热容 $c_0 \sim \dfrac{\partial\,\text{Entropy}}{\partial t}$, $\quad$ Entropy $= \dfrac{\partial \psi_0}{\partial t} \simeq r_1 m_0^2 \begin{cases} 0, & t>0 \\ m_0 \sim |t|^{\frac{1}{2}}, & t<0 \end{cases}$

[Discussion] The concept of "**Universality Class(普适类)**". 以 critical exponents 对相变进行分类. 比如 Ising Model 和 Van der Waals gas 属于同类($\alpha = \alpha' = 0, \beta = \frac{1}{2}, \gamma = \gamma' = 1, \delta = 3$). $q(t), r(t), s(t)$ 不影响 critical exponents, 而是描述具体实验.

[Discussion] Wriss model @ 1907

$$F = U - TS, \quad \mathrm{d}U = -\int H \mathrm{d}M, \quad H = H_{\text{ext}} + b, \quad b \propto M : \text{mean field} \Rightarrow U = -H_{\text{ext}} M + \alpha M^2$$

$$S = S(m), \quad m = \frac{N_+ - N_-}{N}, \quad S(m) = -N k_B \sum_j P_j \ln P_j, \quad P_\pm(m) = \frac{1 \pm m}{2}$$

$$F = -hm + \alpha m^2 - N k_B T[(1+m)\ln(1+m) + (1-m)\ln(1-m)]$$

Landau Free Energy 物态方程: $\left.\dfrac{\partial F}{\partial m}\right|_{m_0} = 0 \Rightarrow h = 2 r_1 m + 4 s_0 m^3 \Rightarrow |m_0| = \sqrt{\dfrac{r_1 |t|}{2 s_0}}, \quad t \to 0^-$.

$$2^{\frac{1}{2}}\left[2\,\mathrm{sgn}\,(t)\left(\frac{m}{r_1^{\frac{1}{2}}|t|^{\frac{1}{2}}/s_0^{\frac{1}{2}}}\right) + 4\left(\frac{m}{r_1^{\frac{1}{2}}|t|^{\frac{1}{2}}/s_0^{\frac{1}{2}}}\right)^3\right] = \frac{h}{r_1^{\frac{3}{2}}|t|^{\frac{3}{2}} s_0^{\frac{1}{2}}} \Leftrightarrow 2^{\frac{1}{2}}\left[2\,\mathrm{sgn}\,(t)\tilde{m} + \tilde{m}^3\right] = \tilde{h}, \quad \tilde{\psi} = -\tilde{h}\tilde{m} + \mathrm{sgn}\,(t)\tilde{m}^2 + \tilde{m}^4$$

约化自由能: $\tilde{\psi} = \dfrac{\psi}{r_1^2 |t|^2 / s_0} \sim \tilde{h}$, 或 $\dfrac{\psi}{|t|^2} \sim \dfrac{h}{|t|^{\frac{3}{2}}}$. 于是有 $\boxed{\psi = C_2 |t|^2 f\left(\dfrac{C_1 h}{|t|^{\frac{3}{2}}}\right)}$.

Beyond MFT: 将指数延拓为 $\psi = C_2 |t|^{2-\alpha} f\left(\dfrac{C_1 h}{|t|^{\Delta}}\right)$, $m_0 \sim \lim_{h\to 0}\left(\dfrac{\partial \psi}{\partial h}\right) \sim \lim_{h \to 0} |t|^{2-\alpha-\Delta} f'\left(\dfrac{C_1 h}{|t|^{\Delta}}\right) \Rightarrow \beta = 2 - \alpha - \Delta$

$\gamma = \gamma' = \alpha + 2\Delta - 2, \quad \delta = \dfrac{\Delta}{\beta}$. 不需要知道具体的 Hamiltonian.

0.1.4.2 Fluctuations & Correlation Functions

无关联体系: $\langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle$. 定义**关联函数** $g_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle = \langle \delta\sigma_i \delta\sigma_j \rangle$, 其中 $\delta\sigma = \sigma - \langle \sigma \rangle$.

