

# Square-Gradient Model for Inhomogeneous Systems: From Simple Fluids to Microemulsions, Polymer Blends and Electronic Structure

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## 1 Introduction

Statistical mechanics is concerned with the properties of many-body systems, i.e., systems containing a large number of either quantum or classical particles [1, 2]. Common examples of such particles include electrons and photons for quantum systems, or diverse microscopic objects for classical systems (e.g., atoms, inert-gas molecules, the repeating units of a polymer or macromolecule, colloidal particles, and globular proteins). To describe the inter-particle interactions, we may divide the elementary quantum particles into bosons and fermions, depending on the symmetric/antisymmetric nature of their wave functions. Such distinction is unnecessary for classical particles because the Newton's equation, often in the context of a semi-empirical potential, is used to describe the particle dynamics.

Regardless of the physical nature of particles, a number of common mathematical procedures may be taken to utilize statistical-mechanical principles to describe a wide variety of phenomena arising from many-body interactions. One of the best-known procedure is Monte Carlo (MC) simulation [3], applicable to calculating the configurational properties of virtually any thermodynamic system. The square-gradient approximation (SGA) discussed in this chapter represents another common but computationally much more efficient procedure. The basic ideas of SGA were introduced by van der Waals to describe the interfacial properties of coexisting vapor and liquid phases over a hundred years ago [4]. Because of its simplicity, SGA remains a popular choice for predicting the microscopic structure and thermodynamic properties of diverse inhomogeneous systems. Similar procedures have been extensively used, for example, to describe phase transitions in condensed-matter systems such as macroscopic phase separations, fluid wetting at solid surfaces, and formation of microemulsions or polymeric mesoscopic phases. In a slightly different context, the

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gradient expansion method is also commonly used in theoretical descriptions of electronic properties for both chemical systems and materials.

In contrast to simulation methods, the universal applicability of SGA to various simple and complex fluids and electronic systems is rarely discussed as a common theme. Because the gradient expansion method was often introduced from the perspectives of seemingly unrelated physical phenomena with utterly different practical applications, SGA was “rediscovered” for a number of times and often named after re-inventors from different subfields of condensed matter physics. This chapter intends to establish a generic linkage among several incarnations of SGA. For pedagogy, our discussion begins with some basic concepts from statistical mechanics applicable to both quantum and classical systems. While for simplicity our discussion is mostly focused on systems containing only one type of particles, it should be straightforward to extend similar ideas (and equations) to multicomponent systems. In addition to pedagogical purposes, this chapter intends to forge a common ground for better communication among different subfields of statistical mechanics and to facilitate future cross-field developments.

## 2 Statistical Mechanics

For a many-body system of practical concern, the dynamic and energetic properties are inevitably related to the particle positions or the spatial distributions of the microscopic constituents. A quantity of fundamental importance is thus the one-body particle density profile, viz. the average local number density of individual particles. For a system containing  $N$  indistinguishable particles of spherical shape, the instantaneous particle distribution may be specified by a summation of the Dirac- $\delta$  functions:

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (1)$$

where  $\mathbf{r}_i$  represents the position to locate the center of mass for particle  $i$ . The one-body density profile is defined as an ensemble average of the instantaneous density

$$\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle = \sum_{i=1}^N \langle \delta(\mathbf{r} - \mathbf{r}_i) \rangle \quad (2)$$

where the angle brackets  $\langle \dots \rangle$  denote an ensemble average, which is determined by the probability of the many-body system in different microstates  $\{v\}$

$$\langle \dots \rangle = \sum_v p_v(\dots). \quad (3)$$

The Dirac- $\delta$  function specifies the probability density distribution for a particle located at a specific position. Accordingly, the density profile  $\rho(\mathbf{r})$  reflects the microscopic structure of the many-body system.

The grand canonical ensemble provides a convenient starting point to describe the properties of a many-particle system in terms of the one-body density profiles. For a one-component system at absolute temperature  $T$ , chemical potential  $\mu$ , and volume  $V$ , the microstate probability is given by

$$p_v = \exp [\beta (\mu N_v - E_v)] / \Xi \quad (4)$$

where  $\Xi$  represents the grand partition function

$$\Xi \equiv \sum_v \exp [\beta (\mu N_v - E_v)]. \quad (5)$$

In Eqs. (4) and (5),  $\beta = 1/(k_B T)$ ,  $k_B$  is the Boltzmann constant,  $N_v$  and  $E_v$  stand for the number of particles and the total energy at microstate  $v$ , respectively. For an electronic system at 0 K, the microstate probability is defined in terms of the multi-body wave function  $\Psi(\mathbf{r}^N, s^N)$ . In that case, the one-body density profile can be written as

$$\rho(\mathbf{r}) = \int \sum_{s^N} \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \Psi^*(\mathbf{r}^N, s^N) \Psi(\mathbf{r}^N, s^N) d\mathbf{x}^N \quad (6)$$

where  $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ ,  $s^N = (s_1, s_2, \dots, s_N)$  stands for the spin coordinates, and  $\Psi^*$  represents the complex conjugate of the multi-body wave function.

In principle, all equilibrium properties of the system can be derived from the grand potential

$$\Omega \equiv -k_B T \ln \Xi. \quad (7)$$

Taking two important thermodynamic variables as an example, we can calculate entropy from a partial derivative of the grand potential with respect to temperature

$$S \equiv -k_B \sum_v p_v \ln p_v = - \left[ \frac{\partial \Omega}{\partial T} \right]_{\mu, V}, \quad (8)$$

and the internal energy is related to the grand potential by

$$U \equiv \langle K_v + \Gamma_v + \int d\mathbf{r} \hat{\rho}_v(\mathbf{r}) \varphi^{\text{ext}}(\mathbf{r}) \rangle = \left[ \frac{\partial \beta \Omega}{\partial \beta} \right]_{\mu, V} + \mu N \quad (9)$$

where  $K_v$  and  $\Gamma_v$  stand for the kinetic and potential energies of the particles at microstate  $v$ , respectively,  $\varphi^{\text{ext}}(\mathbf{r})$  is the external potential for each particle, and  $N = \langle N_v \rangle$  denotes the average number of particles in the system.

From the grand potential, we can also derive a hierarchy of correlation functions. For example, the first derivative of the grand potential with respect to the one-body potential yields the one-body density profile

$$\frac{\delta\Omega}{\delta u(\mathbf{r})} = \rho(\mathbf{r}) \quad (10)$$

where  $u(\mathbf{r}) \equiv \varphi^{\text{ext}}(\mathbf{r}) - \mu$ , and a second derivative leads to the density-density correlation function  $\chi(\mathbf{r}, \mathbf{r}')$ ,

$$-\frac{\delta^2\Omega}{\delta^2 u(\mathbf{r})} = -\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')} = \beta \langle [\hat{\rho}(\mathbf{r}) - \rho(\mathbf{r})][\hat{\rho}(\mathbf{r}') - \rho(\mathbf{r}')] \rangle \equiv \beta\chi(\mathbf{r}, \mathbf{r}'). \quad (11)$$

Although the basic ideas of statistical mechanics are rather intuitive, the complexity in the dynamics of many particles makes direct evaluation of the grand partition function virtually impossible except for a few highly idealized systems. In MC simulation, the ensemble average is instead evaluated using some stochastic processes to sample the microstates with an electronic computer. Thanks to rapid advances in computing technology and algorithm developments, modern applications of statistical mechanics often hinge on simulation methods. Alternatively, the microstates can be generated following the dynamics of individual particles as in molecular dynamics (MD) simulations. While the numerical procedures for both MC and MD are formally exact and rather straightforward to implement, enumeration of the microscopic states of a many-body system is not only computationally demanding but also unhelpful for capturing the essential features of physical phenomena. Molecular simulation generates a large volume of often unrevealingly information. By contrast, theoretical methods are able to capture the universal principles underlying diverse physical phenomena and permit fast calculation of structural and thermodynamic properties without explicit consideration of the microscopic details.

### 3 Density Functional Theory (DFT)

Density functional theory (DFT) provides a generic mathematic framework to establish quantitative connections between thermodynamic properties of a many-body system and the underlying one-body density profiles. The central idea can be best introduced in terms of the Hohenberg-Kohn-Mermin (HKM) theorem [5, 6], which was established first in the context of inhomogeneous electrons at 0 K. The HKM theorem was later generalized to thermodynamic systems of both quantum and classical particles [7].

