KKS Phase Field Model of Graphene-H_2O system coupled with nucleation

1 Model

Free energy given by:

$$F(\phi,c)=\int_V\left[\frac{1}{2}\varepsilon^2(\theta)\,|\nabla\phi|^2+f_{bulk}(\phi,c)\right]dV \tag{1.1}$$

Where

$$f_{bulk}=f_\alpha(\phi,c)(1-p(\phi))+f_\beta(\phi,c)p(\phi)+Hg(\phi) \tag{1.2}$$

在 KKS 模型中，界面区域被视为α和β相的一个混合，它们浓度分别是c_α和c_β。这种情况下，每相的均匀化自由能 f_α 与 f_β 就是c_α 与 c_β 的函数，而不是c和ϕ的函数。

每相的浓度由下面的方程确定

$$\begin{cases} c=c_\alpha(1-p(\phi))+c_\beta p(\phi) \\ \dfrac{\partial f_\alpha(c_\alpha)}{\partial c_\alpha}=\dfrac{\partial f_\beta(c_\beta)}{\partial c_\beta} \end{cases} \tag{1.3}$$

给出了以下单相均匀自由能的抛物型函数:

$$\begin{cases} f_\alpha(c_\alpha)=A_2c_\alpha^2+A_1c_\alpha+A_0 \\ f_\beta(c_\beta)=B_2c_\beta^2+B_1c_\beta+B_0 \end{cases} \tag{1.4}$$

耦合ϕ和c的控制方程的一般形式为

$$\frac{\partial\phi}{\partial t}=-M_\phi\frac{\delta F}{\delta\phi} \tag{1.5}$$

和

$$\frac{\partial c}{\partial t}=\nabla\left(M_c\nabla\left(\frac{\delta F}{\delta c}\right)\right) \tag{1.6}$$

$\varepsilon(\theta)$是各向异性函数

$$\varepsilon(\theta)=1+\gamma\cos(m(\theta-\theta_0)) \tag{1.7}$$

θ由下面公式给定

$$\tan(\theta)=\frac{\partial\phi/\partial y}{\partial\phi/\partial x} \tag{1.8}$$

2. 控制方程

$$
\begin{aligned}
\frac{\partial\phi}{\partial t}&=-M_{\phi}\frac{\delta F}{\delta\phi}\\
&=M_{\phi}\left(\nabla\left[\left(\varepsilon^{2}(\theta)\frac{\partial\phi}{\partial x}+\gamma m\varepsilon(\theta)\sin\left[m\left(\theta-\theta_{0}\right)\right]\frac{\partial\phi}{\partial y}\right)\hat{x}\right.\right.\\
&\quad+\left(\varepsilon^{2}(\theta)\frac{\partial\phi}{\partial y}-\gamma m\varepsilon(\theta)\sin\left[m\left(\theta-\theta_{0}\right)\right]\frac{\partial\phi}{\partial x}\right)\hat{y}\\
&\quad\left.-H\frac{\partial g(\phi)}{\partial\phi}-\left[f_{\beta}-f_{\alpha}-(c_{\beta}-c_{\alpha})f_{\beta,c\beta}\right]\frac{\partial p(\phi)}{\partial\phi}\right)
\end{aligned}
\tag{1.9}
$$

$$
\begin{aligned}
\frac{\partial c}{\partial t}&=\nabla\cdot\left(M_{c}\nabla\left(\frac{\delta F}{\delta c}\right)\right)\\
&=\nabla\cdot\left(D(\phi)c(1-c)\nabla\left(\frac{\partial f_{bulk}}{\partial c}\right)\right)
\end{aligned}
\tag{1.10}
$$

$$
\frac{\partial f_{bulk}}{\partial c}=f_{\alpha,c}(1-p(\phi))+f_{\beta,c}p(\phi)
\tag{1.11}
$$

3 时间离散

使用显式向前欧拉时间差分，可以得到

$$
\phi^{n+1}=\phi^{n}-\Delta tM_{\phi}\mu_{\phi}
\tag{1.12}
$$

$$
c^{n+1}=c^{n}+\Delta t\left[\nabla\cdot\left(\frac{1}{f_{,cc}}M_{c}\nabla\mu_{c}\right)\right]
\tag{1.13}
$$

4 弱形式

$$
\int_{V}\omega c^{n+1}dV=\int_{V}\omega c^{n}+\omega\Delta t\left[\nabla\cdot\left(\frac{1}{f_{,cc}}M_{c}\nabla\mu_{c}\right)\right]dV
\tag{1.14}
$$

$$
\frac{1}{f_{,cc}}\nabla\mu_{c}=\nabla c+(c_{\alpha}-c_{\beta})p(\phi)_{,\phi}\nabla\phi
\tag{1.15}
$$

$$
\int_{V}\omega c^{n+1}dV=\int_{V}\omega c^{n}+\nabla\omega\cdot\left(-\Delta tM_{c}\frac{1}{f_{,cc}}\nabla\mu_{c}\right)dV
\tag{1.16}
$$

$$
\begin{aligned}
\int_{V}\omega\phi^{n+1}dV&=\int_{V}\omega(\phi^{n}-M_{\phi}\Delta t[Hg'(\phi)+[f_{\beta}-f_{\alpha}-(c_{\beta}-c_{\alpha})f_{\beta,c\beta}]])\\
&\quad+\nabla\omega\cdot\left(-\Delta tM_{\phi}\cdot\left(\begin{array}{l}\left[\varepsilon^{2}(\theta)\frac{\partial\phi}{\partial x}+\gamma m\varepsilon(\theta)\sin\left[m\left(\theta-\theta_{0}\right)\right]\frac{\partial\phi}{\partial y}\right]\hat{x}\\+\left[\varepsilon^{2}(\theta)\frac{\partial\phi}{\partial y}-\gamma m\varepsilon(\theta)\sin\left[m\left(\theta-\theta_{0}\right)\right]\frac{\partial\phi}{\partial x}\right]\hat{y}\end{array}\right)\right)
\end{aligned}
\tag{1.17}
$$

5 成核模型

根据经典成核理论，对于临界成核尺寸 J 的成核速率通过下式给定

$$J^*(r,t) = Zn\beta^* \exp\left(-\frac{\Delta G}{(\Delta c)^{d-1}}\right)\exp\left(-\frac{\tau}{t}\right) \tag{1.18}$$

成核率

$$P(r,t) = 1 - \exp(-J^* \Delta V \Delta t) \tag{1.19}$$

Appendix I:

$$g(\phi) = \phi^2 (1-\phi)^2 \tag{1.20}$$

$$p(\phi) = \phi^2 (3-2\phi) \tag{1.21}$$

Parameters：

各向异性强度 γ 为 0.01

各向异性模数 m 为 4or6

初始偏移角 θ_0 为 0

相场偏移率 M_ϕ 为 1.0

浓度场偏移率 M_c 为 1.0

势垒能 H 为 2.0

初始浓度值 c 为 0.2

抛物线自由能函数 A0=0.0,A1=1.0,calmin=0.0,B0=0.0,B1=4.0,cbtmin=1.0

成核率 K1=498.866，K2=4.14465