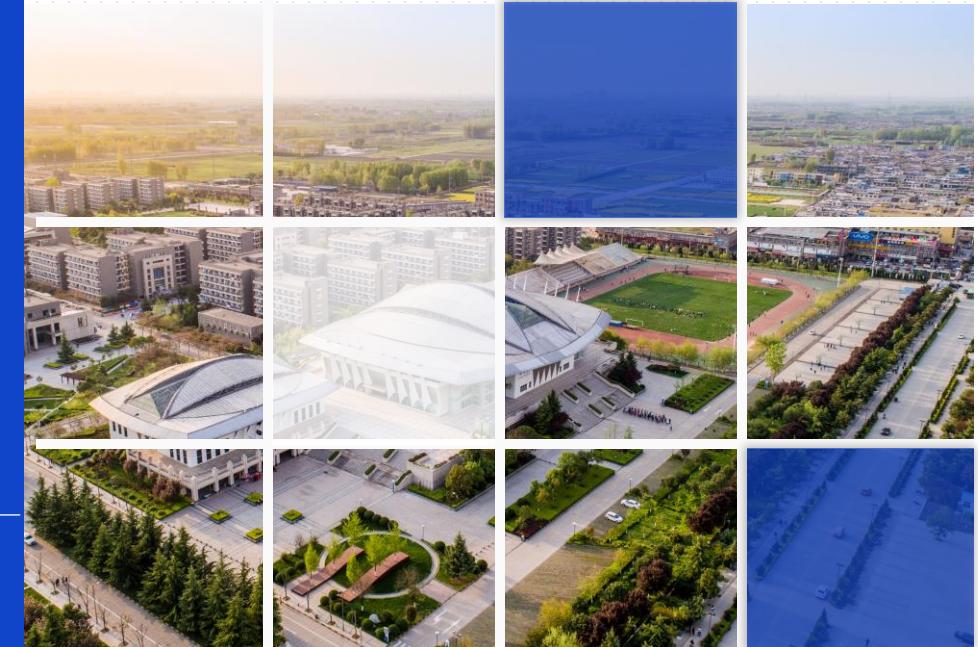


三模晶体相场模型及其对微观组织结构演化的模拟研究



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总结&讨论

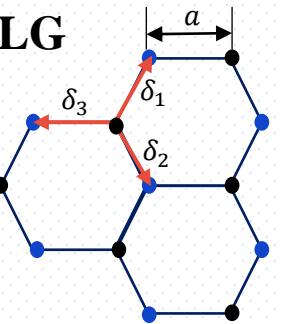


Part One

研究背景

研究背景

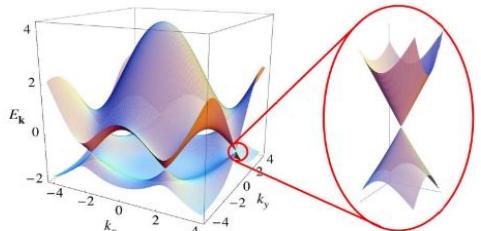
(1) SLG



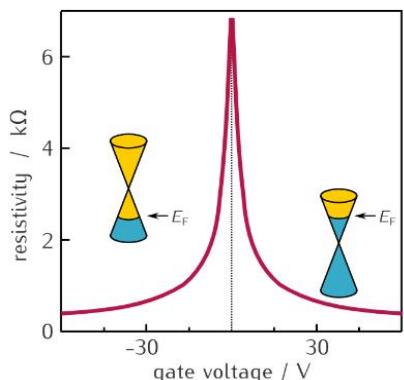
TBA:

$$H = -t \sum_{\vec{r}} \left(b_{\vec{r}+\vec{\delta}_1}^\dagger a_{\vec{r}} + b_{\vec{r}+\vec{\delta}_2}^\dagger a_{\vec{r}} + b_{\vec{r}+\vec{\delta}_3}^\dagger a_{\vec{r}} + h.c. \right)$$

$$E(\mathbf{k}) = \pm t \sqrt{3 + 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{3}{2}k_x a\right) \cos\left(\frac{\sqrt{3}}{2}k_y a\right)}$$



(a)



(b)

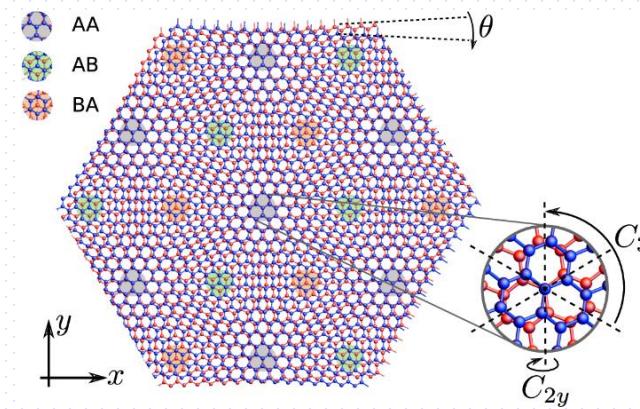
石墨烯的能带结构与电压调控[1]

[1] <https://en.wikipedia.org/wiki/Graphene>

[2] DOI: 10.1103/PhysRevB.98.075109

[3] <https://doi.org/10.1073/pnas.1108174108>

(2) BLG

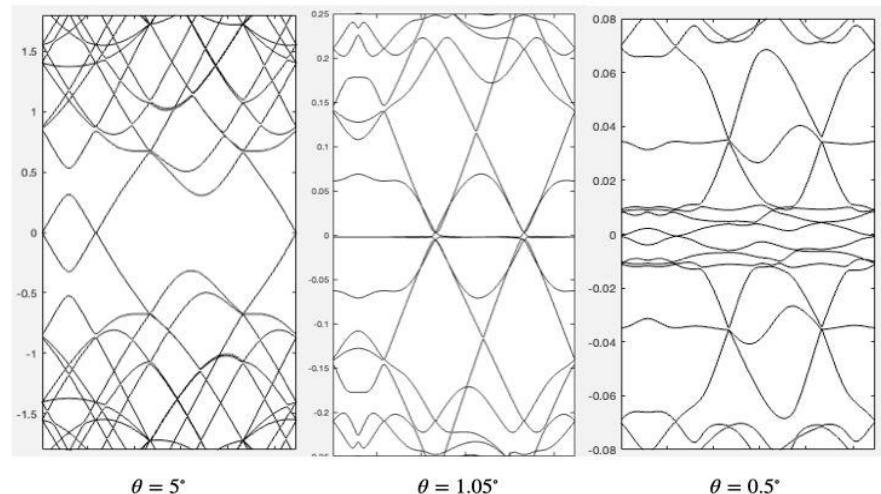


转角石墨烯
结构图[2]

Bistritzer-
MacDonald
Model [3]:

$$H = \begin{pmatrix} -i\nu_F \sigma_{\theta/2} \cdot \nabla & T(\vec{r}) \\ T^\dagger(\vec{r}) & -i\nu_F \sigma_{-\theta/2} \cdot \nabla \end{pmatrix}$$

其中 $T(\vec{r}) = \sum_{j=1}^3 T_j e^{-\vec{q}_j \cdot \vec{r}}$, 且 $T_{j+1} = t_{AA}\sigma_0 + t_{AB} \left(\cos\left(\frac{2\pi}{3}j\right)\sigma_x + \sin\left(\frac{2\pi}{3}j\right)\sigma_y \right)$



转角石墨烯不同转角的能带图[3]

研究背景

(1) 传统方法

➤ Density Functional Theory

$$\hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$
$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \hat{V}_{ext} + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

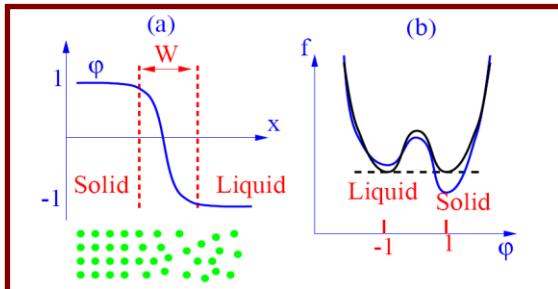
➤ Molecule Dynamics

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$
$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$$

➤ Monte Carlo

$$Z = \sum_{\alpha_0} \langle \alpha_0 | e^{-\beta H} | \alpha_0 \rangle$$

➤ Phase Field



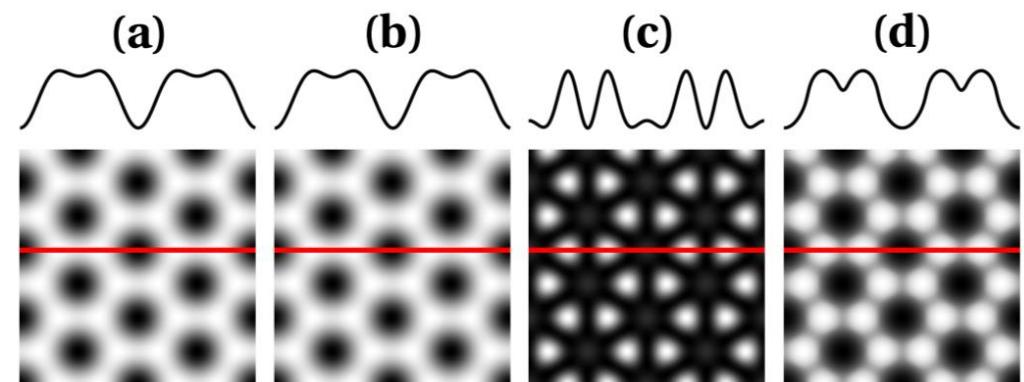
[4] DOI: 10.1103/PhysRevLett.111.035501

[5] DOI: 10.1103/PhysRevB.94.035414

(2) 晶体相场方法^[4] (Phase Field Crystal)



$$F[\psi] = \int d\vec{r} \left\{ \frac{\psi}{2} \left(r + \lambda \prod_{i=1}^3 \left[(\partial_i^2 + \nabla^2)^2 + b_i \right] \right) \psi - \frac{\tau}{3} \psi^3 + \frac{1}{4} \psi^4 \right\}$$



不同晶体相场模型对石墨烯模拟效果图：(a)PFC1 (b)APFC
(c)PFC3 (d)XPFC 其中黑色表示密度小，白色表示密度大^[5]



Part Two

模 型 推 导

模型推导

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

(1) 动能项自由能

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

定义动能项化学势 $\mu^{id} = \frac{\delta F_{id}[\rho(\vec{r})]}{\delta \rho(\vec{r})} = k_B T \ln(\rho(\vec{r}) \lambda_T^3)$

根据自由能表达式 $F = -Nk_B T \ln Z_1 + k_B T \ln N!$

(2) 相互作用项自由能^[6]

$$C^{(m)}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_m; [\rho]) = -\frac{1}{k_B T} \frac{\delta^m F_{ex}[\rho]}{\delta \rho(\vec{r}_1) \dots \delta \rho(\vec{r}_m)}$$