For a one-component system of identical particles, the HKM theorem asserts that the grand potential can be determined by minimization of the density functional

$$\Omega[\rho(\mathbf{r})] \equiv F[\rho(\mathbf{r})] + \int \rho(\mathbf{r})u(\mathbf{r})d\mathbf{r} \quad (12)$$

where  $F[\rho(\mathbf{r})]$  stands for the *intrinsic* Helmholtz energy. Here by intrinsic we mean that the quantity is independent of the system external potential. Formally,  $F[\rho(\mathbf{r})]$  is defined by the microstate probability and the intrinsic energy of the particles

$$F[\rho(\mathbf{r})] = \sum_v p_v (k_B T \ln p_v + K_v + \Gamma_v). \quad (13)$$

According to the HKM theorem, the one-body external potential is a unique functional of the one-body density profile. As a result, both the microstate probability  $p_v$  and, subsequently, the intrinsic Helmholtz energy are unique functionals of the one-body density profile  $\rho(\mathbf{r})$ .

For a specific system, the one-body potential  $u(\mathbf{r})$  is fixed. Minimization of the grand potential functional with respect to the one-body potential leads to

$$\frac{\delta \Omega}{\delta \rho(\mathbf{r})} = \frac{\delta F}{\delta \rho(\mathbf{r})} + u(\mathbf{r}) = 0. \quad (14)$$

Equation (14) is known as the Euler-Lagrange equation. With an explicit expression for the intrinsic Helmholtz energy, Eq. (14) allows us to solve the one-body density profile, which serves as the starting point to predict other thermodynamic and structural properties of the system.

It is worth noting that DFT is formally exact and applicable to both quantum and classical systems. In other words, DFT represents a generic mathematical framework in statistical mechanics. The same procedure is similarly applicable to quantum and classical systems including electronic systems at zero temperature. At  $T = 0$  K, the expression for the grand potential and the Euler-Lagrange equation remain the same but the thermodynamic entropy vanishes. In that case, the intrinsic Helmholtz energy becomes an *internal* energy, depending only on the kinetic and potential energy of the particles

$$F[\rho(\mathbf{r})] = \sum_v p_v (K_v + \Gamma_v) = \langle K_v + \Gamma_v \rangle. \quad (15)$$

For electronic systems, the excitation energy, typically on the order of a few electron volts, is much higher than the thermal energy at room temperature ( $1 \text{ eV} \sim 40 k_B T$ ). As a result, the entropy effects are relatively unimportant for the electronic properties.

While DFT is emerging as one of the most predominant approaches for the theoretical description of inhomogeneous quantum and classical systems, one noticeable caveat is that the HKM theorem does not provide any specific knowledge on the intrinsic Helmholtz energy. Nevertheless, analytical expressions are readily available for the density functional in the absence of inter-particle interactions. The ideal-gas systems provide a useful reference to formulate the *excess* intrinsic Helmholtz energy due to inter-particle interactions. Although exact results are no more attainable

for most practical systems, excellent approximations can be established using analytical tools from both quantum and statistical mechanics [8, 9].

From a mathematical perspective, approximate methods in statistical mechanics are mostly based on perturbation expansions with respect to either the inter-particle energy or the local density inhomogeneity. For systems with a pairwise additive potential  $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ , the total potential energy at each microstate may be written as

$$\Gamma_v = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i) \Gamma(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_2 - \mathbf{r}_j) \quad (16)$$

where a factor of 2 accounts for the fact that each pair potential involves two interacting particles. Using Eqs. (7) and (16), we may show that a functional derivative of the grand potential with respect to the pair potential leads to the two-body density distribution function,  $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ ,

$$\frac{\delta\Omega}{\delta\Gamma(\mathbf{r}_1, \mathbf{r}_2)/2} = < \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) > \equiv \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \quad (17)$$

Equation (17) can be used to evaluate the difference between the intrinsic Helmholtz energy of a real system and that of an ideal system (ID).

At fixed temperature  $T$  and one-body potential  $u(\mathbf{r})$ , a functional integration of Eq. (17) with respect to the pair potential gives [10]

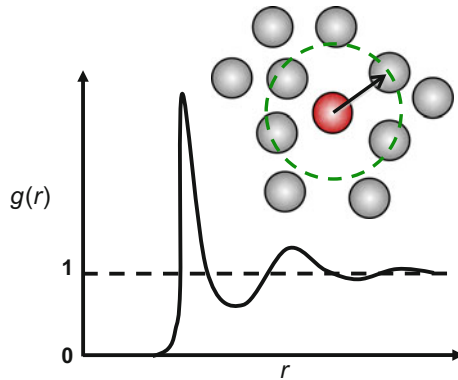
$$F[\rho(\mathbf{r})] = F^{ID}[\rho(\mathbf{r})] + \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \lambda) \Gamma(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (18)$$

where  $F^{ID}[\rho(\mathbf{r})]$  represents the intrinsic Helmholtz energy of the non-interacting system, and  $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \lambda)$  stands for the two-body density correlation function of the system under consideration but with a reduced pair potential,  $\Gamma_\lambda(r) = \lambda\Gamma(r)$ , where  $0 \leq \lambda \leq 1$ . In writing Eq. (18), we assume that the inter-particle potential between spherical particles depends on the center-to-center distance, i.e.,  $\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \Gamma(|\mathbf{r}_1 - \mathbf{r}_2|)$ . The functional integration corresponds to the reversible work to add the inter-particle potential to non-interacting ideal particles [11]. For electronic systems, Eq. (18) is commonly known as the adiabatic connection [8].

For most systems of practical interest, the two-body correlation functions are extremely complicated, depending not only on two positions but also on the local density profile as well as all variables defining the thermodynamic state. For easy understanding, it is convenient to express the two-body density correlation function in terms of the radial distribution function (RDF)

$$g(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) / [\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)] \quad (19)$$

or the total correlation function (TCF)



**Fig. 1** A schematic representation of the radial distribution function (RDF). For a uniform system of spherical particles,  $g(\mathbf{r}_1, \mathbf{r}_2)$  is a function of the distance  $r = |\mathbf{r}_1 - \mathbf{r}_2|$ . For an inhomogeneous system, however, RDF depends on the position and relative orientation. For both uniform and inhomogeneous systems, RDF vanishes at small separation and approaches unity at large distance owing to the short-range repulsion and the rapid decay of long-range inter-particle interactions

$$h(\mathbf{r}_1, \mathbf{r}_2) \equiv g(\mathbf{r}_1, \mathbf{r}_2) - 1. \quad (20)$$

Intuitively, RDF represents the probability of finding a particle given that the position of another particle is fixed at the origin. As shown schematically in Fig. 1, RDF vanishes at small separation due to the inter-particle repulsion and approaches unity at large distance when the particle densities become uncorrelated. In the mean-field approximation, it is commonly assumed  $g(\mathbf{r}_1, \mathbf{r}_2) = 1$  or  $h(\mathbf{r}_1, \mathbf{r}_2) = 0$ , i.e., the total correlation function is completely neglected.

## 4 Square-Gradient Approximation (SGA)

For systems with a nearly uniform one-body density profile, the intrinsic Helmholtz energy may be approximated by a functional Taylor expansion with respect to that of a uniform system with an average density  $\rho_0$ :

$$F[\rho(\mathbf{r})] = F(\rho_0) + \mu \int \Delta\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Delta\rho(\mathbf{r}_1) \Delta\rho(\mathbf{r}_2) K(\mathbf{r}_1, \mathbf{r}_2) + \cdots \quad (21)$$

where  $\Delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$ . In the density expansion above, the reference system has the temperature and the particle chemical potential the same as those corresponding to the real system.

In Eq. (21),  $K(\mathbf{r}_1, \mathbf{r}_2)$  has the units of energy and is referred to as the vertex function. Because the first-order functional derivative of the intrinsic Helmholtz energy with respect to  $\rho(\mathbf{r})$  results in the one-body potential, the vertex function corresponds

to the second-order functional derivative. For a uniform system, it depends only on the distance between  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , i.e.,

$$K(\mathbf{r}_1, \mathbf{r}_2) = - \left. \frac{\delta u(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)} \right|_{\rho(\mathbf{r})=\rho_0} = K(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (22)$$

In writing Eq. (22), we have utilized the Euler-Lagrange equation (i.e., Eq. (14)). Equation (22) suggests that the vertex function specifies the variational of the local one-body potential in response to the change in the particle density at another position.

