Analysis of Otha-Kawasaki Free Energy by Means of the Brazovskii Approach

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Abstract. In this work, we developed the expansion of the Brazovskii type of Otha-Kawasaki free energy used in different condensed matter systems. This expansion makes it easy to evaluate the contributions of the terms of energy involved, usually referred to as short-range, "double-well" potential and long-range. Thus, there is a powerful tool to explore and understand the dynamics of systems evolution out of equilibrium.

1. Introduction
In the weak segregation zone, the free energy of a copolymer system is described through the expression developed by Otha-Kawasaki [1], [2]. It is expressed according to the order parameter, which represents the difference in density between A and B monomers composing the diblock copolymer A-B, \( \phi = \phi_A - \phi_B \) where \( \phi_A \) is A monomer volume fraction, and \( \phi_B \) is B monomer volume fraction. The functional expression of free energy can be expressed as the sum of the contribution of a short-range term and a long-range term,

\[
F[\phi] = F_c[\phi] + F_l[\phi]
\]

The short-range term is [3]:

\[
F_c[\phi] = \int d\mathbf{r} \left[ \frac{D}{2} (\nabla \phi)^2 + W(\phi) \right]
\]

Where \( W(\phi) = -\tau \phi^2 + \frac{g}{2} \phi^4 \) is the so-called "double-well" potential, with phenomenological constants \( \tau \) and \( g \). The gradient term of Equation (1) is associated with the effect of creating interfaces between the two components [4]. The long-range term [5] is

\[
F_l[\phi] = \frac{\alpha}{2} \int d\mathbf{r} \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') (\phi(\mathbf{r}) - \bar{\phi})(\phi(\mathbf{r}') - \bar{\phi})
\]

Where \( \bar{\phi} \) represents average composition. The Green’s function \( G(\mathbf{r}, \mathbf{r}') \) verifies the condition, \( -\nabla^2 G = \delta(\mathbf{r} - \mathbf{r}') \).

The previous equation was initially developed by Leibler [6] and was later supplemented by Otha-Kawasaki [1]. The mesoscopic order is the result of the competition between a short-range attractive interaction — corresponding to the gradient term of (1) — , and a long-range repulsive interaction — corresponding to the long-range term that is imposed to avoid phase macroseparation, and to set the copolymer periodicity. The characteristic wavelength is \( \lambda = 2\pi/k_c = D/\alpha^{-1/4} \).
We use an alternative expression that is obtained from the substitution $\psi(r) = \phi(r) - \bar{\phi}$, [7] then the short-range term is

$$F_s[\psi] = \int dr \left[ \frac{\partial}{\partial \bar{\phi}} (\nabla \psi)^2 + W(\psi) \right]$$

(3)

Where the double well potential

$$W(\psi) = (-\tau \bar{\phi} + g\bar{\phi}^3)\psi + \frac{1}{2} (-\tau + 3 g\bar{\phi}^2)\psi^2 + g\bar{\phi}\psi^3 + \frac{1}{4} g\psi^4$$

(4)

The long-range term is

$$F_l[\psi] = \frac{\alpha}{2} \int d\bar{r} \int dr G(r, \bar{r}) \psi(r) \psi(\bar{r})$$

(5)

The time evolution of the order parameter is determined by the equation

$$\frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta F}{\delta \psi} = \nabla^2 (-D\nabla^2 \psi + A + B\psi + C\psi^2 + g\psi^3) - \alpha \psi + \eta$$

(6)

Where $A = -\tau \bar{\phi} + g\bar{\phi}^3$, $B = -\tau + 3 g\bar{\phi}^2$ and $C = 3 g\bar{\phi}$.

1.1. Brazovskii expansion

In the weak segregation limit, the expression of Otha Kawasaki free energy can be expanded in a setting of critical value $k = k_c$, where $k_c^2 = \frac{\alpha}{D}$ [1]. Then, we proceed to express the gradient term of the short-range contribution in the Fourier representation:

$$F_{ck}[\psi] = \frac{D}{2} \int k^2 \psi_k \psi_{-k} dk$$

(7)

Similarly, the long-range term is:

$$F_{lk}[\psi] = \frac{\alpha}{2} \int \psi_k \frac{1}{k^2} \psi_{-k} dk d(-\hat{k})$$

(8)

Where, $\psi_k$ represents the Fourier Transform of the order parameter.