配分函数为 $Q_N(H,T) = \sum_{\{\sigma_i\}} \exp\left(\beta J \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \beta \mu H \sum_i \sigma_i\right)$, 通过对 $\ln Q_N$ 求偏导以得到期望值:

$$\frac{\partial \ln Q_N}{\partial H} = \beta\mu \left\langle \sum_i \sigma_i \right\rangle = \beta \langle M \rangle, \quad \frac{\partial^2 \ln Q_N}{\partial H^2} = \beta^2\left(\langle M^2 \rangle - \langle M \rangle^2\right);$$

$$\chi = \frac{\partial \overline{M}}{\partial H} = \frac{\partial}{\partial H}\left(\frac{1}{\beta}\frac{\partial \ln Q_N}{\partial H}\right) = \beta\left(\langle M^2 \rangle - \langle M \rangle^2\right) = \beta\mu^2 \sum_{ij} g_{ij},$$

[Discussion] Fluctuation & Response Theorem.

1. 热容 $C_v = \left.\dfrac{\partial \langle E \rangle}{\partial T}\right|_V = \dfrac{\langle (\Delta E)^2 \rangle}{k_B T^2}$;
2. 等温压缩率 $\kappa_T = -\dfrac{1}{\langle V \rangle}\left.\dfrac{\partial \langle V \rangle}{\partial P}\right|_T = \dfrac{\langle (\Delta V)^2 \rangle}{k_B T \langle V \rangle}$.

For homegeneous system, $g_j = g(\vec{r})$, $\quad \chi = \beta\mu^2 N \sum_{\vec{r}} g(\vec{r}) = N\beta\mu^2 \dfrac{1}{a^d}\displaystyle\int \mathrm{d}^d\vec{r} g(\vec{r})$, $\quad a$: lattice constant. 也可理解为再乘上

$e^{i\vec{k}\cdot\vec{r}}$ 进行傅里叶变换得到 $\widetilde{g}\left(\vec{k}\right)$, 但仅取 $\vec{k}=0$ 的分量, 即 $\widetilde{g}\left(\vec{k}=0\right)\to\chi$.

[Discussion] **Linear Response**. $H=H_0[m(x)]-\int \mathrm{d}x m(x)h(x)$, 其中 $m(x)$ 和 $h(x)$ 是 linear coupling 的. 那么

$$F=-k_BT\ln Q,\quad \chi(x,x')=\frac{\partial m(x')}{\delta h(x)}=-\frac{\partial^2 F}{\partial h(x)\partial h(x')}=\beta\left(\langle m(x)m(x')\rangle-\langle m(x)\rangle\langle m(x')\rangle\right)$$

0.1.4.2.1 Generalized Landau Free Energy Correlation Function

一般性地, 自由能 $F=\int \mathrm{d}^d\vec{x}\left\{am\left(\vec{x}\right)^2+b\left[\nabla m\left(\vec{x}\right)\right]^2\right\}$, $m\left(\vec{x}\right)$ 为 order parameter, 其中 $a=kt$, 于是存在关联长度 $\xi=\sqrt{\frac{b}{kt}}$. 尝试求解序参量 $m\left(\vec{x}\right)$ 的关联函数 $\langle m\left(\vec{x}\right)m\left(\vec{x}'\right)\rangle$.

可使用 Fourier 变换 $m\left(\vec{x}\right)=\frac{1}{(2\pi)^d}\int \mathrm{d}^d\vec{q}e^{i\vec{q}\cdot\vec{x}}\widetilde{m}\left(\vec{q}\right),\quad \widetilde{m}\left(\vec{q}\right)=\int \mathrm{d}^d\vec{x}e^{-i\vec{q}\cdot\vec{x}}m\left(\vec{x}\right)$ 将其在 $\vec{q}$ 空间中处理.

规定 $\int e^{i\left(\vec{q}-\vec{q}'\right)\cdot\vec{x}}\mathrm{d}^d\vec{x}=(2\pi)^d\delta(\vec{q}-\vec{q}')$. 变换后自由能为 $F\left[\widetilde{m}\left(\vec{q}\right)\right]=\int\frac{\mathrm{d}^d\vec{q}}{(2\pi)^d}\left(kt+bq^2\right)\widetilde{m}\left(\vec{q}\right)\widetilde{m}\left(-\vec{q}\right)$.

