Soft Matter and Polymer Physics

problem set November 11 , 2016

The string methods – droplet nucleation in the Ginzburg-Landau model

Consider the Ginzburg-Landau free-energy functional in rescaled units

$$\frac{F[m(\mathbf{r})]}{\alpha\sqrt{\bar{\mathcal{N}}}k_{\mathrm{B}}T} = \int \mathrm{d}^3\mathbf{r} \left(-\frac{1}{2}m^2 + \frac{1}{4}m^4 + \frac{1}{2}|\nabla m|^2 \right) \tag{1}$$

$$\frac{\mu(\mathbf{r}|m)}{\alpha\sqrt{\bar{\mathcal{N}}}k_{\mathrm{B}}T} = -m + m^3 - \triangle m \tag{2}$$

with periodic boundary conditions. The spinodal values of the order parameter are given by $m_s = \pm\frac{1}{\sqrt{3}}$. Use the string method [W. E, W. Ren, and E. Vanden-Eijnden, J. Chem. Phys. **126**, 164103 (2007)] to compute the critical nucleus and the concomitant free-energy barrier of a nucleation process.

Discretize the z-axis [0:L] into N intervals of width $\Delta z = L/N$, i.e., $z_0 = 0$, $z_1 = \Delta z$, $\cdots$, $z_k = k\Delta z$, $\cdots$, $z_{N-1} = (N-1)\Delta z = L - \Delta z$, and $z_N = z_0$. A system configuration is completely specified by the vector $m[i_z]$ with $0 \leq i_z \leq N-1$.

Consider the transformation from an initial, homogeneous, metastable state, $m_0[i_z] = m_0$, for all $0 \leq i_z < N$ and $|m_0| > m_s = \frac{1}{\sqrt{3}}$ to the equilibrium state that is comprised of two domains, ± 1, and of sizes, $\frac{l_\pm}{L} = \frac{1\pm m_0}{2}$, which are separated by two interfaces. Use the technique of the previous exercise to calculate the equilibrium configuration $m_{\mathrm{eq}}[i_z]$. Specifically, use the values $m_0 = -0.8$, $L = 100$, and $N = 200$.

The string that describes the transformation is a set of configurations, $m_s[i_z]$, that depends on a continuous contour parameter $0 \leq s \leq 1$. s characterizes the progression of the transformation along the Minimum Free-Energy Path (MFEP). The initial configuration at $s = 0$ corresponds to the homogeneous, metastable state $m_{s=0}[i_z] = m_0[i_z]$, whereas the final configuration corresponds to the equilibrium state $m_{s=1}[i_z] = m_{\mathrm{eq}}[i_z]$. The intermediate states are dictated by the condition that the chemical potential normal to the MFEP vanishes and they can be constructed by the following scheme – the improved and simplified string method.

To this end, we discretize the contour parameter into $n = 20$ points with $s[i_s = 0] = 0$ and $s[i_s = 19] = 1$ and likewise approximate the continuous string of configurations by the set $m[i_s][i_z]$ with $0 \leq i_s < n$ and $0 \leq i_z < N$. The initial and final configurations remain fixed, whereas the "inner" configurations $1 \leq i_s < n-1$ are updated by the following scheme:

1. minimize the free energy of each configuration by a "downhill" step:

$$m[i_s][i_z] \rightarrow m'[i_s][i_z] = m[i_s][i_z] - \mu[i_s][i_z] \cdot \epsilon \qquad (3)$$

for $0 \leq i_z < N$ and $1 \leq i_s < n - 1$. Here $\mu[i_s][i_z]$ denotes the chemical potential of the i_s^{th} configuration at position i_z (cf. Eq. (2)). In the numerical calculations use the value $\epsilon = 0.01$.

2. Calculate the positions $s'[i_s]$ of the updated configurations along the string:

   - calculate the (non-normalized) distance between two neighboring configurations

$$\Delta'_{i_s+1,i_s} = \sqrt{\sum_{i_z=0}^{N} \left(m'[i_s + 1][i_z] - m'[i_s][i_z] \right)^2} \qquad \text{for} \quad i_s = 0, \cdots, n-2$$

   (If $\Delta'_{i_s+1,i_s} < 10^{-6}$ set $\Delta'_{i_s+1,i_s} = 10^{-6}$ in order to preserve order of configurations along string, c.f. initialization)

   - compute the normalized distance

$$s'[i_s] = \frac{\sum_{i=0}^{i_s-1} \Delta'_{i+1,i}}{\sum_{i=0}^{n-2} \Delta'_{i+1,i}}$$

   which fulfills $s'[0] = 0$ and $s'[n-1] = 1$.

3. For each fixed point in space, i_z, compute a third-order spline for the function $f_{i_z}(s) = m'_s[i_z]$ given the n samples $(s'[i_s], m'[i_s][i_z])$. Use this third-order spline to construct the new string in a point-wise manor

$$m[i_s][i_z] = f_{i_z}(s[i_s]) \qquad \text{with} \quad s[i_s] = \frac{i_s}{n-1}$$

   (also compute $t[i_s][i_z]$, see below).

4. let the cycle commence again with step 1 until the perpendicular component of the chemical potential is sufficiently small.

This iterative procedure is converged if the perpendicular component of the chemical potential is small. To this end, we use the spline interpolation to define a tangent vector at each configuration of the string, i.e.,

$$t[i_s][i_z] = t_s[i_z] \equiv \frac{\mathrm{d}}{\mathrm{d}s} m_s[i_z] \approx \frac{\mathrm{d}}{\mathrm{d}s} f_{i_z}(s) \qquad \text{with} \quad s = s[i_s] = \frac{i_s}{n-1} \qquad (4)$$

and define the perpendicular component of the chemical potential as

$$\mu_\perp[i_s][i_z] \equiv \mu[i_s][i_z] - \frac{\sum_{i'_z=0}^{N-1} t[i_s][i'_z] \mu[i_s][i'_z]}{\sum_{i'_z=0}^{N-1} t^2[i_s][i'_z]} \cdot t[i_s][i_z] \qquad (5)$$

Initialize the string according to

$$m[i_s][i_z] = \begin{cases} m_0 & \text{for} \quad 0 < i_s < n/2 \\ m_{\text{eq}}[i_z] & \text{for} \quad n/2 < i_s < n-1 \end{cases} \tag{6}$$

and perform the iterative string calculation until $\mu_\perp[i_s][i_z]$ is sufficiently small (say 0.001). Compute the free-energy change along the string via

$$F_s - F_{s=0} \sim \int \mathrm{d}s \sum_{i_z=0}^{N-1} \mu_s[i_z] t_s[i_z] \tag{7}$$

and compare the result with the direct calculation $F_s \equiv F[m_s(\mathbf{r})]$.