令 $\Delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0$, 并对 $F_{ex}[\rho]$ 取到两点直相关函数即 ($m = 2$)

可以定义相互作用项化学式 μ^{ex} :

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

$$\mu^{ex} = \frac{\delta F_{ex}[\rho]}{\delta \rho(\vec{r})} = -k_B T C^{(1)}(\vec{r}; \rho)$$

$$F_{ex}[\rho] \approx F_{ex}[\rho_0] + \int d\vec{r} \Delta\rho(\vec{r}) \mu_0^{ex}$$

$$- \frac{k_B T}{2} \int \int d\vec{r} d\vec{r}' \Delta\rho(\vec{r}) C^{(2)}(\vec{r}, \vec{r}'; \rho_0) \Delta\rho(\vec{r}')$$

[6] DOI: 10.1103/PhysRevE.70.051605

模型推导

(3) 三模晶体相场的自由能

定义 $\Delta F = F[\rho(\vec{r})] - F[\rho_0]$, 并令平均化学式 $\mu_0 = 0$. 由于密度场 $\rho(\vec{r})$ 通常过于尖锐, 需要定义无量纲数密度 $n(\vec{r})$ 进行平滑处理

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

动能部分进行展开, 取到4阶; 相互作用项构造三模多项式, 以拟合结构因子的前三个峰, 整理得到:

$$F[\psi(\vec{r})] = \int d\vec{r} \left\{ \frac{\psi}{2} \left(r + \lambda \prod_{i=1}^3 [(Q_i^2 + \nabla^2)^2 + b_i] \right) \psi - \frac{\tau\psi^3}{3} + \frac{\psi^4}{4} + V\psi \right\}$$

与朗道铁磁相变自由能进行类比:

$$F[\vec{m}(\vec{r})] = \int d\vec{r} \left\{ \frac{rm^2}{2} + \frac{m^4}{4} + \dots + \frac{K}{2} (\nabla \vec{m})^2 + \frac{L}{2} (\nabla^2 \vec{m})^2 + \dots + \vec{h} \cdot \vec{m} \right\}$$

模型推导

(4) 自由能的迭代方程

根据质量守恒的演化方程：

$$\frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta F[\psi]}{\delta \psi} \quad \rightarrow \quad \frac{\partial \psi}{\partial t} = \nabla^2 \left\{ \left(r + \lambda \prod_{i=1}^N \left[(Q_i^2 + \nabla^2)^2 + b_i \right] \right) \psi - \tau \psi^2 + \psi^3 + V \right\}$$

两边同时进行傅里叶变换，利用 $\mathcal{F}[\nabla^n \psi(\vec{r})] = (i\vec{q})^n \hat{\psi}(\vec{q})$ 得到：

$$\frac{\hat{\psi}_{n+1} - \hat{\psi}_n}{\Delta t} = -q^2 \left\{ \left(r + \lambda \prod_{i=1}^N \left[(Q_i^2 - q^2)^2 + b_i \right] \right) \hat{\psi}_{n+1} - \tau \widehat{\psi_n^2} + \widehat{\psi_n^3} + \hat{V} \right\}$$

整理得到：

$$\hat{\psi}_{n+1} = \frac{\hat{\psi}_n + \Delta t \cdot q^2 (\tau \widehat{\psi_n^2} - \widehat{\psi_n^3} - \hat{V})}{1 + q^2 \Delta t \left(r + \lambda \prod_{i=1}^3 \left[(Q_i^2 - q^2)^2 + b_i \right] \right)}$$

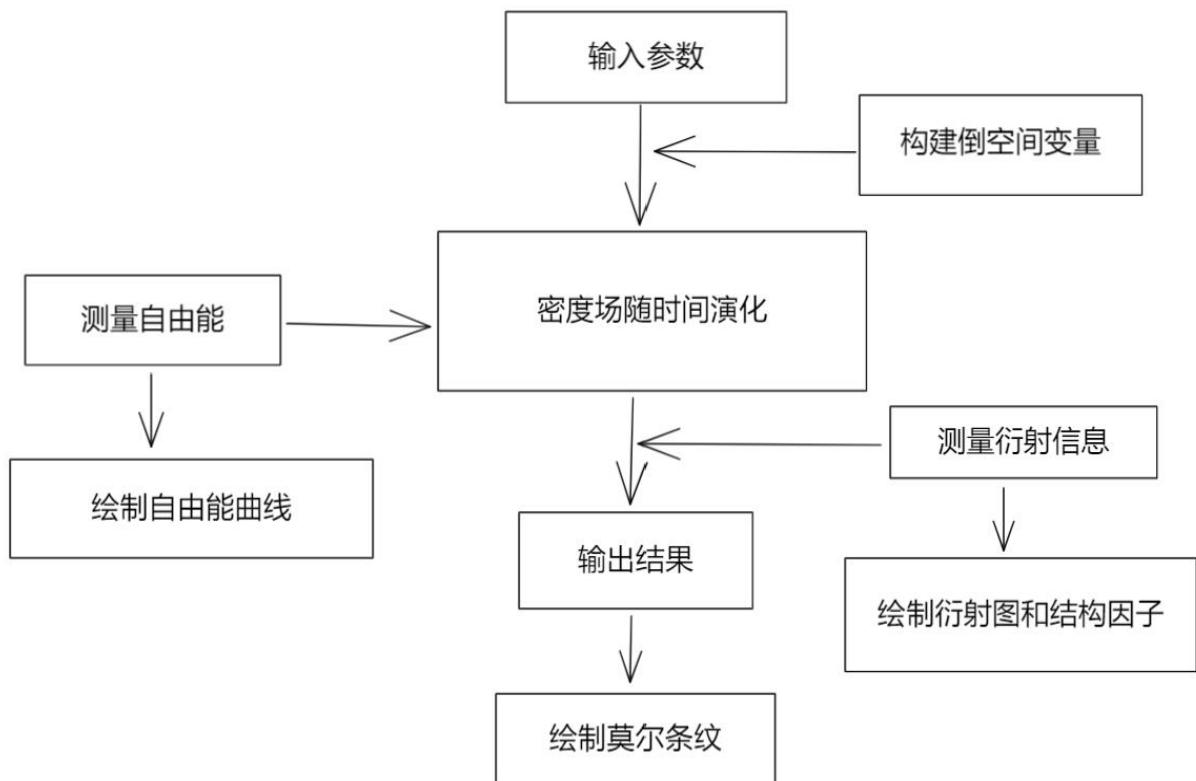


Part Three

程 序 模 拟

程序模拟

(1) 程序设计



程序设计结构图

$$\hat{\psi}_{n+1} = \frac{\hat{\psi}_n + \Delta t \cdot q^2 (\tau \hat{\psi}_n^2 - \hat{\psi}_n^3 - \hat{V})}{1 + q^2 \Delta t (r + \lambda \prod_{i=1}^3 [(Q_i^2 - q^2)^2 + b_i])}$$

系统参数:

$$(dx, dy, dt) = \left(\frac{\pi}{8}, \frac{\pi}{8}, \frac{1}{10}\right)$$

自由能参数:

$$(\psi_0, r, \lambda) = \left(\frac{-1}{5}, \frac{-3}{20}, \frac{1}{50}\right)$$

由于不考虑立方项以及衬底的影响，故：

$$V = \tau = 0$$

- 自由能的测量:

$$F[\psi(\vec{r})] = \int d\vec{r} f \approx \Omega f = N_x N_y dx dy f$$

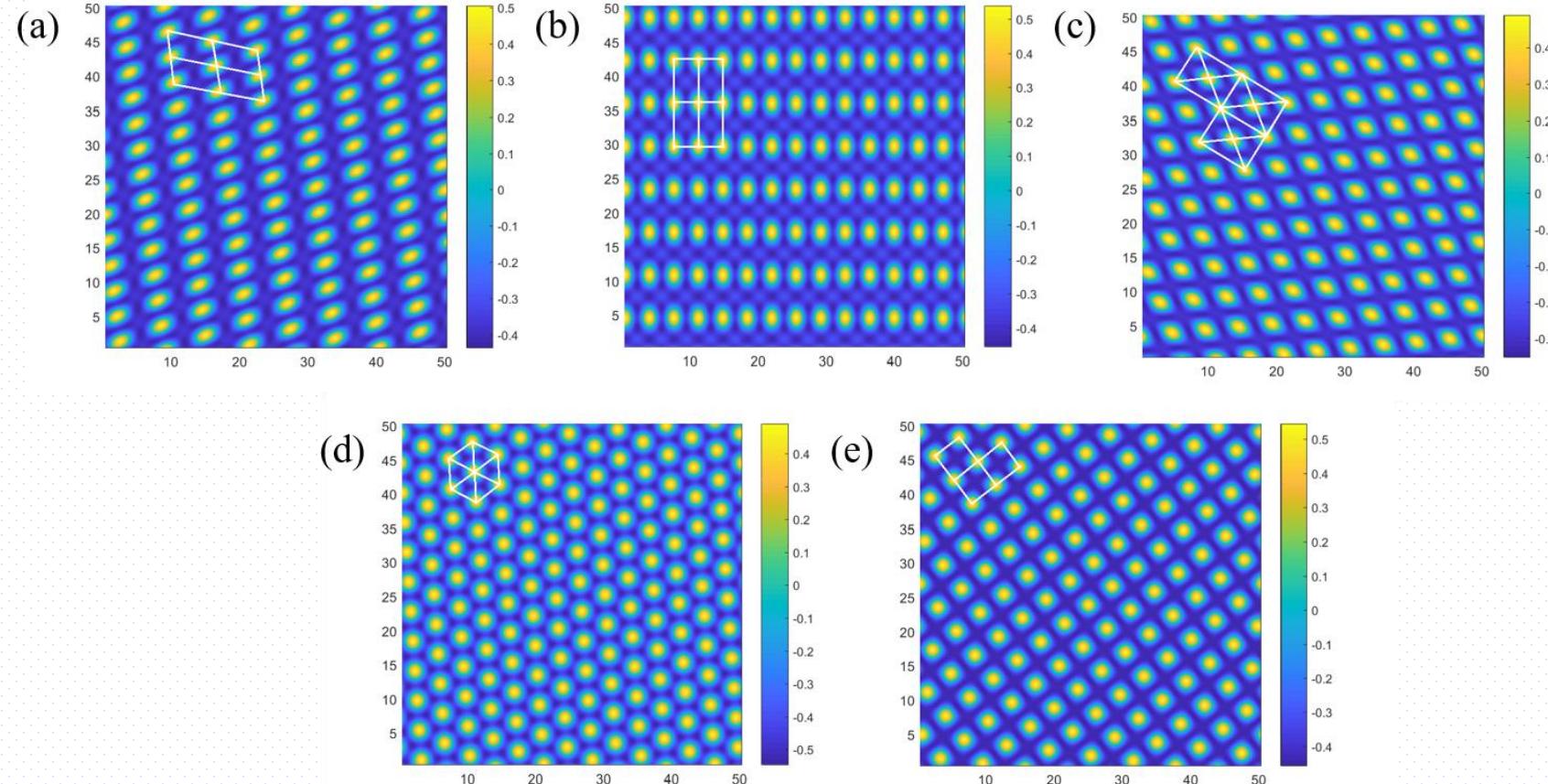
- 结构因子的测量:

$$S(q) \propto \frac{\int_0^{2\pi} |\hat{\psi}(q, \theta)|^2 d\theta}{2\pi q} \sim \frac{\sum_{i=1}^n |\hat{\psi}(q_i)|^2}{n}$$

