晶体相场法公式梳理

推导的重要节点或重要结论，已用方框标出来；引入的新定义，已用下划线勾出!

目录

$$F[\rho(\vec{r})] \to F[n(\vec{r})] \to F[\phi(\vec{r})] \to F[\psi(\vec{r})]$$

1 自由能的导出

通常而言，考虑粒子的动能项和势能项，从而其能量 E 写为：

$$E = \frac{p^2}{2m} + V$$

由此，也将自由能关于粒子密度的泛函 $F[\rho(\vec{r})]$ 分为动能项和相互作用项：

$$F[\rho(\vec{r})] = F_{id}[\rho(\vec{r})] + F_{ex}[\rho(\vec{r})]$$

上式中 $F[\rho(\vec{r})]$ 的内涵是密度标量场 $\rho(\vec{r})$ 映射到某个实数的自由能泛函，F_{id} 和 F_{ex} 分别代表动能项和相互作用项，下面分别对它们的形式进行推导。

1. 动能项 F_{id}

假设粒子服从玻尔兹曼分布，并由动能 ε 可以写出其粒子配分函数 Z_1:

$$\varepsilon = \frac{p^2}{2m} \quad Z_1 = \sum \omega_l e^{-\beta\varepsilon_l} \approx \int \frac{d\vec{r}d\vec{p}}{h^3} e^{-\beta\varepsilon} \quad \Rightarrow \quad \boxed{Z_1 = \frac{V}{h^3}\left(\frac{2m\pi}{\beta}\right)^{3/2}}$$

考虑到同种粒子的全同性，由粒子配分函数可得到自由能的表达式：

$$F = -Nk_BTlnZ_1 + k_BTlnN!$$

由此不难得到自由能密度，并导出 F_{id} 的表达式 (利用 $lnN! \approx NlnN - N$)：

$$f_{id} = \frac{1}{V}(-Nk_BTlnZ_1 + k_BTlnN!) = \frac{k_BT}{V}[Nln(\rho\lambda_T^3) - N] \qquad \lambda_T = \frac{h}{\sqrt{2\pi mkT}}$$

$$\Rightarrow \boxed{F_{id}[\rho(\vec{r})] = \int f_{id}[\rho(\vec{r})]d\vec{r} = \int k_BT[\rho(\vec{r})ln(\rho(\vec{r})\lambda_T^3) - \rho(\vec{r})]d\vec{r}}$$

定义动能项化学势 μ^{id}:

$$\mu^{id} = \frac{\delta F_{id}}{\delta\rho} = \frac{\partial f_{id}}{\partial\rho} = k_BTln(\rho(\vec{r})\lambda_T^3) \quad \Rightarrow \quad \underline{ln(\rho(\vec{r})\lambda_T^3) = \beta\mu^{id}}$$

此外，定义参考密度场 $\underline{\rho_0(\vec{r}) = Const.}$ 从而，利用动能项化学势对 λ_T 进行替换，自由度的动能项可写为：

$$F_{id}[\rho(\vec{r})] = \int k_BT[\rho(\vec{r})ln\left(\rho(\vec{r})\frac{\rho_0}{\rho_0}\lambda_T^3\right) - \rho(\vec{r})]d\vec{r}$$

$$= k_BT\int d\vec{r}\rho(\vec{r})ln\left(\frac{\rho(\vec{r})}{\rho_0}\right) + k_BT\int d\vec{r}\rho(\vec{r})[ln(\rho_0\lambda_T^3) - 1]$$

$$\Rightarrow \boxed{F_{id}[\rho(\vec{r})] = \frac{1}{\beta}\int d\vec{r}\rho(\vec{r})ln\left(\frac{\rho(\vec{r})}{\rho_0}\right) + \frac{1}{\beta}\int d\vec{r}\rho(\vec{r})[\beta\mu_0^{id} - 1]}$$

2. 相互作用项 F_{ex}

首先定义 n 点直相关函数：

$$\underline{C^{(n)}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_n; [\rho]) = -\beta\frac{\delta^n F_{ex}}{\delta\rho(\vec{r}_1)...\delta\rho(\vec{r}_n)}}$$