记关联函数 $C\left(\vec{x}\right)\equiv\langle m\left(\vec{x}\right)m(0)\rangle=\frac{1}{(2\pi)^d}\int \mathrm{d}^d\vec{q}e^{i\vec{q}\cdot\vec{x}}\left\langle\left|\widetilde{m}\left(\vec{q}\right)\right|^2\right\rangle$, 其 Fourier 变换后形式为:

$$\widetilde{C}\left(\vec{q}\right)=\frac{\int\left|\widetilde{m}\left(\vec{q}\right)\right|^2\exp\left\{-\beta F\left[\widetilde{m}\left(\vec{q}\right)\right]\right\}\mathrm{d}^d\vec{q}}{\int\exp\left\{-\beta F\left[\widetilde{m}\left(\vec{q}\right)\right]\right\}\mathrm{d}^d\vec{q}}=\frac{(2\pi)^d}{2}\frac{T}{kt+bq^2}=\frac{(2\pi)^d}{2}\frac{T}{kt(1+\xi^2q^2)}$$

重新变换回 $\vec{x}$ 空间, 得到 $C\left(\vec{x}\right)=\frac{T}{2}\int \mathrm{d}^d\vec{q}e^{i\vec{q}\cdot\vec{x}}\frac{1}{kt+bq^2}$.

1. $d=1$: Residue theorem. $\lim\limits_{r\gg\xi}C(r)\propto r^{-(d-1)/2}e^{-r/\xi}$;
2. $d=3$: $C(r)\sim\frac{1}{r}e^{-r/\xi}$.

[Discussion] New critical exponents. 对于关联现象存在 $\lim\limits_{h\to0,t\to0^+}\xi\sim t^{-\nu},\quad C(r)\Big|_{t=0}\sim r^{-(d-2+\eta)}$.

0.1.4.2.2 Validity of Mean-Field Approximation

平均场理论的生效范围

1. **涨落 v.s. 效应**. 选任意一点 σ_0, 设范围尺度(半径)为 ξ, 圈出范围 Ω. 范围内其余自旋为 σ_r.
If $\int_\Omega\langle\delta\sigma_r\delta\sigma_0\rangle\mathrm{d}^d\vec{r}\ll\int_\Omega\langle\sigma_r\rangle\langle\sigma_0\rangle\mathrm{d}^d\vec{r}\Leftrightarrow T\chi\ll m^2\xi^d\Leftrightarrow T(T_c-T)^{-\gamma}\ll(T_c-T)^{2\beta}(T_c-T)^{-\nu d}\Rightarrow\gamma<\nu d-2\beta$,
即涨落相对效应很小, 则 MFT($\gamma=1,\beta=\nu=\frac{1}{2}$) 较好 $\Rightarrow\boxed{d>4}$.
2. **涨落/关联贡献**. 对相变/关联有贡献的内能: $U_f=-J\sum\limits_{i,j}\left(\langle\sigma_i\sigma_j\rangle-\langle\sigma_i\rangle\langle\sigma_j\rangle\right)=-J\sum\limits_{i,j}g(r_{ij})$,
其中 $g(r)\sim\int \mathrm{d}^d\left(\vec{q}a\right)\frac{e^{-i\vec{q}\cdot\vec{x}}}{t(1+\xi^2q^2)}$ 为关联函数. 关联/涨落部分的热容与 $C_f=-\frac{\partial g(r)}{\partial t}=\int q^{d-1}\frac{e^{-i\vec{q}\cdot\vec{r}}}{t^2(1+\xi^2q^2)}\mathrm{d}q$ 有关.
考虑 Long wavelength limit (small $q\sim\frac{1}{\xi}$): $\Rightarrow C_f\sim\int \mathrm{d}q\frac{q^{d-1}}{t^2(1+\xi^2q^2)}\sim\xi^{-d}t^{-2}\sim\left(t^{-\frac{1}{2}}\right)^{-d}t^{-2}\sim t^{-(d-4)/2}$,
发现 $\lim\limits_{d<4,t\to0}C_f=\infty$, 和 1. 中表述一致.