程序模拟

通过调整倒格矢 Q_1, Q_2, Q_3 , 并固定 $b_1=0$ 得到:

(2) 二维空间五种布拉菲格子



(a) 简单斜方格子(OBL)

$$(b_2, b_3) = (0.01, 0.01)$$

(b) 简单长方(REC)

$$(b_2, b_3) = (0.00, -0.05)$$

(c) 中心长方(RHO)

$$(b_2, b_3) = (0.01, 0.01)$$

(d) 简单六角/三角(TRI)

$$(b_2, b_3) = (-0.40, -0.05)$$

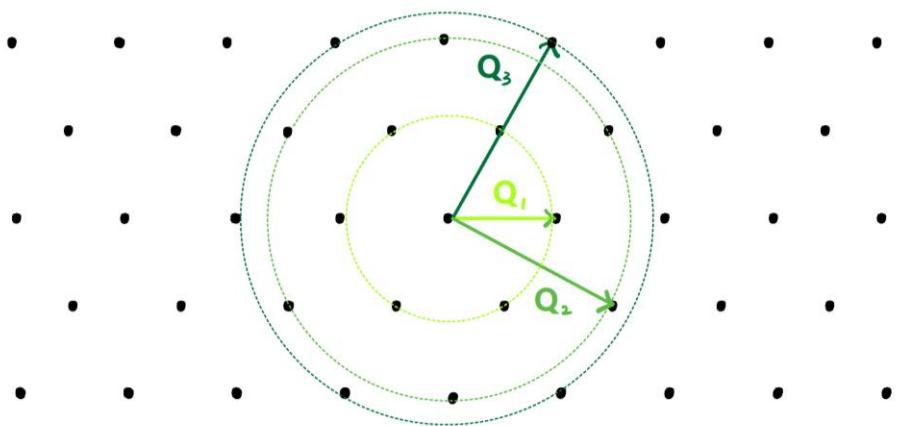
(e) 简单正方(SQU)

$$(b_2, b_3) = (-0.30, 0.00)$$

程序模拟

(3) 三角格子倒格矢下的相图

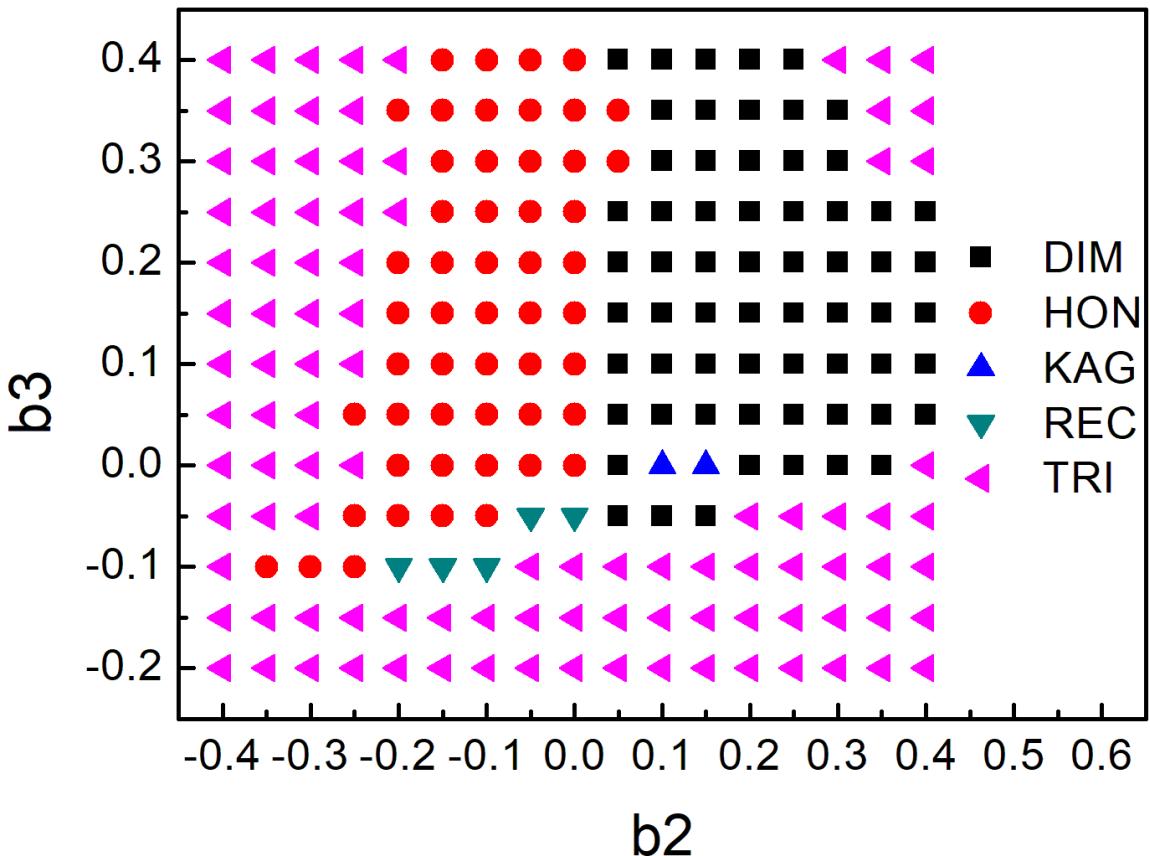
三角格子最近邻倒格矢为 $(Q_1, Q_2, Q_3) = (1, \sqrt{3}, 2)$



选取大小为 $N_x = N_y = 128$, 初始条件为随机密度场:

$$\psi = \psi_0 + 0.01\psi_0 \cdot \text{rand}()$$

其中 $\text{rand}()$ 为 $[-0.5, 0.5]$ 均匀分布的伪随机数



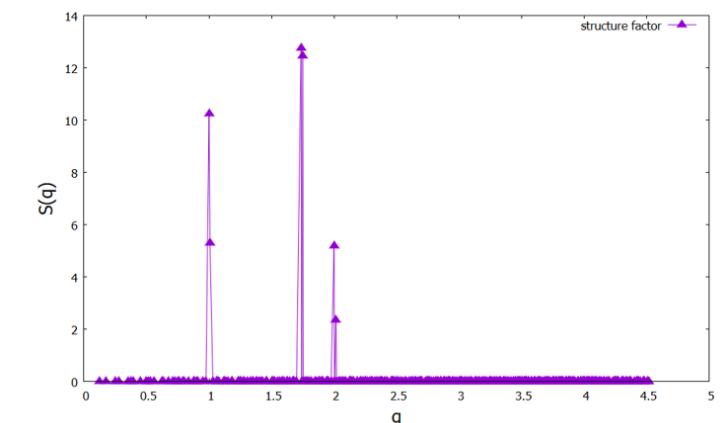
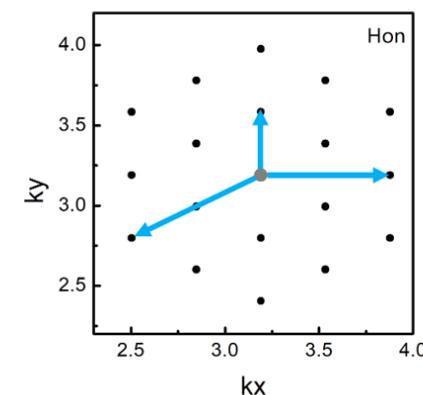
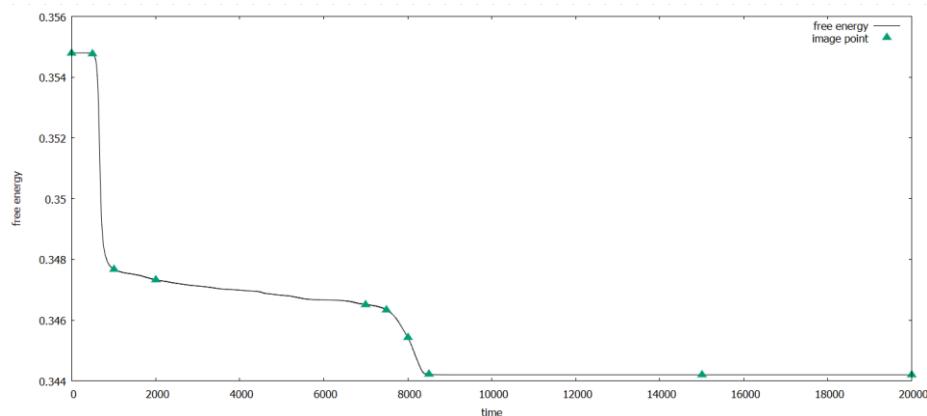
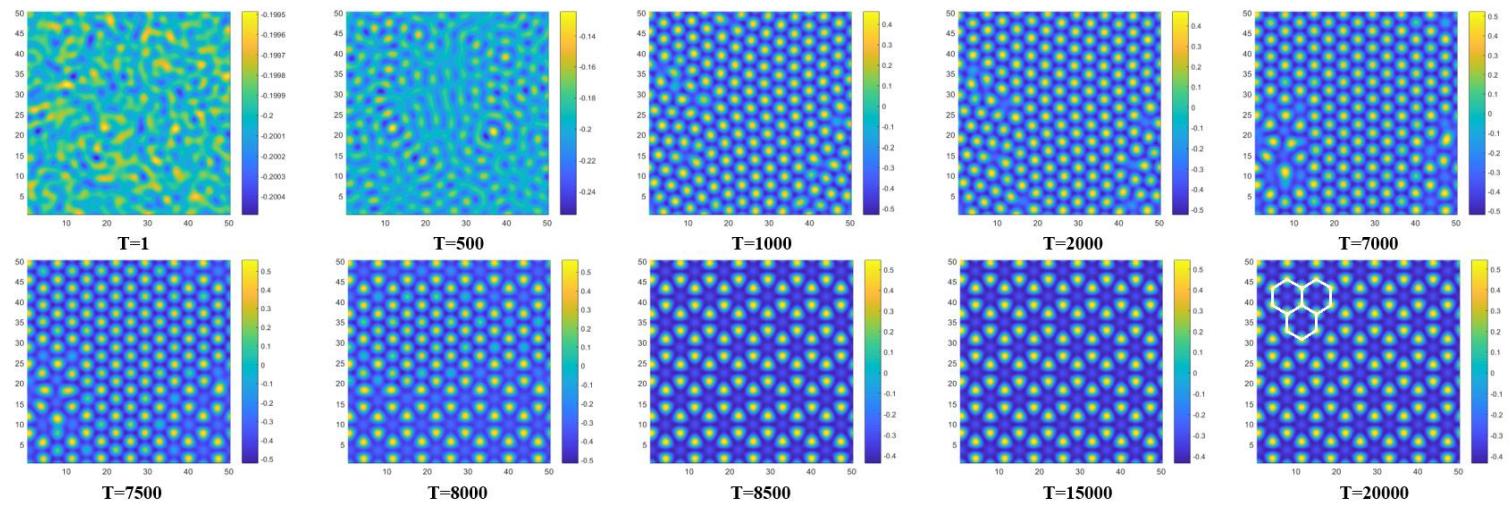
$$b_2 \in [-0.4, 0.4], b_3 \in [-0.2, 0.4]$$