令 $\underline{\Delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0}$，并对 $F_{ex}[\rho(\vec{r})]$ 展开到二阶并代入直相关函数：

$$F_{ex}[\rho(\vec{r})] \approx F_{ex}[\rho_0] - \frac{1}{\beta}\int \Delta\rho(\vec{r})C^{(1)}(\vec{r};\rho_0)d\vec{r} - \frac{1}{2\beta}\int\int \Delta\rho(\vec{r})C^{(2)}(\vec{r},\vec{r'};\rho_0)\Delta\rho(\vec{r'})d\vec{r}d\vec{r'}$$

定义相互作用项的化学势 μ^{ex}:

$$\mu^{ex}=\frac{\delta F_{ex}}{\delta\rho}=-\frac{C^{(1)}(\vec{r};\rho)}{\beta}\quad\Rightarrow\quad\underline{C^{(1)}(\vec{r};\rho)=-\beta\mu^{ex}}$$

由此可将自由能的相互作用项写为：

$$\boxed{F_{ex}[\rho(\vec{r})]\approx F_{ex}[\rho_0]+\int\Delta\rho(\vec{r})\mu_0^{ex}d\vec{r}-\frac{1}{2\beta}\int\int\Delta\rho(\vec{r})C^{(2)}(\vec{r},\vec{r'};\rho_0)\Delta\rho(\vec{r'})d\vec{r}d\vec{r'}}$$

3. 自由能 F

综上，自由能可写作：

$$F[\rho(\vec{r})]=\frac{1}{\beta}\int d\vec{r}\rho(\vec{r})ln\left(\frac{\rho(\vec{r})}{\rho_0}\right)+\frac{1}{\beta}\int d\vec{r}\rho(\vec{r})[\beta\mu_0^{id}-1]+F_{ex}[\rho_0]+\int\Delta\rho(\vec{r})\mu_0^{ex}d\vec{r}$$
$$-\frac{1}{2\beta}\int\int\Delta\rho(\vec{r})C^{(2)}(\vec{r},\vec{r'};\rho_0)\Delta\rho(\vec{r'})d\vec{r}d\vec{r'}$$

为了统一表达化学势和参考密度下的自由能，令：

$$\underline{\mu_0=\mu_0^{id}+\mu_0^{ex}}\qquad\underline{F[\rho_0]=F_{id}[\rho_0]+F_{ex}[\rho_0]}$$

先凑出 $F_{id}[\rho_0]$ 的形式，再利用上式关系，自由能可写为：

$$F[\rho(\vec{r})]=F[\rho_0]+\int d\vec{r}\Delta\rho(\vec{r})\mu_0+\frac{1}{\beta}\int d\vec{r}\left[\rho(\vec{r})ln\left(\frac{\rho(\vec{r})}{\rho_0}\right)-\Delta\rho(\vec{r})\right]$$
$$-\frac{1}{2\beta}\int\int\Delta\rho(\vec{r})C^{(2)}(\vec{r},\vec{r'};\rho_0)\Delta\rho(\vec{r'})d\vec{r}d\vec{r'}$$

定义 $\underline{\Delta F=F[\rho(\vec{r})]-F[\rho_0]}$, 从而不难得到：

$$\frac{\Delta F}{k_BT}=\beta\mu_0\int d\vec{r}\Delta\rho(\vec{r})+\int d\vec{r}\left[\rho(\vec{r})ln\left(\frac{\rho(\vec{r})}{\rho_0}\right)-\Delta\rho(\vec{r})\right]-\frac{1}{2}\int\int d\vec{r}d\vec{r'}\Delta\rho(\vec{r})C^{(2)}(\vec{r},\vec{r'};\rho_0)\Delta\rho(\vec{r'})$$

<u>通常令参考化学势 $\mu_0=0$</u>，于是：

$$\boxed{\frac{\Delta F}{k_BT}=\int d\vec{r}\left[\rho(\vec{r})ln\left(\frac{\rho(\vec{r})}{\rho_0}\right)-\Delta\rho(\vec{r})\right]-\frac{1}{2}\int\int d\vec{r}d\vec{r'}\Delta\rho(\vec{r})C^{(2)}(\vec{r},\vec{r'};\rho_0)\Delta\rho(\vec{r'})}$$