In comparison to the exact expression given in Eqs. (18) and (21) has a major advantage because the vertex function depends on the distance between positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . For systems with a slow varying one-particle density  $\rho(\mathbf{r})$ ,  $\Delta\rho(\mathbf{r})$  is small and the functional Taylor expansion for the intrinsic Helmholtz energy may be truncated after the quadratic term. Similarly, the local density may be expressed as a truncated Taylor series

$$\rho(\mathbf{r}_2) = \rho(\mathbf{r}_1) + (\mathbf{r}_1 - \mathbf{r}_2) \cdot \nabla \rho(\mathbf{r}_1) + \frac{1}{2}(\mathbf{r}_1 - \mathbf{r}_2)(\mathbf{r}_1 - \mathbf{r}_2) : \nabla \nabla \rho(\mathbf{r}_1) + O(\nabla^3 \rho) \quad (23)$$

where  $\nabla \rho(\mathbf{r})$  denotes the density gradient, and symbol “:” is the scalar product of two tensors. As detailed in Appendix, the gradient expansions lead to a simple expression for the intrinsic Helmholtz energy of inhomogeneous systems:

$$F = \int d\mathbf{r} \left\{ f_0[\rho(\mathbf{r})] + \frac{\kappa}{2} |\nabla \rho(\mathbf{r})|^2 \right\} \quad (24)$$

where  $f_0(\rho)$  represents the Helmholtz energy density of the uniform system at system temperature  $T$  and local density  $\rho(\mathbf{r})$ , and  $\kappa$  is called the influence parameter. The first term on the right side of Eq. (24) corresponds to the local density approximation (LDA) for the intrinsic Helmholtz energy, and the gradient term accounts for a correction to the intrinsic Helmholtz energy due to the local density inhomogeneity.

For a uniform system,  $\nabla \rho(\mathbf{r}) = 0$ , and Eq. (24) reduces the bulk Helmholtz energy. Because the correction to the local density approximation is a quadratic function of the density gradient, Eq. (24) is referred to as the square-gradient approximation (SGA). Alternatively, the mathematical form is also known as the Ginzburg–Landau theory or the Landau expansion. Similar methods are used extensively to describe structure formation in inhomogeneous systems and phase transitions [12].

As shown in Appendix, the influence parameter is related to the vertex function of the uniform system  $K_0(r)$

$$\kappa = -\frac{2\pi}{3} \int_0^\infty r^4 K_0(r) dr = \lim_{q \rightarrow 0} [\tilde{K}_0(q) - \tilde{K}_0(0)]/q^2 \quad (25)$$



where  $\tilde{K}_0(q)$  represents the 3-dimensional (3D) Fourier transform of  $K_0(r)$

$$\tilde{K}_0(q) = \tilde{K}_0(\mathbf{q}) \equiv \int K_0(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \int \frac{\sin(qr)}{qr} K_0(r) d\mathbf{r}. \quad (26)$$

Alternatively, it may be expressed in terms of the density-density correlation function

$$\beta\kappa = \lim_{q \rightarrow 0} [1/\tilde{\chi}_0(q) - 1/\tilde{\chi}_0(0)]/q^2 \quad (27)$$

where  $\tilde{\chi}_0(q)$  corresponds to the 3D Fourier transform of the density–density correlation

$$\chi(\mathbf{r}, \mathbf{r}') \equiv \langle [\hat{\rho}(\mathbf{r}) - \langle \hat{\rho}(\mathbf{r}) \rangle] [\hat{\rho}(\mathbf{r}') - \langle \hat{\rho}(\mathbf{r}') \rangle] \rangle. \quad (28)$$

In deriving the influence parameter, we assume that the vertex function is independent of the local density. Accordingly,  $\kappa$  is determined from the correlation functions of the uniform reference system. For better numerical performance, however,  $\kappa$  is often evaluated from  $K_0(r)$  of a uniform system at the local density.

SGA requires as an input the local Helmholtz energy density and the vertex function (or the density–density correlation function) of the corresponding uniform system. On the one hand, the Helmholtz energy density is typically provided by an equation of state or an excess free-energy model for corresponding bulk systems. Alternatively, the local Helmholtz energy density may be obtained from an empirical correlation based on simulation results. For classical systems, the correlation functions can be solved from the integral-equation theories (e.g., the Ornstein-Zernike equation) or from mean-field approximations and analytical functions derived for ideal systems (e.g., correlation functions for Gaussian chains). Because gradient expansions are applied to both the intrinsic Helmholtz energy and the one-body density profile, we expect SGA to perform well for inhomogeneous systems with near uniform density profiles. With the influence parameter evaluated from the local densities (or locally averaged densities [13], however, SGA may also be used for highly inhomogeneous systems.

## 5 Simple Fluids

A simple fluid consists of argon-like molecules. In addition to noble gases, other examples of simple fluids include a large number of nonpolar gases of low molecular weight such as methane and, from a thermodynamics perspective, colloidal dispersions and aqueous solutions of globular proteins.

For a simple fluid, the bulk Helmholtz energy can be readily derived from an equation of state. Taking the van der Waals theory as an example, the reduced Helmholtz energy density per volume is given by

$$\beta f_0(\rho) = \rho \left[ \ln\left(\frac{\rho \Lambda^3}{1 - b\rho}\right) - 1 - \beta \rho a \right] \quad (29)$$

where  $a$  and  $b$  are van der Waals' parameters,  $\Lambda$  represents the thermal wavelength. More accurate expressions for the Helmholtz energy density are available [14].

The vertex function of a simple fluid may be expressed in terms of the direct correlation function (DCF),  $c(\mathbf{r}, \mathbf{r}')$ ,

$$\beta K(\mathbf{r}, \mathbf{r}') = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\rho(\mathbf{r})} - c(\mathbf{r}, \mathbf{r}'). \quad (30)$$

Mathematically,  $c(\mathbf{r}, \mathbf{r}')$  corresponds to the second-order functional derivatives of the excess Helmholtz energy,  $F^{\text{ex}} \equiv F - F^{\text{ID}}$

$$c(\mathbf{r}, \mathbf{r}') \equiv -\frac{\delta^2 \beta F^{\text{ex}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (31)$$

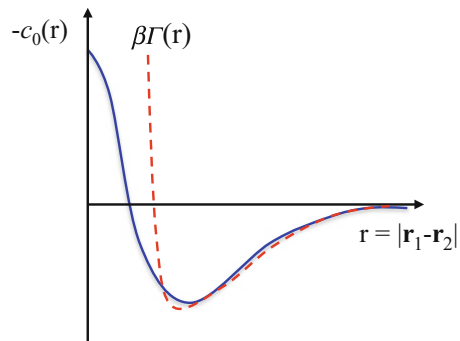
Without inter-particle interactions, the Helmholtz energy of the ideal system is exactly known

$$F^{\text{ID}} = k_B T \int \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r}) \Lambda^3] - 1 \} d\mathbf{r}. \quad (32)$$

As shown in Appendix, DCF and RDF are related through the Ornstein-Zernike equation, which provides a basis for numerical solutions of the correlation functions. Analytical expressions of  $c_0(r)$  are also available for a number of simple fluids over a broad range of thermodynamic conditions [15].

Figure 2 shows schematically the direct correlation function for a uniform fluid. While there is an apparent connection between the direct correlation function and the reduced pair potential at large distance, it is important to recognize that  $c_0(r)$  depends not only on the distance but also on thermodynamic parameters defining the equilibrium state. At large distance, the direct correlation function approaches to the reduced pair potential as

**Fig. 2** A schematic representation of the direct correlation function of a simple fluid  $c_0(r)$ . At large distance, the direct correlation function is virtually identical to the reduced pair potential  $-\beta\Gamma(r)$ . At short distance, the pair potential diverges while the direct correlation function remains finite



$$c_0(r) \approx -\beta\Gamma(r) \quad \text{as } r \rightarrow \infty. \quad (33)$$

For uniform systems, Eq. (30) reduces to

$$\beta K_0(r) = \delta(r)/\rho_0 - c_0(r). \quad (34)$$

Substituting Eq. (34) into (25), we can calculate the influence parameter from the DCF of a uniform system

$$\kappa = \frac{2\pi k_B T}{3} \int_0^\infty dr r^4 c_0(r). \quad (35)$$

Because of the asymptotic behavior of  $c_0(r)$ , Eq. (35) suggests that SGA is not valid if the inter-particle potential behaves as  $1/r^n$ ,  $n < 6$  at large  $r$ .

### Case study I: Interfacial tension

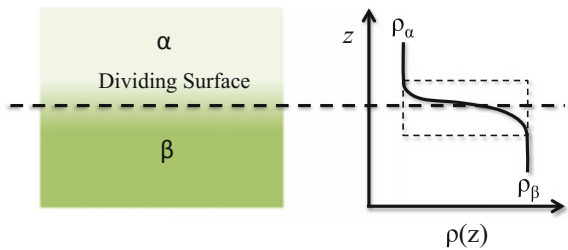
The interfacial tension between two coexisting phases, say  $\alpha$  and  $\beta$ , is defined as the change in free energy in response to variation of the interfacial area. For two bulk phases at equilibrium, the interfacial area refers to that of an imaginary surface dividing the total mass of a particular component in the system into those corresponding to two bulk phases. The imaginary surface is called the Gibbs dividing surface.