程序模拟

(3-1) 蜂窝状结构(Honeycomb)

$$(b_2, b_3) = (-0.10, 0.10)$$

应用：石墨烯、氮化硼等材料，
以及冷原子光晶格模拟、量子模
拟、量子计算等领域都有着广泛
的应用。

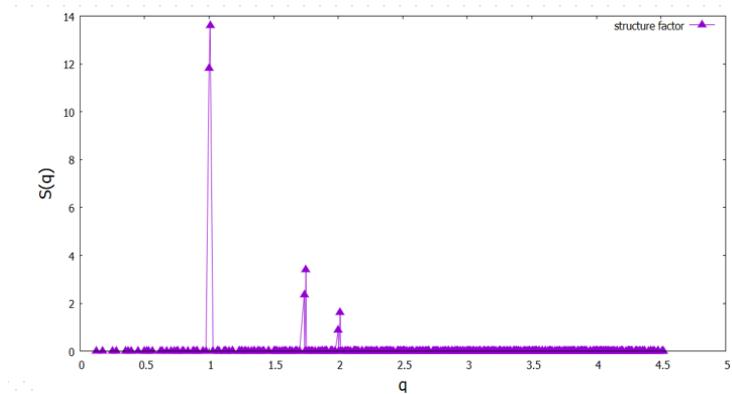
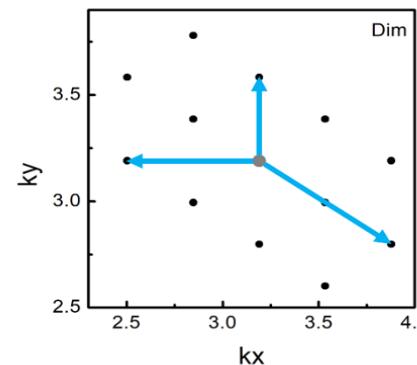
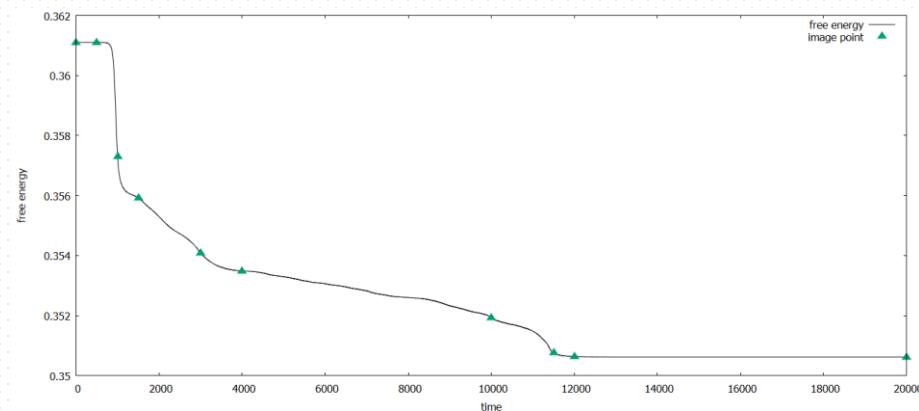
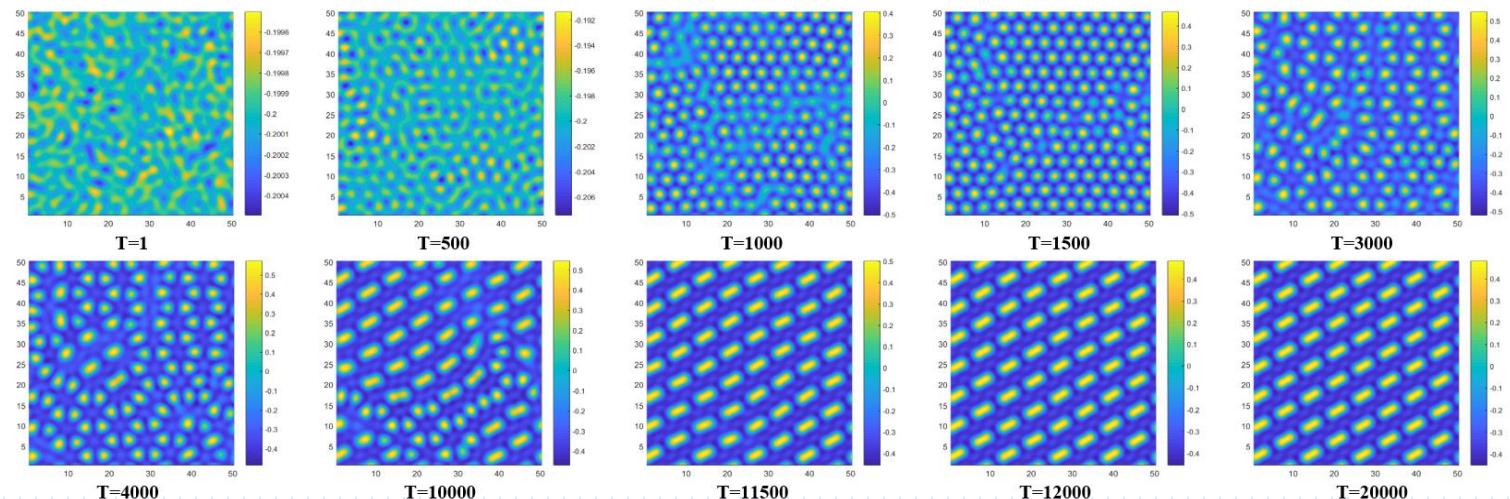


程序模拟

(3-2) 二聚结构(Dimer)

$$(b_2, b_3) = (0.05, 0.10)$$

应用：二维派尔斯相变、二维
Su-Schrieffer-Heeger模型以及二
聚化的研究

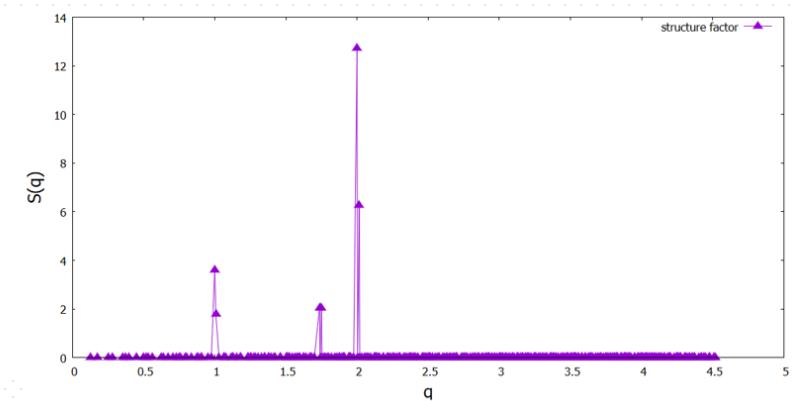
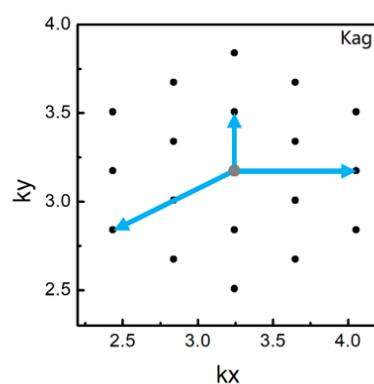
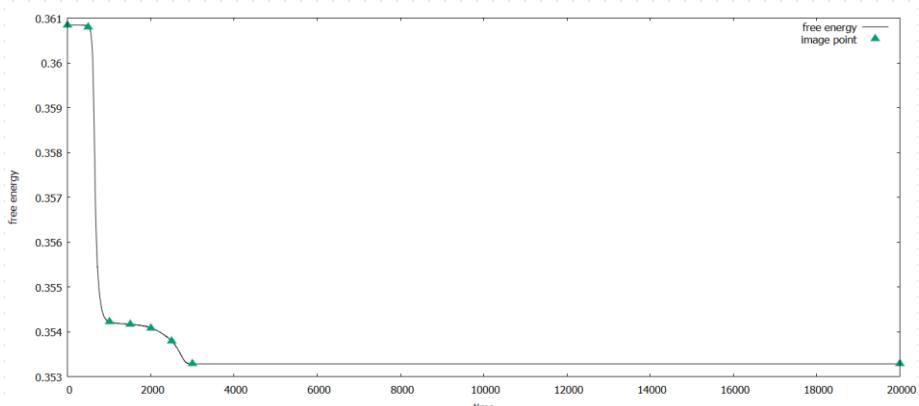
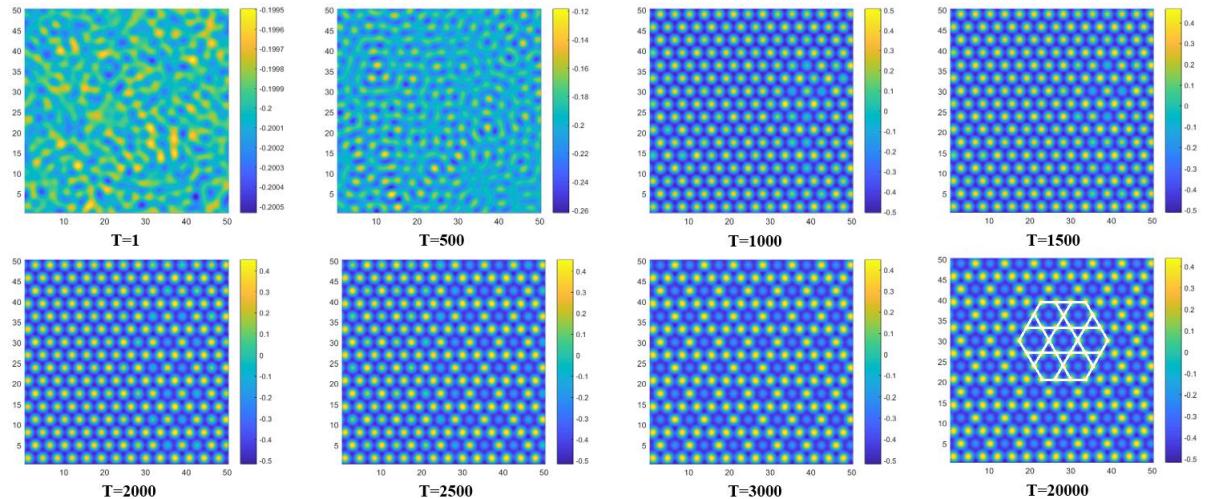