0.1.5 Scale Transformation

对 2D spin lattice 进行标度变换: $\begin{bmatrix}x&o&x\\o&o&x\\x&x&x\end{bmatrix}\xrightarrow{N_x>N_o}X$. 观察发现, 对于 Critical state($\xi\to\infty$), 会保持 Scale invariance.

[Discussion] Symmetry consideration (**Noether's theorem**).
$L=\left(\dot{x}^2+\dot{y}^2\right)+V(x-y)$, 对 $(x,y)\to(x+\delta,y+\delta)$ 表现出平移不变性; $L=\dot{x}^2+\dot{y}^2+x^2+y^2$, 表现出旋转不变性.

0.1.5.1 Implement Scale Transformation

存在两种尺度变换思路:

1. Block-spin transformation: $\begin{bmatrix} o & o & o & o \\ o & o & o & o \\ o & o & o & o \\ o & o & o & o \end{bmatrix} \xrightarrow{l=2} \begin{bmatrix} \bullet & \bullet \\ \bullet & \bullet \end{bmatrix}$, 晶格常数 $a \to a' = la(l=2)$; 自旋个数 $N \to N' = l^{-d}N(d=2)$;
尺度 $r \to r' = l^{-1}r$. Number density invariant: $\dfrac{N}{a^d} = \dfrac{N'}{(a')^d}$. $\sigma = \pm 1 \to \sigma' = \pm 1$.

2. $\begin{bmatrix} \phi & o & \phi & o & \phi & o \\ o & \phi & o & \phi & o & \phi \\ \phi & o & \phi & o & \phi & o \\ o & \phi & o & \phi & o & \phi \\ \phi & o & \phi & o & \phi & o \\ o & \phi & o & \phi & o & \phi \end{bmatrix}$, $Q_N = \sum_{\sigma_i} \exp\left[-\beta H_N(\{\sigma_i\}, J)\right] = \sum_{\sigma'_j} \exp\left[-\beta H_{N'}\left(\{\sigma'_j\}, J'\right)\right]$, $N' = \dfrac{N}{2}$, $a' = \sqrt{2}a$, $l = \dfrac{a'}{a} = \sqrt{2}$.

考察对相变有贡献的自由能(Landau 自由能是 Helmholtz 自由能), Single point: $N'\psi^{(s)}(t', h') = N\psi^{(s)}(t, h)$,
类比 $N \to N' = l^{-d}N$, 线性假设 $t \to t' = l^{y_t}t, h \to h' = l^{y_h}h$. 于是将 $\psi^{(s)}$ 变换写作 $\psi^{(s)}(t,h) = l^{-d}\psi^{(s)}\left(l^{y_t}t, l^{y_h}h\right)$ 形式.
已知自由能 $\psi^{(s)}(t,h) = |t|^\beta \widetilde{\psi}\left(\dfrac{h}{|t|^\alpha}\right)$, 变换前后分别代入得 $|t|^\beta \widetilde{\psi}\left(\dfrac{h}{|t|^\alpha}\right) = l^{-d}\left|t'\right|^\beta \widetilde{\psi}\left(\dfrac{h'}{|t'|^\alpha}\right)$,
比较可得 $\dfrac{h}{|t|^\alpha} = \dfrac{h'}{|t'|^\alpha}$, $\quad |t|^\beta = l^{-d}\left|t'\right|^\beta$. 因此指数间存在关系 $\alpha = \dfrac{y_h}{y_t}, \quad \beta = \dfrac{d}{y_t}$.

0.1.5.2 Scale Transformation in 1D & 2D Ising Models

0.1.5.2.1 1D Ising Model 研究 $J \to J', \quad B \to B'$ 变换的具体形式. 将配分函数写作形式:

$$Q_N = \sum_\sigma \exp\left\{\beta \sum_i \left[J\sigma_i\sigma_{i+1} + \frac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\} = \sum_\sigma \exp\left\{\sum_i \left[K_0 + K_1\sigma_i\sigma_{i+1} + \frac{1}{2}K_2(\sigma_i + \sigma_{i+1})\right]\right\}$$