Schematically, Fig. 3 presents a Gibbs dividing surface between two bulk phases (e.g., vapor and liquid) and the local density profile across the interface for a one-component system. Here the density profile varies only in the direction perpendicular to the interface, i.e.,  $\rho(\mathbf{r}) = \rho(z)$ , where  $z$  represents the coordinate in perpendicular to the surface. Because the dividing surface possesses no volume, its position, here set at  $z = 0$ , can be determined from the one-body density profile

$$\int_{-\infty}^0 dz [\rho(z) - \rho_\alpha] + \int_0^\infty dz [\rho(z) - \rho_\beta] = 0. \quad (36)$$

Equation (36) is also applicable to multi-component systems. In that case, the location of the dividing surface depends on a specific component selected such that its density profile satisfies Eq. (36).

**Fig. 3** The Gibbs dividing surface between two bulk phases ( $\alpha$  and  $\beta$ ) and a schematic of the density profile in the interfacial region



For an inhomogeneous system containing two coexisting bulk phases, SGA predicts that the grand potential per unit area is given by

$$\Omega/A = \int_{-\infty}^{\infty} dz \left\{ f_0[\rho(z)] + \frac{\kappa}{2} |\rho'(z)|^2 - \mu\rho(z) \right\} \quad (37)$$

where  $\rho'(z) \equiv d\rho(z)/dz$ . For the bulk systems, the grand potential reduces to  $\Omega = -PV$  where pressure  $P$  is the same for the coexisting phases. The surface tension is defined as the grand potential per unit area relative to those corresponding to the bulk phases

$$\gamma \equiv \frac{\Omega - \Omega^\alpha - \Omega^\beta}{A} = \int_{-\infty}^{\infty} dz \left\{ f_0[\rho(z)] + \frac{\kappa}{2} |\rho'(z)|^2 - \mu\rho(z) - P \right\}. \quad (38)$$

To use Eq. (38), we need an equation of state for the bulk phase and the density profile. As discussed, above, the latter can be calculated by minimization the grand potential Eq. (37):

$$\mu_0[\rho(z)] - \kappa\rho''(z) - \mu = 0 \quad (39)$$

where  $\mu_0 \equiv (\partial f_0/\partial \rho)_T$ ,  $\rho''(z) \equiv d^2\rho(z)/dz^2$ . Because of the inhomogeneity in local density,  $\mu_0 \neq \mu$ ;  $\mu_0$  reduces to the bulk chemical potential only when the density is constant. Using the boundary conditions far from the interface, i.e.,  $\rho(-\infty) = \rho_\beta$  and  $\rho(\infty) = \rho_\alpha$ , one may solve the density profile from a numerical integration of Eq. (39).

To obtain an explicit expression for the surface tension, we may rewrite Eq. (39) in terms of the local grand potential density,  $\omega(\rho) = f^0(\rho) - \rho\mu$ ,

$$\kappa\rho''(z) = \frac{\partial\omega(\rho)}{\partial\rho}. \quad (40)$$

Multiplying both sides of Eq. (40) by  $\rho'(z)$  leads to

$$\frac{d}{dz} \left[ \frac{\kappa}{2} \rho'(z)^2 - \omega(\rho) \right] = 0. \quad (41)$$

Using boundary conditions  $\rho'(z) = 0$  and  $\omega = -P$  for the bulk phases, we can integrate Eq. (41) with respect to  $z$  and find

$$\frac{\kappa}{2} \rho'(z)^2 - \omega(\rho) = -P. \quad (42)$$

Substituting Eq. (42) into (38) leads to a simplified expression for the surface tension

$$\gamma = \kappa \int_{-\infty}^{\infty} \rho'(z)^2 dz. \quad (43)$$

According to Eq. (43), the surface tension and the influence parameter have the same sign. Because the direct correlation function is negative at small separation and positive at larger distance, Eq. (35) suggests that the influence parameter may be negative under certain conditions. In that case, the surface tension is negative, favoring spontaneous formation of the interfacial area (e.g., in microemulsions as discussed below).

A nice feature of SGA for predicting surface tension is that Eq. (43) can be evaluated without knowing the density profile explicitly. According to Eq. (42), we have

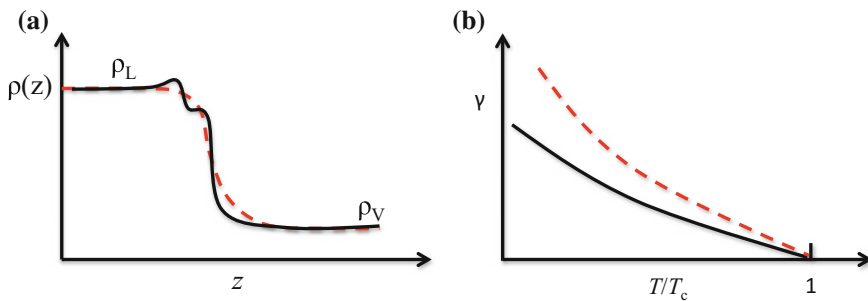
$$dz = -d\rho / \sqrt{2[\omega(\rho) - P]/\kappa}. \quad (44)$$

Here a negative sign is taken with the assumption that the density declines in the  $z$  direction. We now substitute Eq. (44) into (43) and integrate by parts,

$$\gamma = \int_{\rho_\alpha}^{\rho_\beta} \sqrt{2\kappa[\omega(\rho) - P]} d\rho. \quad (45)$$

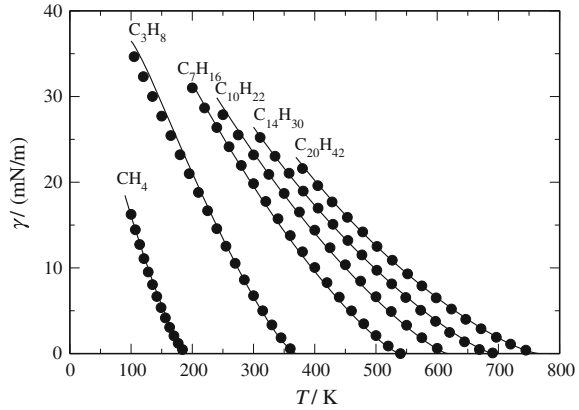
Equation (45) indicates that SGA can be used to predict the surface tension directly from the correlation functions and the equation of state for the uniform systems without computing the density profile.

SGA is able to capture the essential features of interfacial inhomogeneity and surface tension. In comparison to exact results from experiments or molecular simulations, however, its performance is mostly qualitative [16]. As shown in Fig. 4, SGA often gives a too broad one-body density profile at the interfacial region. Besides, it misses density fluctuations near the liquid side of a vapor-liquid interface.



**Fig. 4** A schematic comparison of the density profile at the vapor-liquid interface and the surface tension versus temperature predicted from SGA (*dashed lines*) with those from experiments (*solid lines*). Here  $T_c$  stands for the critical temperature for the vapor-liquid coexistence

**Fig. 5** The vapor-liquid interfacial tension of normal alkanes. Here the symbols are experimental data and the solid lines are SGA predictions. Adopted from Garrido et al. *AIChE Journal* (2016)



Because SGA predicts a too-broad interfacial region, it overestimates the surface tension over the entire range of the coexisting temperature. A quantitative representation of the surface tension can be accomplished by using an accurate equation of state for the bulk phases and an optimized influence parameter. For example, Fig. 5 shows that, even with the assumption that the influence parameter is independent of the local density, the SGA is able to describe vapor-liquid interfacial tensions of several normal alkanes in excellent agreement with experimental data [17].

## 6 Microemulsions

Microemulsions are thermodynamically stable heterogeneous mixtures of oil, water and surfactants forming microscopic structures of various sizes and shapes. In microemulsions, oil and water droplets are dispersed in “water in oil (w/o)”, “oil in water (o/w)”, or bicontinuous structures stabilized by pure or mixed surfactants adsorbed at the oil-water interfaces. Microemulsions have industrial applications such as polymer synthesis, drug delivery, and enhanced oil recovery in the petrochemical industry [18].

To capture the gross features of microemulsions, Teubner and Strey proposed the following phenomenological equation for the deviation of the intrinsic Helmholtz energy from that of a uniform system

$$\Delta F = \int d\mathbf{r} \{a_2 \phi^2 + c_1 |\nabla \phi(\mathbf{r})|^2 + c_2 |\nabla \cdot \nabla \phi(\mathbf{r})|^2\} \quad (46)$$

where  $\phi(\mathbf{r})$  stands for an order parameter to account for the deviation of the local water or oil concentration from the corresponding mean value,  $a_2 > 0$ ,  $c_1 < 0$  and  $c_2 > 0$  are phenomenological parameters with their signs fixed to ensure thermodynamic stability of the inhomogeneous system. It is worth noting that  $c_1 < 0$  implies

a negative surface tension in microemulsions, favoring spontaneous formation of surface area. In Eq. (46), the 4th-order gradient term is introduced to ensure that the system will be stabilized without unlimited growth of the interface area.