程序模拟

(3-3) 笼目状结构(Kagome)

$$(b_2, b_3) = (0.10, 0.00)$$

应用：量子自旋液体的构型，并且是近几年高温超导领域比较重要的晶体结构。例如笼状 CsV_3Sb_5 超导体的新奇特性，为高温超导领域的
发展提供新思路。

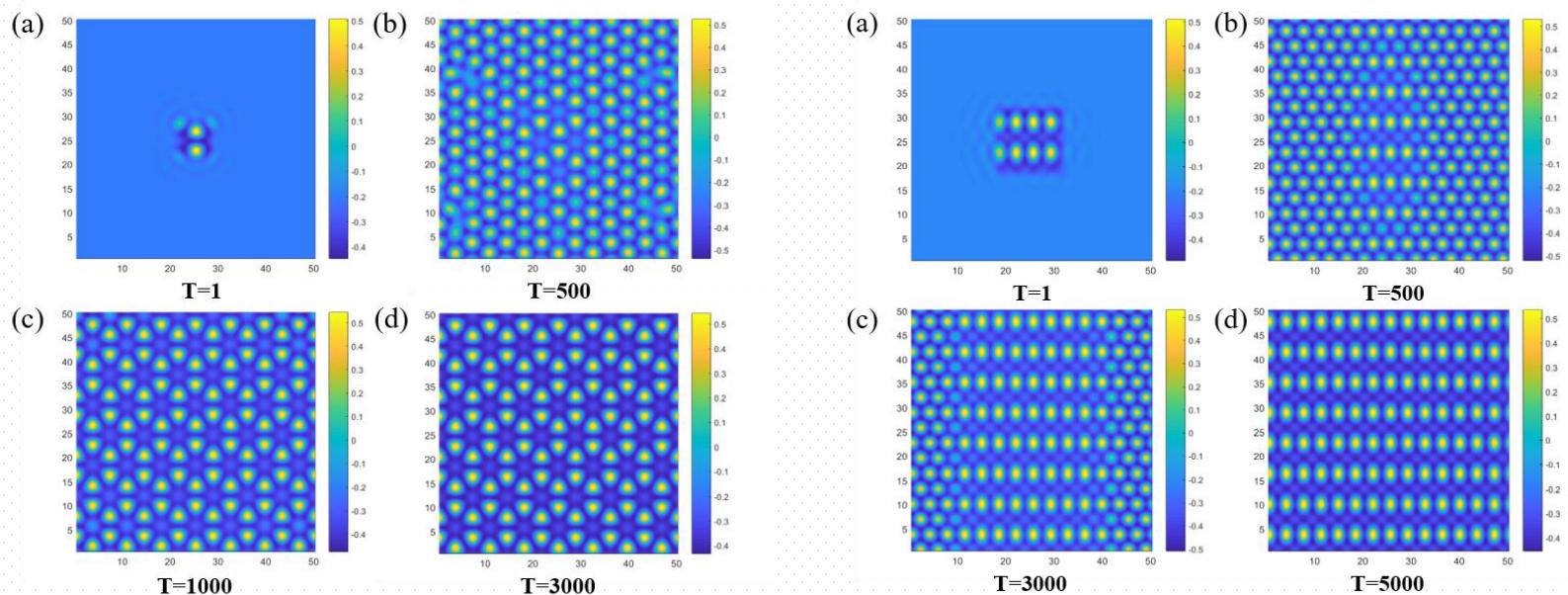


程序模拟

(4) 单晶生长与竞争形核

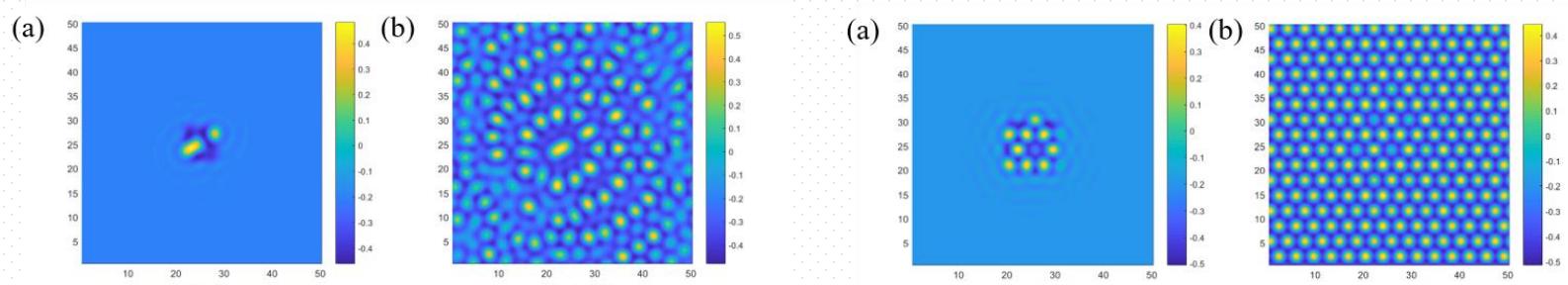
HON:

T=8000 → T=3000



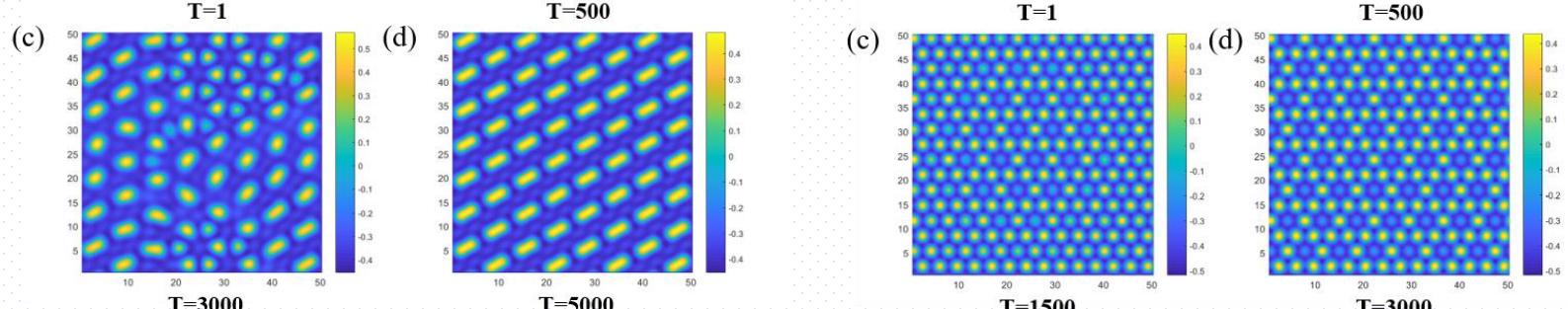
DIM:

T=12000 → T=5000



REC:

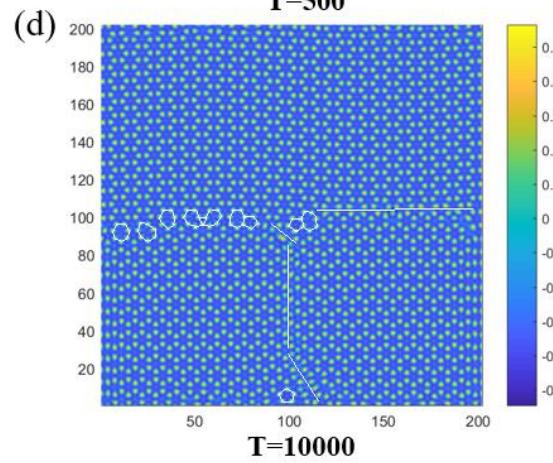
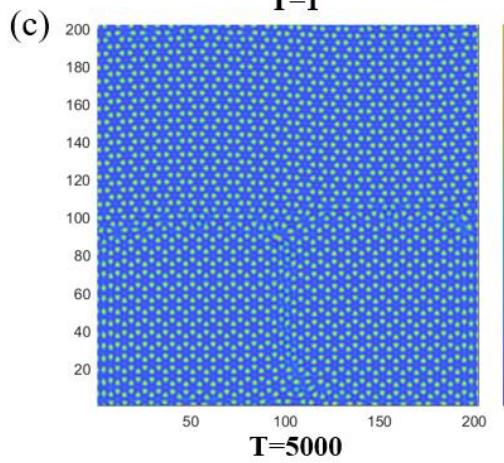
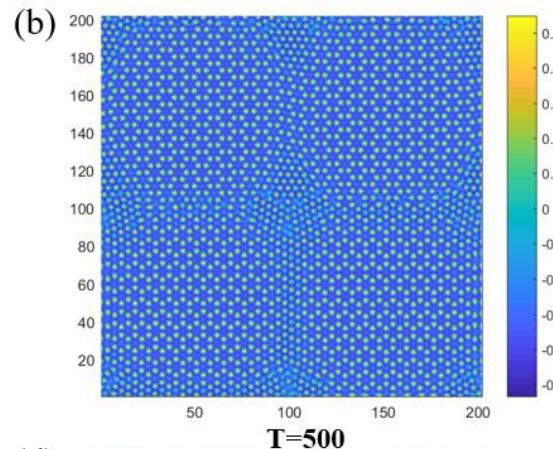
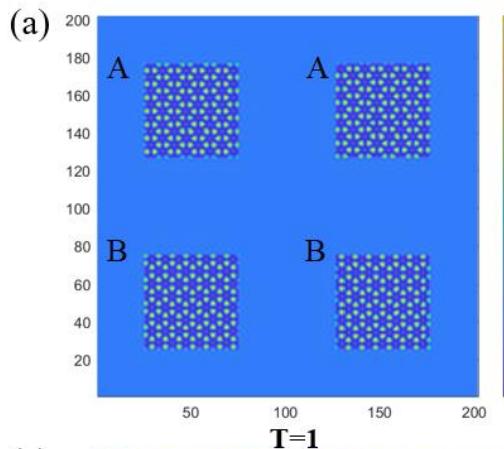
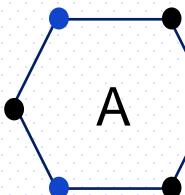
T=11000 → T=5000