==================== 补充内容 ====================

类似地，将上式推广到多元体系，并对相互作用项完全展开：

$$\frac{\Delta F}{k_B T} = \int d\vec{r} \sum_i \left[\rho_i(\vec{r}) ln \left(\frac{\rho_i(\vec{r})}{\rho_0^i} \right) - \Delta \rho_i(\vec{r}) \right]$$

$$- \sum_{n=2}^{\infty} \frac{1}{n!} \int d\vec{r}_1 ... d\vec{r}_n \sum_{i,...,j} C_{i,...,j}^{(n)}(\vec{r}_1, ..., \vec{r}_n) \Delta \rho_i(\vec{r}_1) ... \Delta \rho_j(\vec{r}_n)$$

其中 $i, ...j = A, B, C...$，即不同种类的物质，因而 $C_{i,...,j}^{(n)}$ 表示不同种类物质之间的相互作用。这便是处理二元或二元以上晶体相场法自由能的基本公式。

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定义无量纲数密度 $n(\vec{r})$:

$$n(\vec{r}) = \frac{\Delta \rho(\vec{r})}{\rho_0} = \frac{\rho(\vec{r}) - \rho_0}{\rho_0} \quad \Rightarrow \quad \underline{\Delta \rho(\vec{r}) = \rho_0 n(\vec{r})} \quad \underline{\rho(\vec{r}) = \rho_0 [n(\vec{r}) + 1]}$$

根据上式，将密度场无量纲化，得到自由能的最终形式：

$$\boxed{\frac{\Delta F}{k_B T \rho_0} = \int d\vec{r} \{ [n(\vec{r}) + 1] ln [n(\vec{r}) + 1] - n(\vec{r}) \} - \frac{\rho_0}{2} \int \int d\vec{r} d\vec{r'} n(\vec{r}) C^{(2)} n(\vec{r'})}$$

2 直相关函数的选择

将自由能分为不含直相关函数的第一项和含直相关函数的第二项，对第一项进行展开：

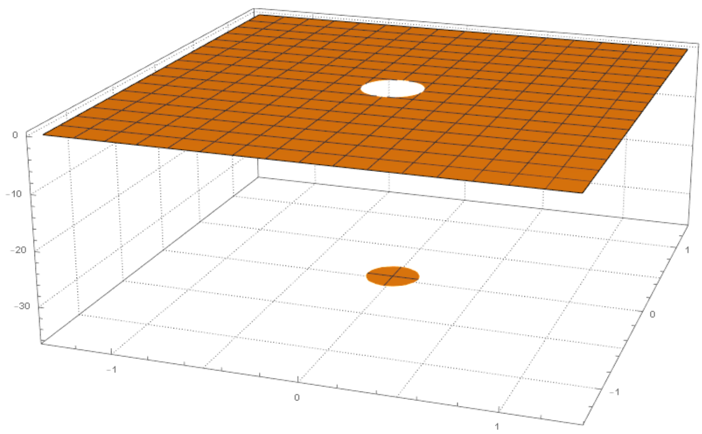
$$\boxed{\int d\vec{r} \{ [n(\vec{r}) + 1] ln [n(\vec{r}) + 1] - n(\vec{r}) \} \approx \int d\vec{r} \{ \frac{1}{2} n(\vec{r})^2 - \frac{a}{6} n(\vec{r})^3 + \frac{b}{12} n(\vec{r})^4 \}}$$

其中 a 和 b 为经验参数，为之后进一步简化做准备。

至于第二项，关键取决于 $C^{(2)}(|\vec{r} - \vec{r'}|)$ 的选取，令 $r = |\vec{r} - \vec{r'}|$，设：

$$\underline{\rho_0 C^{(2)}(|\vec{r} - \vec{r'}|) = \rho_0 C^{(2)}(r) = -\frac{R}{\pi r_0^2} circ \left(\frac{r}{r_0} \right)}$$

注意这里讨论的是二维空间，因而矢量也是二维的：$\vec{r} = (x, y), \vec{r'} = (x', y')$，从而 $\underline{r = \sqrt{(x - x')^2 + (y - y')^2}}$. 下图即直相关函数在实空间中的图像。