The polynomial form given by Eq. (46) is commonly known as the Landau expansion for the free energy of an inhomogeneous system. Intuitively, it may be understood as an empirical gradient expansion relative to an unstructured uniform phase without invoking any specific knowledge on the local Helmholtz energy density and correlation functions. As a result, the Landau expansion is applicable as a simple mathematical procedure to structure formation in any thermodynamic systems. The Taylor expansion is expected to be adequate when the order parameter is small as in the early stage of phase transitions or structure formation in heterogeneous systems.

A conventional experimental approach to monitor the structure of microemulsions is by small angle neutron or X-ray scattering. The scattering experiments provide information on the structures of microemulsions at nanometer or even smaller length scales. The intensity of neutron or X-ray scattering is proportional to the Fourier transform of the density-density correlation function

$$I(q) \sim \tilde{\chi}(q). \quad (47)$$

As shown in Appendix,  $\tilde{\chi}(q)$  is inversely proportional to the vertex function in the Fourier space,  $\tilde{K}(q)$

$$\beta \tilde{K}(q) \tilde{\chi}(q) = 1. \quad (48)$$

As the order parameter is defined linearly proportional to the local density of water or oil molecules, Eq. (46) can be used to derive the density-density correlation function. Taking a second-order functional derivative of the empirical Helmholtz energy with respect to  $\phi(\mathbf{r})$  and making the Fourier transform, we find the vertex function in the Fourier space

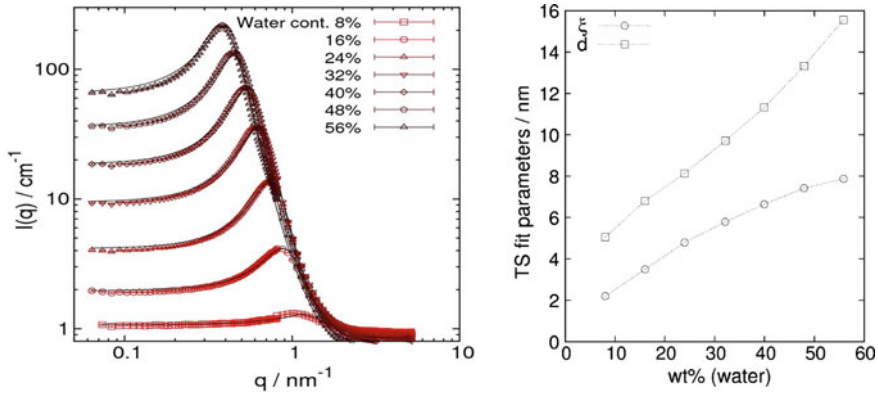
$$\beta \tilde{K}(q) \sim (a_2 + c_1 q^2 + c_2 q^4). \quad (49)$$

Accordingly, the density-density correlation function is

$$\tilde{\chi}(q) \sim \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \quad (50)$$

Equation (50) provides a theoretical basis for interpreting the physical meanings of the scattering spectra obtained from neutron or X-ray experiments. The spectra obtained from small angle scattering experiments is most relevant to the long-range limit of the density-density correlation function of the inhomogeneous system. According to Eq. (50), the asymptotic limit of the density-density correlation function may be written in the real space as

$$\chi(r) \sim \frac{de^{-r/\xi}}{2\pi r} \sin\left(\frac{2\pi r}{d}\right), \quad r/\xi \gg 1 \quad (51)$$



**Fig. 6** Small angle neutron scattering (SNAS) spectra for nonionic microemulsions containing water, Brij 96 surfactant, ethyl oleate and hexanol [19]. The solid lines represent correlations with the Teubner-Strey (TS) model with two fit parameters  $\xi$  and  $d$  changing with the water content (right panel). (Adapted from Kaur et al. Langmuir 2012)

where

$$\xi = \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} + \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2} \quad (52)$$

$$d = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2}. \quad (53)$$

Equation (51) suggests that  $d$  is related to a characteristic domain size of the microemulsion, and  $\xi$  may be understood as the correlation length for the density fluctuations. For water in oil (W/O) or oil in water (O/W) microemulsions, the domain size corresponds to the diameter of spherical droplets for the dispersed phase, and the correlation length reflects density fluctuation within each spherical domain. For bicontinuous microemulsions, the sinusoidal term accounts for the alternating domains of oil and water phases with an average periodicity of  $d$ , and the exponential term is related to the short-range correlation within the water or oil domain.

The Teubner-Strey (TS) model has been routinely used to describe the scattering spectra of a wide variety of microemulsions. The domain size and correlation length obtained from the fit parameters provide insights into the microscopic structure. For example, Fig. 6 shows the small angle neutron scattering (SANS) spectra for nonionic microemulsions containing water, a surfactant (Brij 96), ethyl oleate and hexanol [19]. The system is relevant for a number of pharmaceutical and cosmetic formulations. We see that the scattering intensity curves are near perfectly reproduced by the TS model. From the fit parameters, the domain size and correlation length at different water contents can be determined. Figure 6 shows that the domain size is linearly increasing with the amount of water contained, implying that the microscopic



structure swells proportionally upon the addition of water. This example illustrates how the scattering experiments shed lights for systematic formulation of microemulsions with desired microscopic structures. As the structure is not directly detected, the statistical-mechanical model becomes indispensable for interpretation of the experimental spectra.

## 7 Polymer Blends

Pierre-Gilles de Gennes was often credited as the first to use the square-gradient approximation (SGA) for inhomogeneous polymer blends [20]. The so-called Flory-Huggins-de Gennes (FHdG) model remains a popular choice for describing the thermodynamic properties of inhomogeneous polymeric systems and phase transactions. The FHdG theory may also be relevant to biological systems because recent studies suggest that the physics of polymer phase transitions are applicable to the formation of intracellular membrane apartments [21].

To illustrate the basic concepts behind the FHdG theory, we consider an inhomogeneous blend of two polymers A and B. According to SGA, the intrinsic Helmholtz energy is given by

$$F = \int d\mathbf{r} \left\{ f_0[\rho_A, \rho_B] + \frac{\kappa_{AA}}{2} [\nabla \rho_A(\mathbf{r})]^2 + \kappa_{AB} \nabla \rho_A(\mathbf{r}) \cdot \nabla \rho_B(\mathbf{r}) + \frac{\kappa_{BB}}{2} [\nabla \rho_B(\mathbf{r})]^2 \right\} \quad (54)$$

where  $\rho_A(\mathbf{r})$  and  $\rho_B(\mathbf{r})$  stand for the segment densities,  $\kappa_{ij}$  are influence parameters to account for the effect of local density inhomogeneity, and  $f_0$  represents the Helmholtz energy density of a homogeneous polymer at the local segment densities.

For uniform polymer systems, the Flory-Huggins theory is commonly used to describe the Helmholtz energy of mixing. The reduced Helmholtz energy per polymer segment, relative to those of pure species, is given by

$$\beta v_0 \Delta f_0 = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi_F \phi_A \phi_B, \quad (55)$$

where  $v_0$  represents the volume per lattice site,  $N_i$  denotes the degree of polymerization for polymer  $i = A$  or  $B$ ,  $\phi_i = \rho_i v_0$  stands for the polymer volume fraction, and  $\chi_F$  is the Flory parameter.

As discussed above, the influence parameters can be determined from the vertex functions

$$\kappa_{ij} = \lim_{q \rightarrow 0} [K_{0,ij}(q) - K_{0,ij}(0)]/q^2. \quad (56)$$

In terms of the polymer volume fractions, the vertex function is related to the density fluctuations in the binary polymer mixture

$$K_{ij}^{-1}(\mathbf{r}_1, \mathbf{r}_2) = \beta \langle \delta \hat{\rho}_i(\mathbf{r}_1) \delta \hat{\rho}_j(\mathbf{r}_2) \rangle = \frac{\beta}{v_0^2} \langle \delta \hat{\phi}_i(\mathbf{r}_1) \delta \hat{\phi}_j(\mathbf{r}_2) \rangle \quad (57)$$

where  $\hat{\phi}_i(\mathbf{r}) = \hat{\rho}_i(\mathbf{r})v_0$ , and  $\delta \hat{\phi}_i(\mathbf{r}) \equiv \hat{\phi}_i(\mathbf{r}) - \phi_{i,0}$  stands for the deviation of the instantaneous local volume fraction from the mean value  $\phi_{i,0}$ .