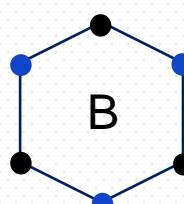
KAG:

T=3000 → T=3000

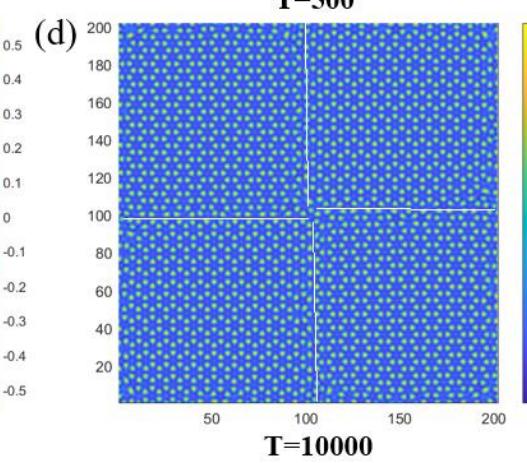
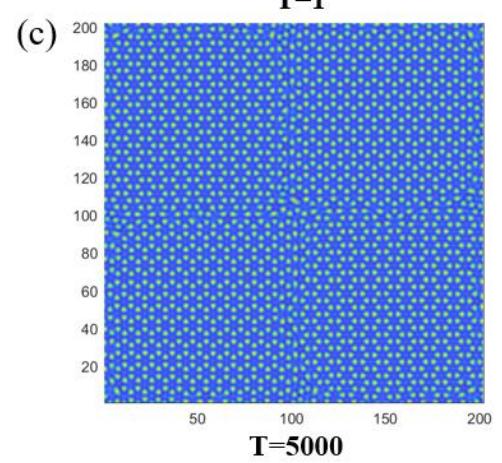
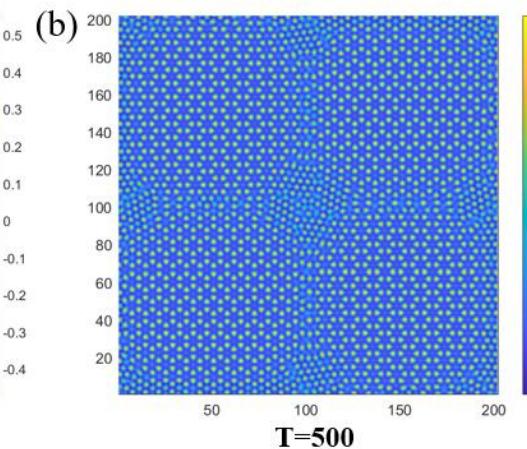
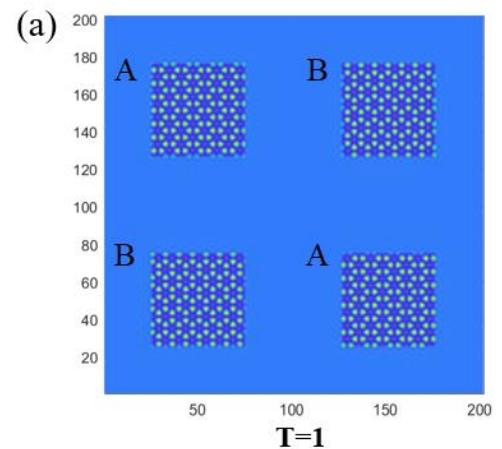
程序模拟



AABB型蜂窝状结构竞争形核



$$N_x = N_y = 514$$



ABBA型蜂窝状结构竞争形核

程序模拟

(5) 莫尔条纹的模拟

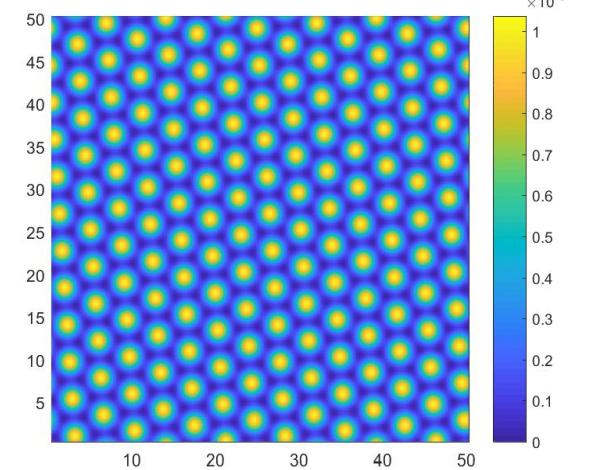
$$N_x = N_y = 128$$

$$(Q_1, Q_2, Q_3) = (1, \sqrt{3}, 2)$$

$$(b_2, b_3) = (-0.10, 0.10)$$

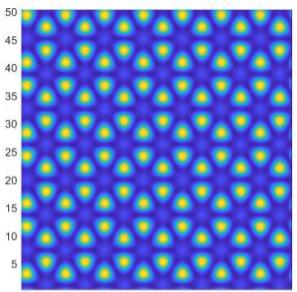
$$V = V_0 \psi_{sub}$$

$$V_0 \in [10^{-6}, 10^{-1}]$$



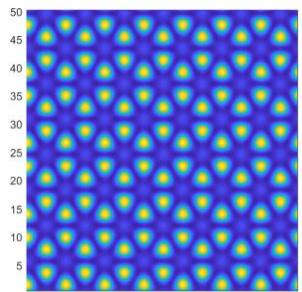
三角衬底

$$V_0=10^{-6}$$



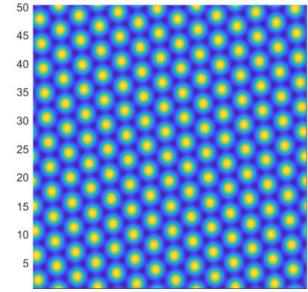
(A-f-1)

$$V_0=10^{-5}$$



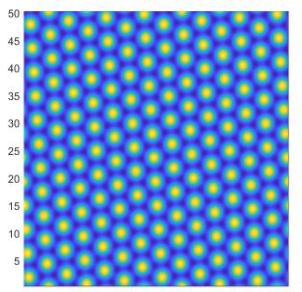
(A-f-2)

$$V_0=10^{-4}$$



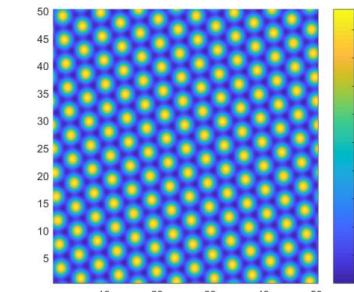
(A-f-3)

$$V_0=10^{-3}$$



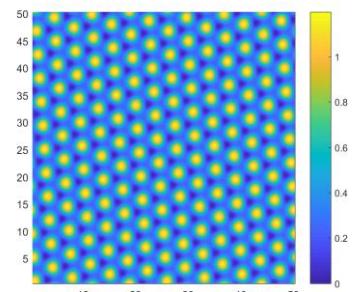
(A-f-4)

$$V_0=10^{-2}$$



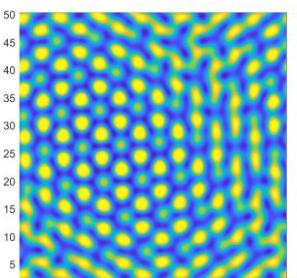
(A-f-5)

$$V_0=10^{-1}$$

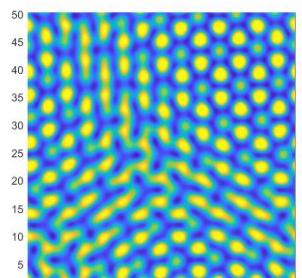


(A-f-6)

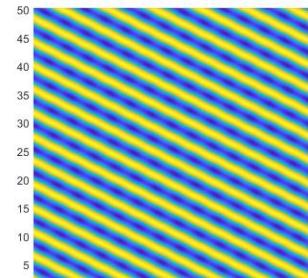
薄膜



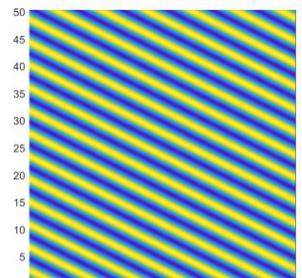
(A-m-1)



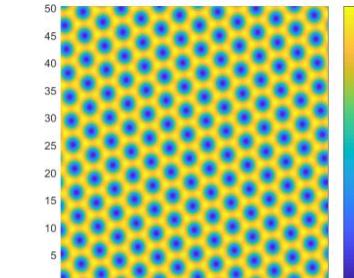
(A-m-2)



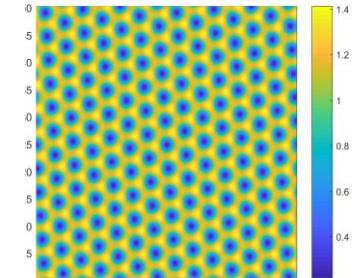
(A-m-3)



(A-m-4)



(A-m-5)

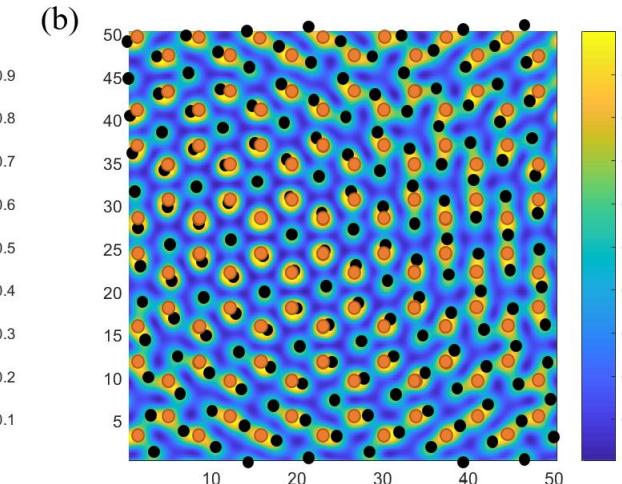
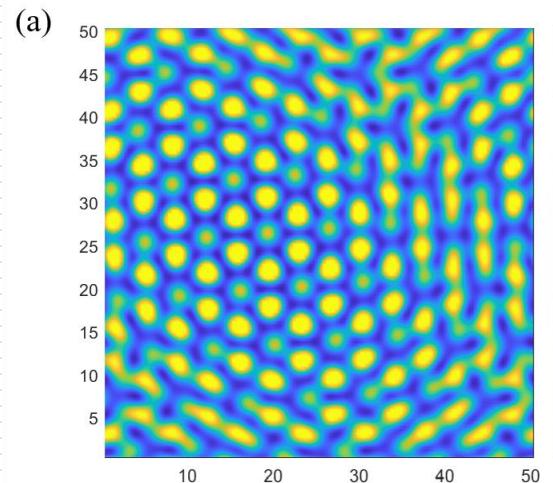