A generic function can be expanded in a series of power in the setting to an $a$-value according to the expression [8]

$$f(x) = f(a) + f'(a)(x - a) + \frac{1}{2} f''(a)(x - a)^2 + \cdots$$

(9)

Where the order of the derivative of the function is represented by the primacy. By using the above expression, we can expand the function

$$f(k) = \frac{1}{k^2}$$

(10)

in the setting of $k^2 = k_c^2$, we obtain

$$\frac{1}{k^2} \approx \frac{1}{k_c^2} - \frac{1}{k_c^4} (k^2 - k_c^2) - \frac{1}{k_c^6} (k^2 - k_c^2)^2 + \cdots$$

(11)
Replacing in the expression of the long-range term—equation (8)—, we obtain

\[
F_{lk}[\psi] \approx \frac{\alpha}{2} \iint \psi_k \left( \frac{1}{k_c^2} - \frac{1}{k_c^2} (k^2 - k_c^2) \right) \psi_{-k} dk d(-k)
\]  \hspace{1cm} (12)

Where we have developed the first-order expansion in \(k^2\).

Combining in real space with the gradient term, both contributions of free energy can be expressed according to the differential operators, i.e.:

\[
\frac{D}{2} (\nabla \psi)^2 + \frac{\alpha}{2} G(\mathbf{r}, \mathbf{r}) \psi(\mathbf{r}) \psi(\mathbf{r}) \approx -\frac{\alpha}{k_c^2} (\nabla \psi)^2 + \frac{3}{2} \frac{\alpha}{k_c^2} \psi^2 + \frac{\alpha}{2k_c^2} (\nabla^2 \psi)^2 + \ldots
\]  \hspace{1cm} (13)

that, when combined with the double-well term, we finally obtain the expansion of Otha-Kawasaki energy:

\[
F[\psi] = F_S + F_l = \int d\mathbf{r} \left[ \frac{\alpha}{2k_c^2} (\nabla^2 \psi)^2 - \frac{\alpha}{k_c^2} (\nabla \psi)^2 + \frac{3}{2} \frac{\alpha}{k_c^2} \psi^2 + W(\psi) \right]
\]  \hspace{1cm} (14)

The sought expansion or approximation of Brazovskii corresponds to the previous expression, and can be calculated numerically in a simple way, as we will see in the following section.

2. Numerical simulation

The Equation (6) has been solved numerically using a semi-implicit algorithm pseudospectral [9] with periodic boundary conditions. To obtain an adequate numerical stability and an accurate resolution, the time steps and spatial resolution have been selected. According to the typical values used in these numerical schemes, \(\Delta t \sim 10^{-4}\) is used for time steps and \(\Delta x \sim 10^{-2}\) is used for spatial discretization. The size of the simulated system is \(L_xL = 512\times512\).

The time evolution of a cololymer system is represented in Figure (1), starting from an initial random composition and with \(\tau = D = \alpha = g = 1\), \(\bar{\phi} = 0.1\), the chosen values correspond to a lamellae configuration. The energy in the presented system decreases in the time as can be seen in Figure (2), where the contribution of each term of energy and the total energy are illustrated.

![Figure 1](image1.png)

**Figure 1.** Time evolution of a copolymer system in accordance with equation (6). Lamellae configuration. The values used are: \(\tau = 2.1\), \(D = 1\), \(\alpha = 1\), \(g = 1\), \(\bar{\phi} = 0.0\).

Times: a- \(t=10\)  b- \(t=50\)  c- \(t=200\)  d- \(t=1000\)

Similarly, a system with values \(\tau = 2.1,D = 1,\alpha = 1,\ g = 1,\ \bar{\phi} = 0\) was simulated, once again, starting from a random configuration. In this case, the system symmetry is hexagonal. The time evolution is illustrated in Figure (3), while the energy evolution can be seen in Figures (4) and (5).

These examples allow for observing the ease with which energy can be evaluated and thus, allow for having a very useful tool in the analysis of systems that respond to the free energy equation of Otha-Kawasaki.
3. Results and discussion

Figures (2) and (5) show the evolution of the different free energy terms which were obtained by means of the approximation made in section 1.1. As it can be seen, the different energy contributions—short-range and long-range—are easy to evaluate, and they allow for understanding the dynamics of the system evolution in the most complete way.

Figure 2. Time evolution of the energy for the system presented in Fig. 1.

Figure 3. Time evolution of a copolymer system in accordance with equation (16). Hexagonal configuration. The values used are: $\tau = 2.1$, $D = 1$, $\alpha = 1$, $g = 1$, $\bar{\phi} = 0.1$.

Times: a-t=10  b-t=50  c-t=200  d-t=1000

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Figure 4. Representation of the total energy in accordance with the approximation made in Section 1.1. a- Copolymer patterns, b- total energy (a.u.). Note how at long times, the energy is located at the grain boundaries.
5. Time evolution of the energy for the system presented in Fig. 3.

4. Conclusions
The expansion of the free energy of Brazokskii to the free energy for Otha-Kawasaki in the weak segregation regime is presented in this paper. The development of energy based on differential operators, that can be easily calculated in a numerical way, allows for the access to the energy analysis during the time evolution towards the equilibrium of a copolymer system as it was exemplified in Section 1.1.

5. References
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