The Flory-Huggins lattice model assumes that the polymer mixture is incompressible. In other words, each lattice site is occupied by one and only one polymer segment of either type A or B such that the local volume fraction is normalized

$$\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r}) = 1. \quad (58)$$

Using the identity

$$\nabla \phi_A(\mathbf{r}) = -\nabla \phi_B(\mathbf{r}), \quad (59)$$

we may simplify Eq. (54) and derive the Helmholtz energy of mixing for the inhomogeneous system

$$\Delta F = \int d\mathbf{r} \left\{ \Delta f_0(\phi) + \frac{\kappa}{2} [\nabla \phi]^2 \right\} \quad (60)$$

where  $\phi = \phi_A$ , and  $\kappa$  is an effective influence parameter given by

$$\kappa \equiv (\kappa_{AA} + \kappa_{BB} - 2\kappa_{AB})/v_0^2. \quad (61)$$

Because of the incompressibility hypothesis, the densities of polymer segments are inter-related and the Helmholtz energy for the binary mixture resembles that for a one-component system (viz. Eq. (24)).

To derive the influence parameter, the FHDG theory assumes further that, in a polymer melt, the local fluctuation of the polymer volume fractions behaviors as that corresponding to non-interacting polymers (viz. Gaussian chains). In other words, the density-density correlation functions are determined by the intra-chain connectivity of polymer segments. Because segments from different polymer chains are uncorrelated, we have  $\chi_{0,AB}(r) = \chi_{0,BA}(r) = 0$ .

As shown in the Appendix, the intra-chain density-density correlation for polymer A can be approximated by

$$\tilde{\chi}_{0,AA}(q) \approx \frac{N_A \phi_{0,A}}{v_0^2} \left( 1 - \frac{q^2 R_A^2}{3} \right) \quad (62)$$

where  $R_A \equiv N_A l_A^2/6$  is the radius of gyration for an ideal polymer chain, and  $l_A$  represents the bond length for polymer A. Substituting Eq. (62) into (56) yields the influence parameter for polymer A

$$\kappa_{AA} = \frac{1}{\beta} \lim_{q \rightarrow 0} [\chi_{0,AA}^{-1}(q) - \chi_{0,AA}^{-1}(0)]/q^2 = \frac{v_0^2 R_A^2}{3\beta N_A \phi_{0,A}} = \frac{v_0^2 l_A^2}{18\beta \phi_{0,A}}. \quad (63)$$

Similarly, the influence parameter for polymer B is

$$\kappa_{BB} = \frac{v_0^2 l_B^2}{18\beta\phi_{0,B}} \quad (64)$$

where  $l_B$  represents the bond length for polymer B. Because there is no correlation between segments from different ideal polymer chains, the cross inference parameters are

$$\kappa_{AB} = \kappa_{BA} = 0. \quad (65)$$

Substituting Eqs. (64)–(65) into (61), we derive the effective influence parameter for the polymer blend

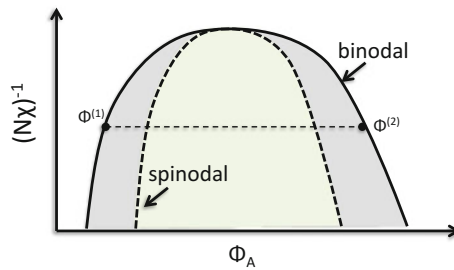
$$\kappa = \frac{1}{18\beta} \left( \frac{l_A^2}{\phi_{0,A}} + \frac{l_B^2}{\phi_{0,B}} \right). \quad (66)$$

### Case study II. Kinetics of polymer phase separation

A binary polymer mixture may exist either as a single uniform phase or as two coexisting phases, depending on its composition and temperature. As shown in Fig. 7, the binodal curve separates regions of the phase diagram into single and two phases. In the two-phase region, spontaneous phase separation occurs when the system exists inside the spinodal line. The demixing process is called spinodal decomposition.

When a polymer blend undergoes spinodal decomposition, its morphology, i.e., the inhomogeneous distribution of polymer segments, is controlled by the dynamics of the phase-separation. The change of the polymer composition can be described by the phenomenological diffusion equation

$$\frac{\partial \phi(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{J}, \quad (67)$$



**Fig. 7** A schematic phase diagram for a binary polymer blend. Here  $\Phi^{(1)}$  and  $\Phi^{(2)}$  represent the volume fraction of polymer A in two coexisting curves. The system exists as one single phase outside the *binodal* curve and two phases otherwise. Inside the *spinodal* curve, the mixture is spontaneously separated into two phases

where  $\phi(\mathbf{r}, t)$  is the volume fraction of polymer A at position  $\mathbf{r}$  and time  $t$ ,  $\mathbf{J}$  is the local flux of polymer A. The polymer flux may be related to the local chemical potential  $\mu_A$  through the generalized Fick's law

$$\mathbf{J} = -\Lambda \nabla \beta \mu_A \quad (68)$$

where  $\Lambda$  represents the Onsager coefficient [9]. In general,  $\Lambda$  is nonlocal, depending on the polymer size and the self-diffusion coefficient.

If polymers A and B are symmetric, i.e.,  $N_A = N_B = N$  and  $l_A = l_B = l$ , the Helmholtz energy functional for the inhomogeneous polymer blend becomes

$$\beta \Delta F = \frac{1}{v_0} \int d\mathbf{r} \left\{ \frac{1}{N} \ln \phi + \frac{1-\phi}{N} \ln (1-\phi) + \chi_F \phi(1-\phi) + \frac{l^2 [\nabla \phi]^2}{36 \phi(1-\phi)} \right\} \quad (69)$$

Accordingly, the local chemical potential for polymer A is

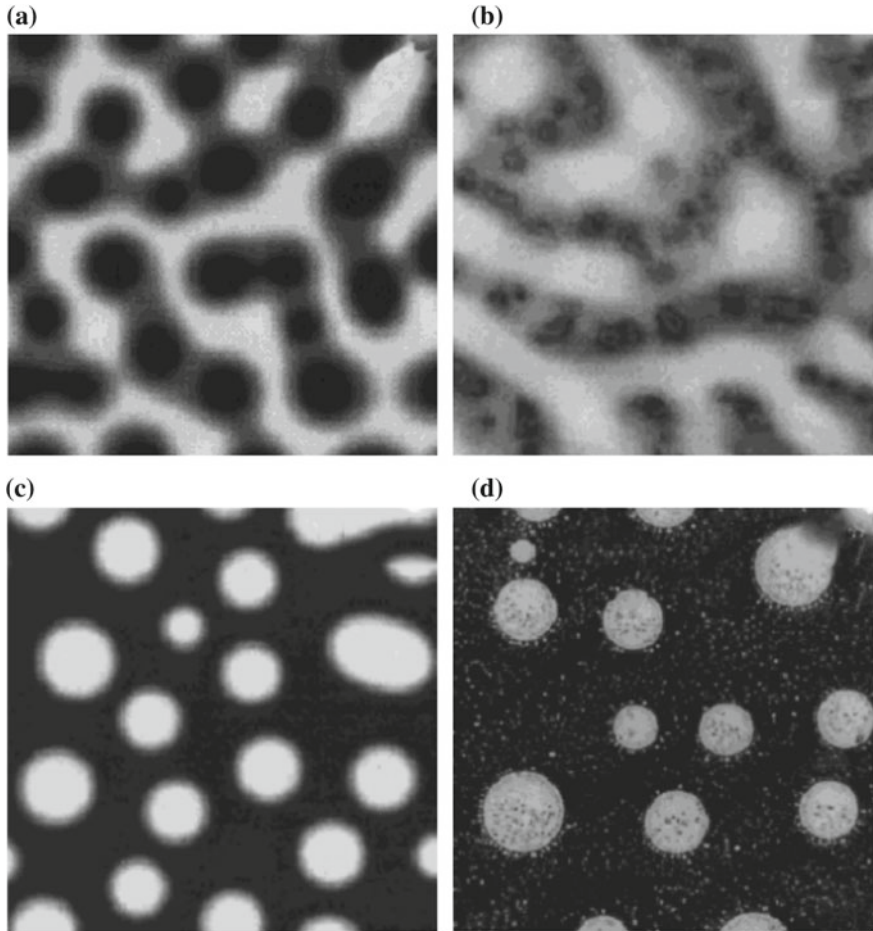
$$\beta \mu_A(\mathbf{r}) = \frac{1}{N} \ln \frac{\phi}{1-\phi} + \chi_F(1-2\phi) - \frac{l^2}{18} \frac{\nabla^2 \phi}{\phi(1-\phi)} + \frac{l^2 (\nabla \phi)^2}{36} \left[ \frac{1}{\phi^2} - \frac{1}{(1-\phi)^2} \right] \quad (70)$$

Substituting Eq. (70) into Eqs. (67) and (68), we can calculate the evolution of the segment density profile during phase transitions. In general, spinodal decomposition in a polymer blend results in a highly interconnected bicontinuous structure at the early stage of phase separation. Spherical structures are possible at relatively late stages. The fully developed morphology is mainly determined by the polymer composition, and less by other parameters such as polymer chain lengths and binary interaction parameters.