(A-m-6)

莫尔
条纹

程序模拟

$$V_0 \in [10^{-6}, 10^{-5}]$$



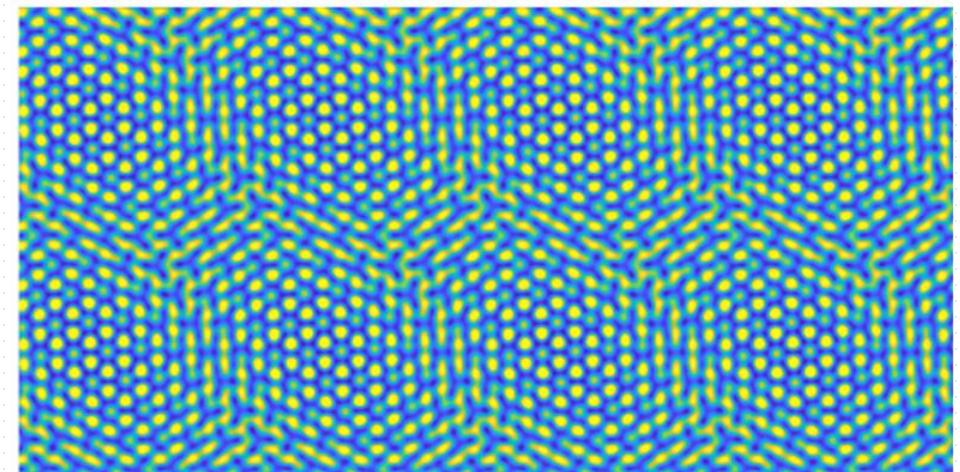
● 衬底原子
● 薄膜原子

$$\psi_{\text{Moiré}} = \psi + \psi_{\text{sub}}$$

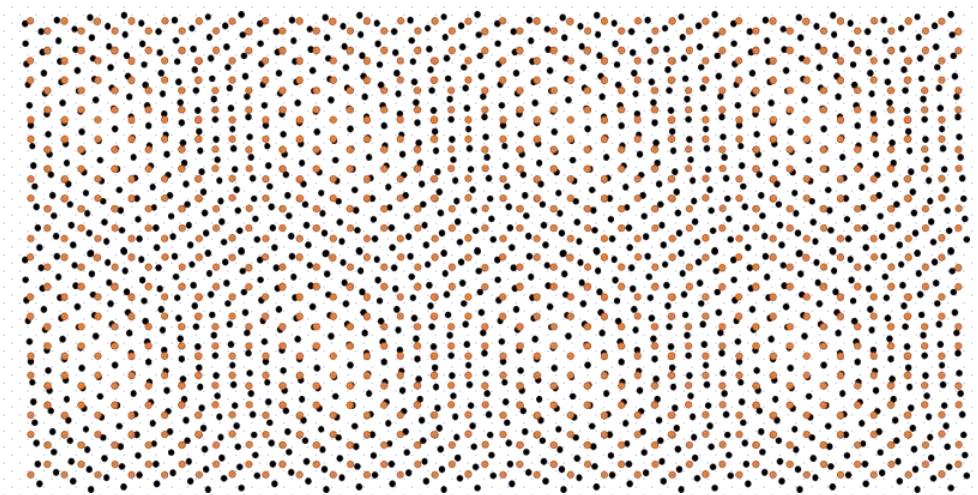
$$F \sim V\psi = V_0\psi_{\text{sub}}\psi$$

在保证薄膜周期性结构的条件下，尽可能使得薄
膜原子与衬底原子重叠最小！

(a)



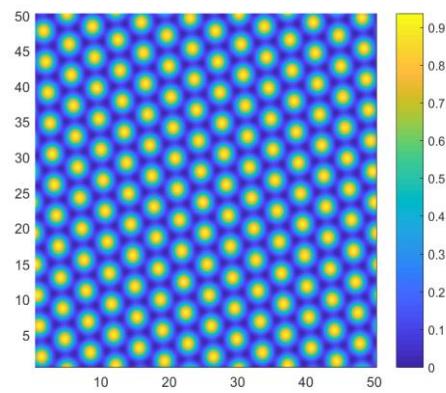
(b)



大面积的莫尔条纹

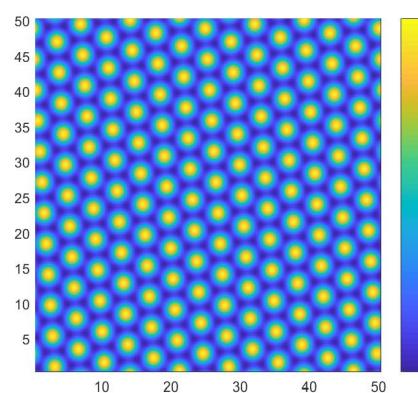
程序模拟

$$V_0 \in [10^{-4}, 10^{-3}]$$

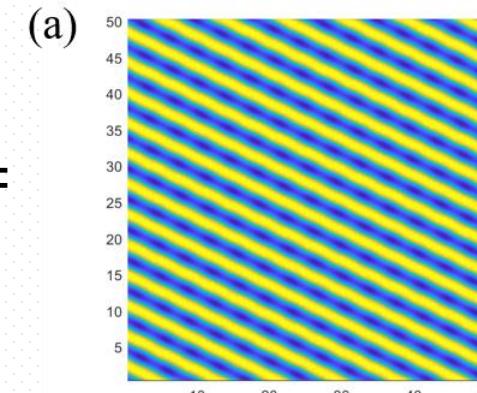


薄膜

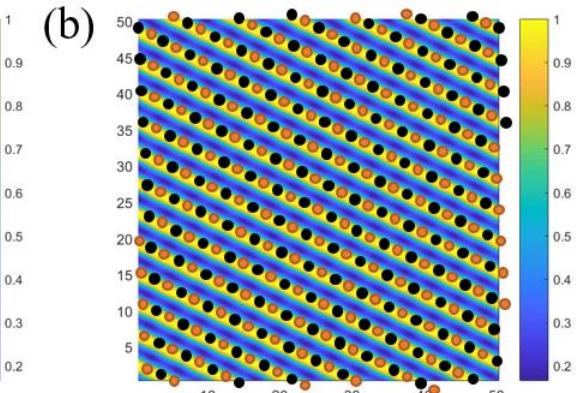
+



衬底

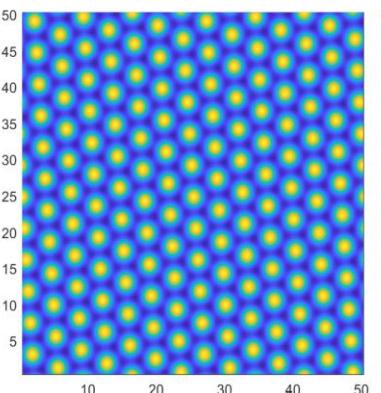


(a)



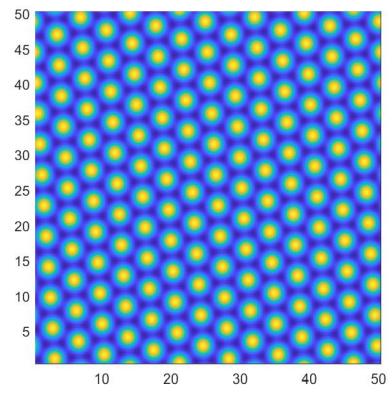
(b)

莫尔条纹

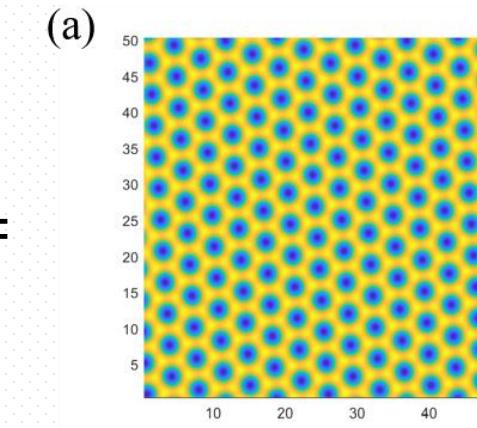


薄膜

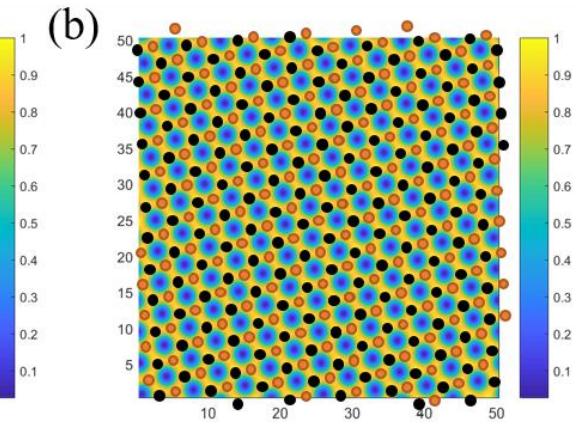
+



衬底



(a)

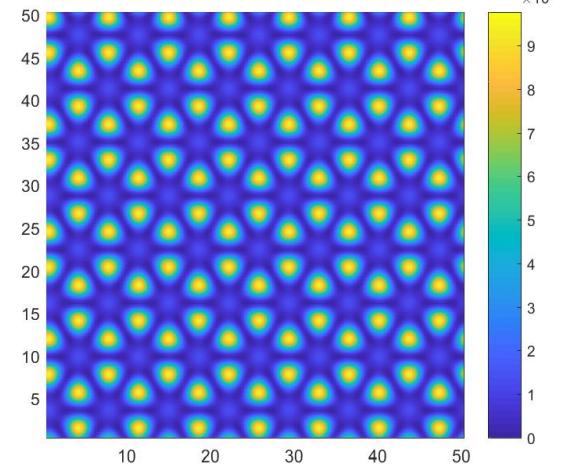


(b)