将系数写作矢量形式 $\vec{K} = (K_0, K_1, K_2) = (0, \beta J, \beta\mu B)$. 可知变换时有 $\vec{K} \to \vec{K}'$, 其蕴含具体变换的信息.
不妨假定总自旋数 N 为偶数, 则取自旋链环中所有偶数位置, 则自旋数变换: $N \to N' = \dfrac{N}{2}$. 变换前后的配分函数相等:

$$Q_N = \sum_{\sigma'_j} \prod_{j=1}^{\frac{N}{2}} e^{2K_0} e^{\frac{1}{2}K_2\left(\sigma'_j + \sigma'_{j+1}\right)} 2\cosh\left[K_1\left(\sigma'_j + \sigma'_{j+1}\right) + K_2\right] = \sum_{\sigma'_j} \prod_{j=1}^{\frac{N}{2}} e^{K'_0 + K'_1\sigma'_j\sigma'_{j+1} + \frac{1}{2}K'_2\left(\sigma'_j + \sigma'_{j+1}\right)}$$

$\sigma \to \sigma'$ 的变换即相邻自旋求和, 涉及 3 类情况: $\sigma_{2j} = \sigma_{2j+1} = \pm 1 \Rightarrow \sigma'_j = \pm 1; \quad \sigma_{2j} = -\sigma_{2j+1} \Rightarrow \sigma'_j = 0$, 作为约束方程.
解得 $\vec{K} \to \vec{K}'$ 的具体表达式:
$e^{K'_0} = 2e^{2K_0}\left[\cosh(2K_1 + K_2)\cosh(2K_1 - K_2)\cosh^2 K_2\right]^{\frac{1}{4}} = \natural_0(K_0, K_1, K_2), \quad e^{K'_1} = \natural_1(K_1, K_2), \quad e^{K'_2} = \natural_2(K_1, K_2)$
[Discussion] 研究无外场条件($K_2 = 0$)下各量. 配分函数变换为 $Q_N(K_1, K_2) = e^{N'K'_0}Q_{N'}(K'_1, K_2)'$,
因此自由能变换为 $F_N(K_1, K_2) = -N'K'_0 + F_{N'}(K'_1, K'_2)$.
设单自旋自由能为 $f(K_1, K_2)$ 形式: $f(K_1; K_2 = 0) = -\dfrac{1}{2}\ln\left[2\cosh^{\frac{1}{2}}(2K_1)\right] + \dfrac{1}{2}f\left(K'_1 = \ln\left[\cosh^{\frac{1}{2}}(2K_1)\right]; K'_2 = 0\right)$
令 $x = K_1$, 即有 $f(x) = -\dfrac{1}{2}\ln\left[2\cosh^{\frac{1}{2}}(2x)\right] + \dfrac{1}{2}f\left(\ln\left[\cosh^{\frac{1}{2}}(2x)\right]\right)$, 代入 $x = 0$ 发现 $f(0) = -\ln 2$.
猜测 $f(x) = -\ln[2y(x)]$, 代入单自旋自由能变换式: $\dfrac{y^2(x)}{y\left\{\ln\left[\cosh^{\frac{1}{2}}(2x)\right]\right\}} = \cosh^{\frac{1}{2}}(2x)$, 解得 $y(x) = \cosh(x)$.
因此 $\boxed{f(K_1; K_2 = 0) = -\ln(2\cosh K_1)}$.

0.1.5.2.2 2D Ising Model $Q_N = e^{NK_0}\sum_{\sigma_i}\exp\left\{K\sum_{\langle i,j\rangle}\sigma_i\sigma_j + L\sum\sigma_i\sigma_j + M\sum\sigma_j\sigma_r\sigma_l\sigma_m\right\}$

0.1.5.2.3 Origin of Fixed Point 变换 $K' = R_l(K)$ 可以视为点在 $\vec{K}$ 空间中的 flow(轨迹).
那么可能存在点 K^*, 使得 $R_l(K^*) = K^*$. 这类点即 **Fixed Point**.
[Example] $X_{i+1} = \lambda X_i(1 - X_i)$, 存在两个不动点 $X^* = 0, 1$.