利用卷积 $A(\vec{r}) * B(\vec{r}) = \int A(|\vec{r'} - \vec{r}|) \cdot B(\vec{r}) d\vec{r}$ 的性质：

$$\mathcal{F}[A(\vec{r}) * B(\vec{r})] = \mathcal{F}[A(\vec{r})] \cdot \mathcal{F}[B(\vec{r})] = \hat{A}(\vec{k}) \cdot \hat{B}(\vec{k})$$

$$\Rightarrow \underline{A(\vec{r}) * B(\vec{r}) = \mathcal{F}^{-1}[\hat{A}(\vec{k}) \cdot \hat{B}(\vec{k})]}$$

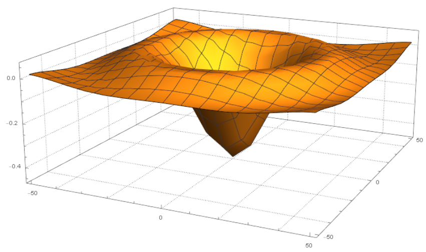
即两函数的卷积可以等同于两函数在傅里叶空间相乘的逆变换，因而利用这种技巧对第二项进行处理：

$$-\frac{1}{2} \int d\vec{r} n(\vec{r}) \int d\vec{r'} \rho_0 C^{(2)}(|\vec{r} - \vec{r'}|) n(\vec{r'}) = -\frac{1}{2} \int d\vec{r} n(\vec{r}) \mathcal{F}^{-1}[\rho_0 \hat{C}^{(2)}(\vec{k}) \cdot \hat{n}(\vec{k})]$$

对于 $\rho_0 \hat{C}^{(2)}(\vec{k})$，可由二维傅里叶变换得到：

$$\boxed{\rho_0 \hat{C}^{(2)}(\vec{k}) = \int -\frac{R}{\pi r_0^2} circ\left(\frac{r}{r_0}\right) e^{-i\vec{k}\cdot\vec{r}} d\vec{r} = -2R \frac{J_1(r_0 k)}{r_0 k}}$$

这里 $\vec{k} = (k_x, k_y)$，从而 $k = \sqrt{k_x^2 + k_y^2}$. 下图即直相关函数在傅里叶空间中的图像。



===================== 补充内容 =====================

对函数 $f(\vec{r})$ 进行傅里叶变换：

$$\hat{f}(\vec{k}) = \mathcal{F}[f(\vec{r})] = \int f(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d\vec{r}$$

可以证明有如下关系（证明略）：

$$\boxed{\mathcal{F}^{-1}[\vec{k}^n \cdot \hat{f}(\vec{k})] = (-i\nabla)^n f(\vec{r})}$$

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由此，对 $\rho_0 \hat{C}^{(2)}(\vec{k})$ 进行展开：

$$\rho_0 \hat{C}^{(2)}(\vec{k}) = -R \sum_{n=0}^{\infty} \frac{1}{n!(n+1)!} \left(\frac{r_0}{2}\right)^{2n} (ik)^{2n}$$

进而利用补充内容中的结论，得到：

$$\mathcal{F}^{-1}[\rho_0 \hat{C}^{(2)}(\vec{k}) \cdot \hat{n}(\vec{k})] = -R \sum_{n=0}^{\infty} \frac{1}{n!(n+1)!} \left(\frac{r_0}{2}\right)^{2n} (\nabla^2)^n n(\vec{r})$$

由此第二项化为：

$$\boxed{\frac{1}{2} \int d\vec{r} n(\vec{r}) 2Rf(\nabla^2) n(\vec{r})}$$

其中 $f(\nabla^2)$ 算符定义如下：

$$\underline{f(\nabla^2) = \frac{1}{2} \sum_{n=0}^{\infty} \frac{1}{n!(n+1)!} \left(\frac{r_0}{2}\right)^{2n} (\nabla^2)^n}$$

综上，加入直相关函数的具体形式之后，最终得到：

$$\boxed{\frac{\Delta F}{k_B T \rho_0} = \int d\vec{r} \left\{ \frac{n(\vec{r})}{2} [1 + 2Rf(\nabla^2)] n(\vec{r}) - \frac{a}{6} n(\vec{r})^3 + \frac{b}{12} n(\vec{r})^4 \right\}}$$