莫尔条纹

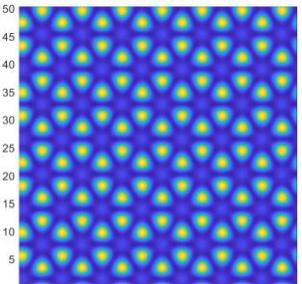
程序模拟

相同的条件下，改变衬底为蜂窝状结构



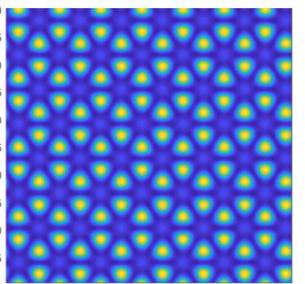
蜂窝状衬底

$$V_0=10^{-6}$$



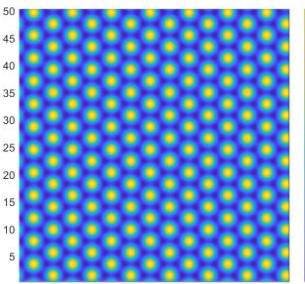
(B-f-1)

$$V_0=10^{-5}$$



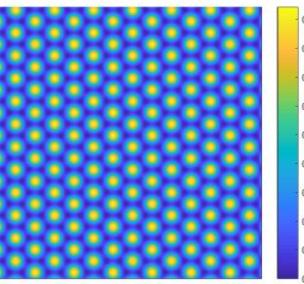
(B-f-2)

$$V_0=10^{-4}$$



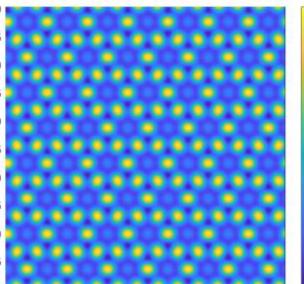
(B-f-3)

$$V_0=10^{-3}$$



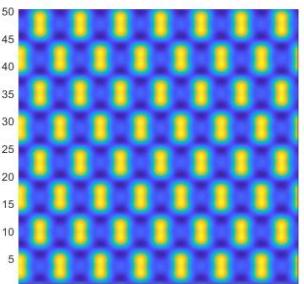
(B-f-4)

$$V_0=10^{-2}$$



(B-f-5)

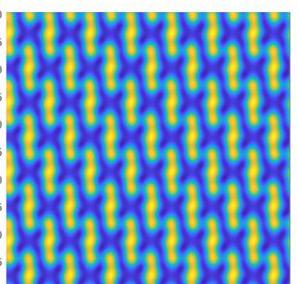
$$V_0=10^{-1}$$



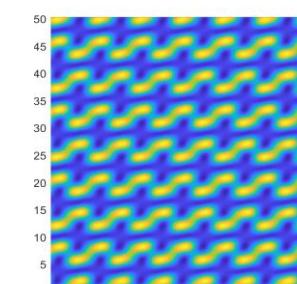
(B-f-6)

薄膜

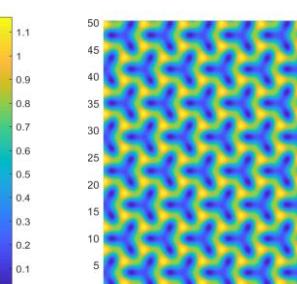
莫尔条纹



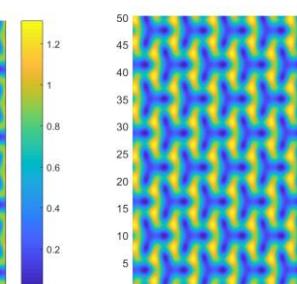
(B-m-1)



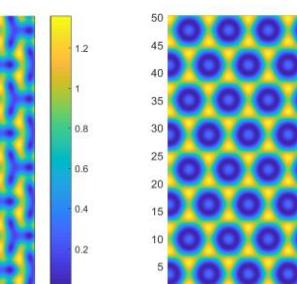
(B-m-2)



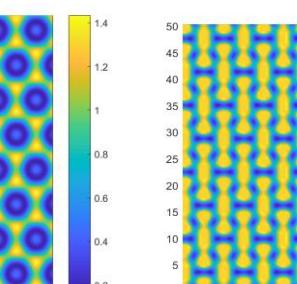
(B-m-3)



(B-m-4)



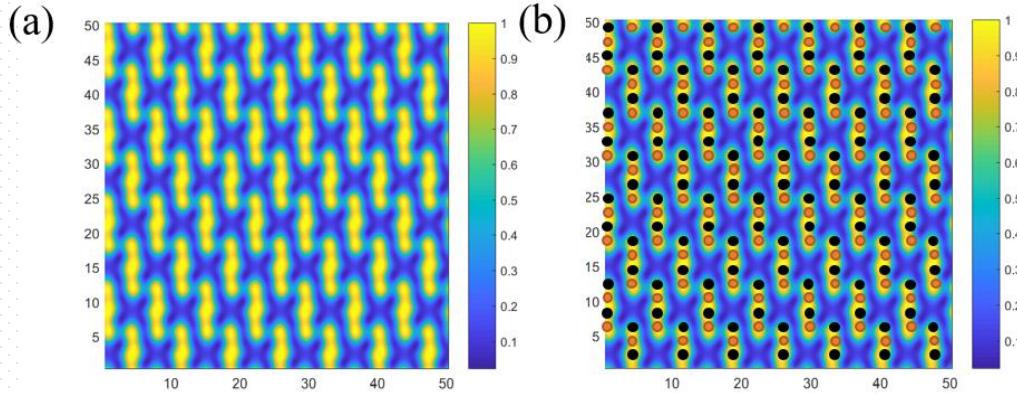
(B-m-5)



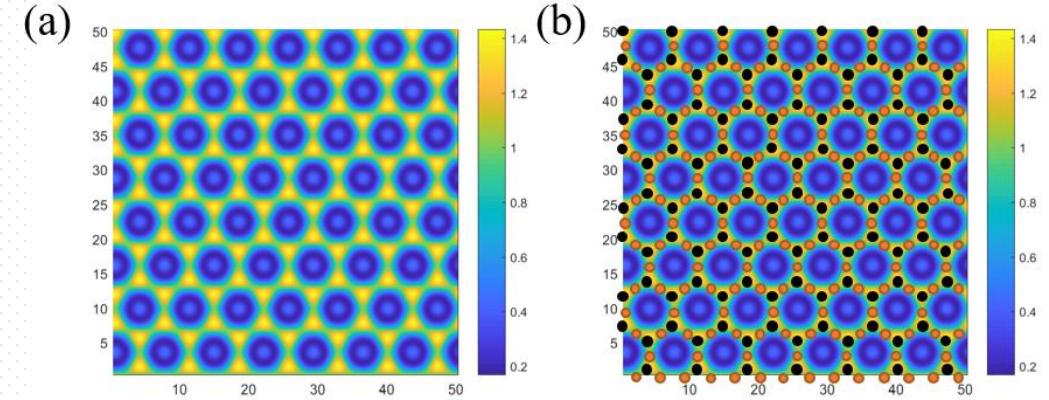
(B-m-6)

程序模拟

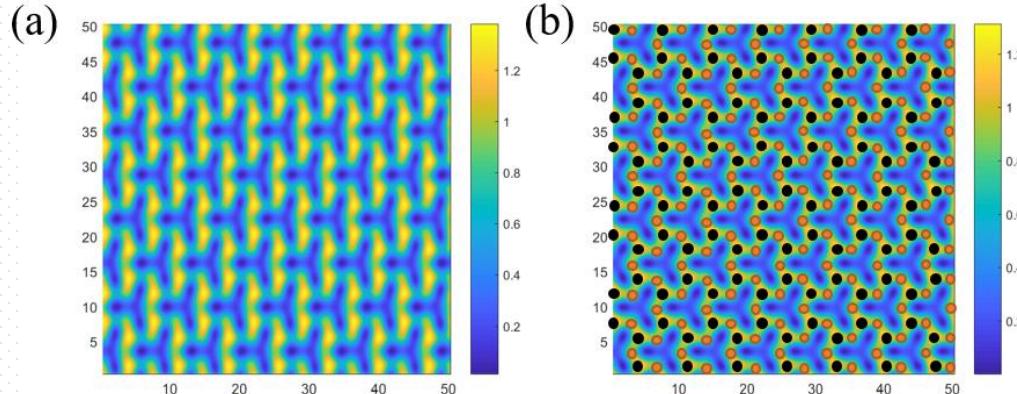
$$V_0 \in [10^{-6}, 10^{-5}]$$



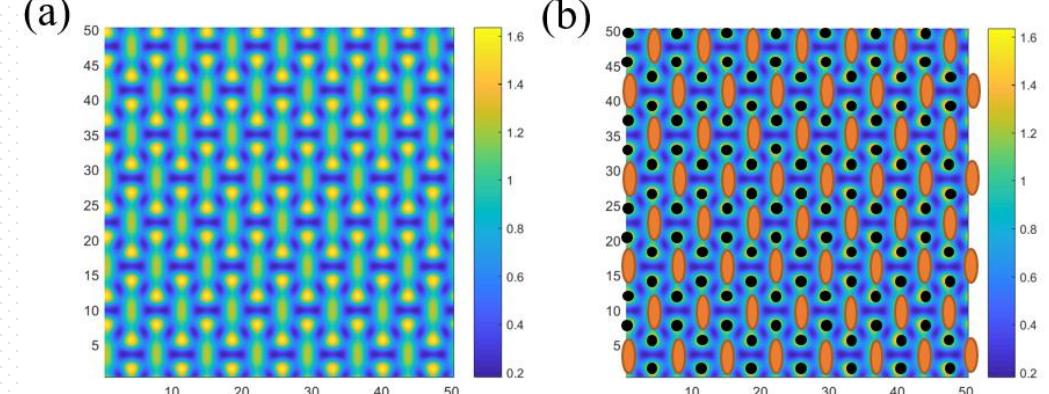
$$V_0 = 10^{-2}$$



$$V_0 \in [10^{-4}, 10^{-3}]$$



$$V_0 = 10^{-1}$$





Part Four

总结 & 讨论

总结&讨论

1. 得到了三模晶体相场模型的自由能表达式，并对三模晶体相场进行离散化，得到迭代式进行程序编写。
2. 通过程序模拟，绘制了不同对称性下的晶体相貌，一方面，得到了二维空间中五种布拉菲格子，说明三模晶体相场具有模拟二维空间所有晶格结构的潜质；另一方面，我们着重研究了三角对称性下的形貌特征，并绘制了相图，通过分析相图中的形貌，可以更好的理解三模晶体相场能够模拟复杂结构的原因。
3. 基于之前建立的程序框架，对晶核生长进行模拟。单晶生长可以极大的提高迭代的效率，多晶形核竞争会产生晶界等缺陷，并形成多晶结构。
4. 对于莫尔条纹的模拟，本文采用了三角结构和蜂窝状结构两种衬底，通过调节薄膜衬底耦合强度，使得周期性的薄膜生长出不同的形貌，通过分析可知，这一演化过程的机理，主要是由衬底对薄膜原子的排斥作用与薄膜晶体结构之间的竞争效应决定的。



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