变换对应于矩阵, 即可用特征值来进行描述. 令变换无穷小, 则 $R_{l_2}[R_{l_1}(K)] = R_{l_1 * l_2}(K) \longrightarrow \lambda_{l_1}\lambda_{l_2} = \lambda_{l_1 * l_2}$.
这说明特征值可能为 $\lambda(l) \sim l^\alpha$ 形式, 从而满足 $l_1^\alpha l_2^\alpha = (l_1 \cdot l_2)^\alpha$.

研究 $\vec{K}$ 的连续变换. 记 $R_l^n(K^*)=K^{(n)}$ 为对 $\vec{K}$ 进行了 n 次 R_l 变换的结果. 那么关联长度将会满足变换式 $\xi^{(n)}=l^{-n}\xi^{(0)}$.
对于不动点 K^* 而言, 将会有 $\xi(K^*)=l^{-1}\xi(K^*)$. 该方程具有两个解 $\{\overset{\text{trivial}}{0},\overset{\text{critical}}{\infty}\}$.

[Discussion] 若经过 n 次变换后的关联长度 $\xi\left[K^{(n)}\right]$, 能推导出初始点 $K^{(0)}=R_l^0(K)$ 的关联长度 $\xi(K^{(0)})=\infty$ 吗?
由于 $l>1$, 则关联长度有 $\xi(K')=l^{-1}\xi(K)<\xi(K)$. 可见 $\xi\left[K^{(n)}\right]$ 递减, 其仍发散说明初项 $\xi\left[K^{(0)}\right]=\infty$.
可见 $\xi=\infty$ 不仅会在不动点/Critical point 出现, 也会在 $\vec{K}$ 空间中连续出现而形成 **Critical Curve**.

0.1.5.2.4 RG Flow Near the Critical/Fixed Point in $\vec{K}$ Space 研究不动点附近的 $\vec{K}=\vec{K}^*+\vec{k}$, 其中 $\vec{k}\to\vec{0}$.

那么可将 $K\to K'$ 变换写作 Taylor 展开: $\vec{K}'=\vec{K}^*+\vec{k}'=R_l\left(\vec{K}^*+\vec{k}\right)=R_l\left(\vec{K}^*\right)+\left.\dfrac{\partial R_l\left(\vec{q}\right)}{\partial\vec{q}}\right|_{\vec{q}=\vec{K}^*}\vec{k}+\cdots$,

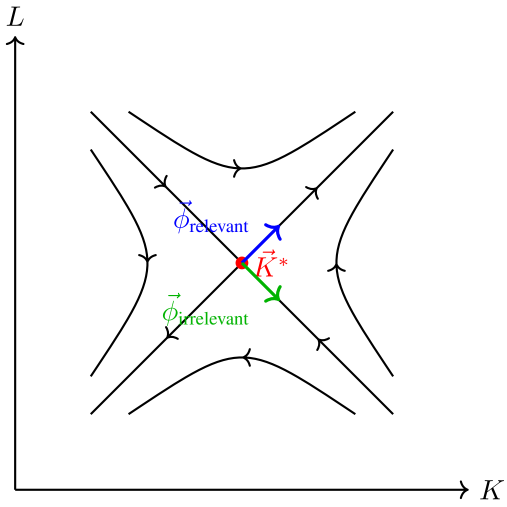
其中 $\vec{k}'=A_l\vec{k}$, $\quad A_l=\left.\dfrac{\partial R_l\left(\vec{q}\right)}{\partial\vec{q}}\right|_{\vec{q}=\vec{K}^*}$. 将 $\vec{k}$ 以基矢展开 $\vec{k}=\sum\limits_i u_i\hat{\phi}_i$, 则变换式 $\vec{k}'=A_l\vec{k}$ 即可写作 $\sum\limits_i u_i'\hat{\phi}_i=A_l\sum\limits_i u_i\hat{\phi}_i$.

特征方程 $A_l\hat{\phi}_i=\lambda_i\hat{\phi}_i$, 代入为 $\sum\limits_i u_i'\hat{\phi}_i=\sum\limits_i u_i\lambda_i\hat{\phi}_i$, 即得分量变换式 $u_i\to u_i'=\lambda_i u_i=l^{y_i}u_i$.

n 次变换后, 分量 $u_i^{(n)}=l^{ny_i}u_i^{(0)}=\lambda_i^n u_i^{(0)}$; 可见:

1. $\lambda_i>1$, 则分量发散, 此时 u_i 为 **Relevant Variable**(有相变贡献);
2. $\lambda_i<1$, 则分量收敛于 0, 此时 u_i 为 **Irrelevant Variable**(无相变贡献).