3 进一步化简

为了进一步化简，引入以原子数密度为单位的序参量 $\phi(\vec{r})$，$\overline{n}$ 为常数：

$$\underline{n(\vec{r}) \to \overline{n} + \frac{\phi(\vec{r})}{\rho_0}}$$

代入自由能中得到：

$$\frac{\Delta F}{k_B T \rho_0} = \int d\vec{r} \left\{ \frac{\overline{n} + \frac{\phi(\vec{r})}{\rho_0}}{2} [1 + 2Rf(\nabla^2)] \left(\overline{n} + \frac{\phi(\vec{r})}{\rho_0} \right) - \frac{a}{6} \left(\overline{n} + \frac{\phi(\vec{r})}{\rho_0} \right)^3 + \frac{b}{12} \left(\overline{n} + \frac{\phi(\vec{r})}{\rho_0} \right)^4 \right\}$$

<u>忽略常数项和一次项</u>，化简整理得到：

$$\Delta F = \int d\vec{r} \left\{ \frac{(1 - a\overline{n} + b\overline{n}^2 + 2Rf(\nabla^2))}{2\rho_0} k_B T \phi(\vec{r})^2 + \frac{(-a + 2b\overline{n})}{6\rho_0^2} k_B T \phi(\vec{r})^3 + \frac{b k_B T \phi(\vec{r})^4}{12\rho_0^3} \right\}$$

考虑到自由能的对称性，只含偶数幂级数，从而令 $\underline{\overline{n} = \frac{a}{2b}}$ ，代入得到：

$$\Delta F = k_B T \int d\vec{r} \left\{ \frac{b\phi(\vec{r})^4}{12\rho_0^3} + \frac{(1 - \frac{a^2}{4b} + 2Rf(\nabla^2))}{2\rho_0} \phi(\vec{r})^2 \right\}$$

令：

$$\underline{\alpha = \frac{k_B T}{\rho_0} \left(1 - \frac{a^2}{4b} \right)} \qquad \underline{\lambda = \frac{2Rk_B T}{\rho_0}} \qquad \underline{u = \frac{k_B T b}{3\rho_0}}$$

得到：

$$\boxed{\Delta F = \int d\vec{r} \left\{ \frac{\phi(\vec{r})}{2} [\alpha + \lambda f(\nabla^2)] \phi(\vec{r}) + u \frac{\phi(\vec{r})^4}{4} \right\}}$$

再令：

$$\underline{\psi = \phi \sqrt{\frac{u}{\lambda}}} \qquad \underline{\varepsilon = -\frac{\alpha}{\lambda}} \qquad \underline{\Delta \mathcal{F} = \frac{u}{\lambda^2} \Delta F}$$

得到：

$$\boxed{\Delta \mathcal{F} = \int d\vec{r} \left\{ \frac{\psi}{2} [-\varepsilon + f(\nabla^2)] \psi + \frac{\psi^4}{4} \right\}}$$

4 离散化处理

根据动力学方程：

$$\frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta \Delta \mathcal{F}}{\delta \psi}$$

代入得到：

$$\frac{\delta \Delta \mathcal{F}}{\delta \psi} = [-\varepsilon + f(\nabla^2)]\psi + \psi^3$$

即：

$$\boxed{\frac{\partial \psi}{\partial t} = \nabla^2 \left\{[-\varepsilon + f(\nabla^2)]\psi + \psi^3\right\}}$$

离散化之后：

$$\frac{\hat{\psi}_{n+1} - \hat{\psi}_n}{\Delta t} = -k^2 \left[-\varepsilon + \frac{J_1(r_0 k)}{r_0 k}\right] \hat{\psi}_{n+1} - k^2 \hat{\psi}_n^3$$

$$\Rightarrow \boxed{\hat{\psi}_{n+1} = \frac{\hat{\psi}_n - k^2 \Delta t \hat{\psi}_n^3}{1 + k^2 \Delta t \left[-\varepsilon + \frac{J_1(r_0 k)}{r_0 k}\right]}}$$