Nauman and coworkers applied the FHdG theory to investigate the morphologies of ternary polymer blends after spinodal decomposition [22]. They found that, as shown in Fig. 8, the morphologies of the polymer blends predicted by Eq. (68) closely resemble those obtained from experiments. The theoretical results may help design polymer blends with minimal experimentation.

## 8 Electronic Systems

The square-gradient approximation (SGA) is independent of the physical significance of the density functional or inter-particle potentials, making it universally applicable to both quantum as well as classical systems. For its application to electronic systems, a quantity of central importance is the exchange-correlation functional,  $E_{xc}[\rho(\mathbf{r})]$ , which is introduced in the Kohn-Sham (KS) *ansatz* for calculating the energy and the electronic structure at the ground state [23]. In essence, the KS theory asserts the existence of a non-interacting reference system with an effective external potential  $v_s(\vec{r})$  such that both its ground-state energy and the density profile are the same as those corresponding to the real system.



**Fig. 8** Morphologies of polymer blends from theoretical predictions (**a**, **c**) and from electron microscopy (**c**, **d**). Here (**a**) and (**b**) are for a 40/40/20 blend of poly (methyl methacrylate) (PMMA), polystyrene (PS) and polybutadiene (PB); (**c**) and (**d**) are for a 34/33/33 blend of PS-PB-polyisoprene (PI). The morphologies shown here are fully developed (long time). (Adapted from Brunswick et al. Journal of Applied Polymer Science (1998))

For a non-interacting electronic system in the presence of a one-body potential  $v_s(\vec{r})$ , the wave function of electrons can be solved from the KS equation (viz. the single-particle Schrödinger equation)

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right] \psi_i = \varepsilon_i \psi_i \quad (71)$$

where  $\hbar$  denotes the Dirac constant,  $m$  is the electron mass,  $\varepsilon_i$ ,  $i = 1, 2, \dots, N$ , stands for the  $i$ th lowest energy of the non-interacting system, and  $N$  is the number of electrons. The one-body electron density is related to the wave function

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (72)$$

The exchange-correlation functional is introduced to reproduce the ground-state energy of the real system

$$E[\rho(\mathbf{r})] = T_0[\rho(\mathbf{r})] + \int d\mathbf{r} \rho(\mathbf{r}) V^{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}[\rho(\mathbf{r})] \quad (73)$$

where  $T_0$  stands for the kinetic energy of non-interacting electrons, and  $V^{\text{ext}}(\mathbf{r})$  represents the one-body external potential. In Eq. (73) and thereafter, all physical quantities are given in atomic units.

From the KS wave functions, we can calculate the kinetic energy of the non-interacting system

$$T_0 = -\frac{1}{2} \sum_{i=1}^N \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}). \quad (74)$$

The external energy and the classical electron-electron repulsion energy on the right side of Eq. (73) are directly related to the one-body density profile.

While there is no a priori knowledge on the exchange-correlation energy,  $E_{XC}[\rho(\mathbf{r})]$  is clearly a functional of the one-body density as all other terms in Eq. (73) are. Intuitively, we may divide  $E_{XC}$  in terms of contributions from the difference between the kinetic energy of the real system and that of the non-interacting electrons, the exchange (Pauli exclusion) effects, and multi-body correlations. Because  $\rho(\mathbf{r})$  minimizes the ground-state energy of both the reference and the real systems, the effective one-body potential for the non-interacting reference system, up to a constant of little relevance, can be written as

$$v_s(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{XC}(\mathbf{r}) \quad (75)$$

where

$$v_s(\mathbf{r}) = \frac{\delta E_{XC}}{\delta \rho(\mathbf{r})}. \quad (76)$$

As discussed above (see Eq. (18)), we can derive an exact equation for the grand-state energy of the real system using the non-interacting system as a reference

$$E[\rho(\mathbf{r})] = T_0[\rho(\mathbf{r})] + \int d\mathbf{r} \rho(\mathbf{r}) V^{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')g(\mathbf{r}, \mathbf{r}', \lambda)}{|\mathbf{r} - \mathbf{r}'|} \quad (77)$$

where  $g(\mathbf{r}, \mathbf{r}', \lambda)$  represents the pair-correlation function between electrons with the Coulomb interaction between the electrons reduced by a factor of  $\lambda$ . In the electronic DFT literature, Eq. (77) is commonly known as the adiabatic connection.

A comparison of Eqs. (73) and (77) indicates that the exchange-correlation energy corresponds to the indirect energy for “charging up” the non-interacting electrons:

$$E_{XC}[\rho(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')\bar{h}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (78)$$

where

$$\bar{h}(\mathbf{r}, \mathbf{r}') \equiv \int_0^1 d\lambda [g(\mathbf{r}, \mathbf{r}', \lambda) - 1] \quad (79)$$

stands for the average hole-correlation function (viz., the average total correlation function). Because the electrostatic energy diverges at zero separation, the hole correlation function is precisely known,  $h(\mathbf{r}, \mathbf{r}, \lambda) = -1$ . In addition, it must satisfy the normalization conditions because the hole correlation function is defined relative to one electron at position  $\mathbf{r}$ ,

$$\int d\mathbf{r}' h(\mathbf{r}, \mathbf{r}', \lambda) = -1. \quad (80)$$

With an analytical expression for  $E_{XC}$  or  $\bar{h}(\mathbf{r}, \mathbf{r}')$ , we can determine the electron density profile and the ground-state energy from Eqs. (72) and (73), respectively. From these quantities, other ground-state properties of the electronic system can be readily calculated.

As for classical systems discussed above, the KS-DFT does not provide any systematic procedure to determine the exchange-correlation energy of the two-body correlation functions. Since the publication of the KS equation in 1965, tremendous efforts have been devoted to the development of accurate exchange-correlation functionals for inhomogeneous electrons and such efforts are still well ongoing [8]. Existing applications of the KS equation are mostly based on various forms of the generalized gradient approximations (GGA). As in SGA, the GGA functional includes an exchange-correlation energy corresponding to that of a uniform system at the local density and a gradient correction to account for the local density inhomogeneity. For a uniform electron gas, the local exchange-correlation energy as a function of the density is known from quantum Monte Carlo simulations [24]. However, the development of gradient corrections for the exchange and correlation energy is mathematically very complex. Among numerous versions of GGA, PBE [25] and B3LYP [26, 27] are two main functionals broadly used in the KS-DFT calculations for molecular and materials systems, respectively.

We may illustrate the basic procedure to use SGA for electronic systems by considering the kinetic energy of non-interacting electrons at 0 K. According to the Thomas-Fermi theory, the kinetic energy as a functional of the local density is given by

$$T_{TF}[\rho(\mathbf{r})] = \frac{3(3\pi^2)^{2/3}}{10} \int d\mathbf{r} \rho(\mathbf{r})^{5/3}. \quad (81)$$

The gradient correction to the kinetic energy can be derived again from Eq. (24) using the density-density correlation function of the corresponding uniform system as the input. For non-interacting electrons in the bulk, the density-density correlation function in the Fourier space is known as the Lindhard function [28]

$$\chi_0(q) = -\frac{k_F}{2\pi^2} \left\{ 1 - \frac{s}{4} \left( 1 - \frac{4}{s^2} \right) \ln \left( \left| \frac{s+2}{s-2} \right| \right) \right\} \quad (82)$$

where  $k_F = (6\pi^2 \rho_0/g)^{1/3}$  is the Fermi momentum,  $g = 2$  is the spin degeneracy for an unpolarized electronic system, and  $s \equiv q/k_F$ . At small  $q$ , we have

$$K_0(q) = 1/\chi_0(q) = \frac{2\pi^2}{k_F} \left( \frac{1}{2} + \frac{s^2}{24} + \dots \right). \quad (83)$$

Therefore, the influence parameter for the non-interacting electrons is

$$\kappa = \frac{1}{3} \lim_{q \rightarrow 0} [K_0(q) - K_0(0)]/q^2 = \frac{\pi^2}{12k_F^3} = \frac{g}{72\rho_0}. \quad (84)$$

Together with the local kinetic energy for ideal Fermions, we have the kinetic energy functional

$$T_{TFW}[\rho(\mathbf{r})] = \int d\mathbf{r} \left\{ \frac{3(3\pi^2)^{2/3}}{10} \rho(\mathbf{r})^{5/3} + \frac{|\nabla \rho(\mathbf{r})|^2}{72\rho(\mathbf{r})} \right\} \quad (85)$$

where we have replaced  $\rho_0$  with local density  $\rho(\mathbf{r})$ . Equation (85) corresponds to Weiszacker's correction to the Thomas-Fermi equation for inhomogeneous electrons [29].