[Discussion] Scale transformation 是一个信息丢失的过程, 所以重整化群严格来说不能被称为群结构.
现在研究 2D Ising Model 中的 RG flow. 取公式中的 K 和 L 作为坐标轴, 得到大致的 RG flow 示意图:



在不动点附近存在 $\vec{\phi}_{\text{relevant}}$ 和 $\vec{\phi}_{\text{irrelevant}}$, 两本征矢所指的方向. 亦即, 若要流沿着指向 K^* 的曲线移动, 要求分量 $u_{\text{relevant}}\to 0$.

[Discussion] Emergence of Non-analyticity/singularity

1. 回忆: 在研究配分函数时, 每一项都是解析的, 若要产生 singularity(奇点), 则需要求和项数无穷大, 而某些物理量保持有限值(e.g. $\lim\limits_{N,V\to\infty}n=\dfrac{N}{V}=n_0$);

2. 不动点也是通过无穷连续变换产生的;

3. 微分方程 $\dfrac{\mathrm{d}u}{\mathrm{d}t}=-2u\left(u^2-1\right)$ 的精确解为 $u(t)=\dfrac{u_0}{\sqrt{u_0^2-(u_0^2-1)e^{-4t}}}$, 其中 $u_0=u\Big|_{t=0}$. 存在不动点 $u^*=\pm1$, 通过 $\lim\limits_{t\to\infty}u(t)=\operatorname{sgn}\left(u_0\right)$ 逼近.

[Example] RG Equ. of 2D Ising Model: $\begin{cases}K'=2K^2+L\\L'=K^2\end{cases}$, 通过 $\begin{cases}K'=K\\L'=L\end{cases}$ 解得 $\begin{cases}K^*=\dfrac{1}{3}\\L^*=\dfrac{1}{9}\end{cases}$. 取不动点附近 $\begin{cases}K=K^*+k_1\\L=L^*+k_2\end{cases}$,

小量变换满足 $\begin{cases}k_1'=\dfrac{4}{3}k_1+k_2\\k_2'=\dfrac{2}{3}k_1\end{cases}$. 将其写作矩阵形式: $\vec{k}'=A_l\vec{k}\Rightarrow A_l=\begin{bmatrix}4/3&1\\2/3&0\end{bmatrix}$. 该矩阵的特征值为 $\lambda_{1,2}=\dfrac{2\pm\sqrt{14}}{3}$.

($\lambda_1>1$, 则 u_1 是 **Relevant Variable**, 表现为 $u_1\neq0$ 时, RG flow 趋于发散.)

特征矢量 $\vec{\phi}_{1,2} = \begin{bmatrix} 2 \pm \sqrt{10} \\ 2 \end{bmatrix}$; 将其作为基矢, 则小量 $\vec{k} = \begin{bmatrix} k_1 \\ k_2 \end{bmatrix} = u_1\vec{\phi}_1 + u_2\vec{\phi}_2$. 反解得到 $u_1 = 2k_1 + (\sqrt{10}-2)k_2$.

令 $u_1 = 0$, 则 $\lambda_1 > 1$ 不影响流的轨迹经过不动点 (K^*, L^*). 此时得到 K-L 空间中的一条斜线 $2k_1 + (\sqrt{10}-2)k_2 = 0$, 该斜线将与 K 轴相交于 $K_c \simeq 0.3979$.

[Discussion] Complexity? Universal behavior?

形如 $x_{j+1} = f(x_i, \lambda)$ 的迭代方程. 如 $x_{i+1} = \lambda x_i(1-x_i)$, 随着 λ 值变化出现不动点 x^* 的分形.

定义 $\delta_n = \dfrac{x_{n+1} - x_n}{x_n - x_{n-1}}$, 发现其存在规律 $\lim\limits_{n\to\infty} \delta_n = 4.6692\cdots$.