A similar but mathematically much more complicated procedure may be applied to derive the gradient correction for the exchange and correlation energies [30]. The mathematical complexity mainly arises from evaluation of the density-density correlation function for real electronic systems. Nevertheless, it is clear that the functional expression from the gradient expansion can be written in terms of a local density contribution and a correction for the density gradient. For example, the PBE exchange energy is given by [25]

$$E_X[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_X F_X(s) \quad (86)$$

where  $\varepsilon_X$  is the local exchange energy per electron for the uniform system



$$\varepsilon_X = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho(\mathbf{r})^{1/3} \quad (87)$$

and

$$s = |\nabla \rho(\mathbf{r})|^2 / 2k_F \rho(\mathbf{r}) \quad (88)$$

is a dimensionless density gradient arising from the gradient expansion.  $F_X(s)$  is a semi-empirical function that was formulated to satisfy various asymptotic results for uniform electron gas

$$F_X(s) = 1.804 - \frac{0.804}{1 + 0.2730s^2}. \quad (89)$$

In derivation of Eq. (86), the local term accounts for the exchange energy with the hole correlation function calculated from that of the non-interacting reference system ( $\lambda = 0$ ). The gradient correction is no more quadratic in the density gradient because it represents a resummation of high-order terms in the gradient expansion of the exchange-correlation energy.

## 9 Summary

This chapter introduces the gradient expansion method, specifically the square-gradient approximation (SGA), as a general scheme to formulate the intrinsic Helmholtz energy of inhomogeneous systems including electrons at 0 K and illustrate its applications for predicting surface tensions, microemulsion structures, and the kinetics of polymer phase transitions. Similar procedures, broadly known as the Landau expansion method, are used to describe a wide range of phase transitions including weak segregation of block copolymers, wetting and drying transitions, and phase diagrams of liquid crystals. Whereas the theoretical procedure has been well established in each individual subfield of physical sciences, little explored is the inter-connection among similarly formulated theoretical methods from different perspectives, not only in terms of mathematical concepts but also the underlying physics principles. Such a connection may be best illustrated in the context of statistical mechanics. In addition to apparent pedagogical values, this work may help to forge a common ground to comprehend fragmented developments in different subfields of statistical mechanics and promote cross-field collaborations.

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## Appendices

### Density-Gradient Expansion

Consider an inhomogeneous system with one-particle number density  $\rho(\mathbf{r})$ . The intrinsic Helmholtz energy can be formally expressed relative to that of a uniform system with density  $\rho_0$  by a functional Taylor expansion with respect to the local density deviation  $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$ :

$$F[\rho(\mathbf{r})] = F_0 + \int \left. \frac{\delta F}{\delta \rho(\mathbf{r})} \right|_0 \Delta\rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \left. \frac{\delta^2 F}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right|_0 \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \quad (90)$$

where  $F_0$  is the intrinsic Helmholtz energy of the uniform system at the same temperature, and subscript 0 denotes the uniform reference system. According to Eq. (90), the intrinsic free energy  $F[\rho(\mathbf{r})]$  is fully specified by a set of functions

$$K(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \delta^n F / \prod_{i=1}^n \delta \rho(\mathbf{r}_i) \quad (91)$$

where  $n = 1, 2, \dots$ .

The one-body density profile satisfies the variational condition, i.e., it minimizes the grand potential  $\Omega$

$$\frac{\delta \Omega}{\delta \rho(\mathbf{r})} = 0 \quad (92)$$

The grand potential relates to the intrinsic Helmholtz energy by the Legendre transformation:

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) u(\mathbf{r}) d\mathbf{r} \quad (93)$$

where  $u(\mathbf{r}) \equiv \varphi^{\text{ext}}(\mathbf{r}) - \mu$  corresponds to a one-body potential define by the chemical potential and the external potential  $\varphi^{\text{ext}}(\mathbf{r})$  of the particles,  $\mu$  is the chemical potential. Combing Eqs. (92) and (93) leads to

$$\frac{\delta F}{\delta \rho(\mathbf{r})} = -u(\mathbf{r}) \quad (94)$$

For a uniform system,  $\varphi^{\text{ext}}(\mathbf{r}) = 0$ , Eq. (94) reduces to

$$\left. \frac{\delta F}{\delta \rho(\mathbf{r})} \right|_0 = \mu. \quad (95)$$

The second-order term in the density functional expansion of the intrinsic Helmholtz energy plays a particularly important role in theoretical developments. The vertex function is defined as

$$K(\mathbf{r}, \mathbf{r}') \equiv \frac{\delta^2 F}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = -\frac{\delta u(\mathbf{r})}{\delta \rho(\mathbf{r}')} \quad (96)$$

It can be shown that the density-density correlation function is related to the functional derivative of the one-body density with respect to the reduced one-body potential

$$\chi(\mathbf{r}, \mathbf{r}') \equiv \langle [\hat{\rho}(\mathbf{r}) - \rho(\mathbf{r})][\hat{\rho}(\mathbf{r}') - \rho(\mathbf{r}')] \rangle = -\frac{\delta \rho(\mathbf{r})}{\delta \beta u(\mathbf{r}')} \quad (97)$$

where the instantaneous density of the system

$$\hat{\rho}(\mathbf{r}) \equiv \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (98)$$

is expressed as a summation of Dirac delta functions, and  $\langle \cdots \rangle$  represents the ensemble average.

From Eqs. (96) and (97), we see that the density-density correlation function corresponds to the inverse functional derivative of the 2nd order coefficient in the functional Taylor expansion of the intrinsic Helmholtz energy

$$\int \beta K(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}', \mathbf{r}'') d\mathbf{r}'' = \delta(\mathbf{r} - \mathbf{r}'). \quad (99)$$

For a uniform system, both  $K_0(\mathbf{r}, \mathbf{r}')$  and  $\chi_0(\mathbf{r}, \mathbf{r}')$  depend only on the distance  $|\mathbf{r} - \mathbf{r}'|$ . In that case, we may apply the translational and rotational symmetry for the correlation functions:

$$\begin{cases} K(\mathbf{r}, \mathbf{r}') = K(0, \mathbf{r} - \mathbf{r}') \equiv K_0(|\mathbf{r} - \mathbf{r}'|) \\ \chi(\mathbf{r}, \mathbf{r}') = \chi(0, \mathbf{r} - \mathbf{r}') \equiv \chi_0(|\mathbf{r} - \mathbf{r}'|) \end{cases} \quad (100)$$

Substituting Eq. (100) into (99) gives

$$\int \beta K_0(|\mathbf{r} - \mathbf{r}''|) \chi_0(|\mathbf{r}' - \mathbf{r}''|) d\mathbf{r}'' = \delta(\mathbf{r} - \mathbf{r}') \quad (101)$$

A 3D Fourier transform of Eq. (101), reveals a simple relationship between  $\tilde{K}_0(q)$  and  $\tilde{\chi}_0(q)$

$$\beta \tilde{K}_0(q) \tilde{\chi}_0(q) = 1 \quad (102)$$

where

$$\tilde{K}_0(q) = \tilde{K}_0(\mathbf{q}) \equiv \int K_0(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \frac{4\pi}{q} \int_0^\infty r \sin(qr) K_0(r) dr \quad (103)$$

$$\tilde{\chi}_0(q) = \tilde{\chi}_0(\mathbf{q}) \equiv \int \chi_0(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \frac{4\pi}{q} \int_0^\infty r \sin(qr) \chi_0(r) dr \quad (104)$$

Applying Eq. (97) to a uniform system of average density  $\rho_0$ , we have

$$\begin{aligned} \chi_0(|\mathbf{r} - \mathbf{r}'|) &= \chi(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle - \rho_0^2 \\ &= \langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle_{\mathbf{r} \neq \mathbf{r}'} + \langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle_{\mathbf{r}=\mathbf{r}'} - \rho_0^2 \\ &= \rho^{(2)}(\mathbf{r}, \mathbf{r}') + \rho_0 \langle \hat{\rho}(\mathbf{r}') \rangle_{\mathbf{r}=\mathbf{r}'} - \rho_0^2 \\ &= \rho_0^2 h_0(|\mathbf{r} - \mathbf{r}'|) + \rho_0 \delta(\mathbf{r} - \mathbf{r}') \end{aligned} \quad (105)$$

where  $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$  is the two-body density function, and

$$h_0(|\mathbf{r} - \mathbf{r}'|) \equiv \left. \frac{\rho^{(2)}(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r})\rho(\mathbf{r}')} \right|_0 - 1 \quad (106)$$

denotes the total correlation function. In the Fourier space, Eq. (105) becomes

$$\tilde{\chi}_0(q) = \rho_0^2 \tilde{h}_0(q) + \rho_0 \quad (107)$$

With the help of Eqs. (95), (102) and (107), we can evaluate the intrinsic free energy functional  $F[\rho(\mathbf{r})]$  up to the quadratic term. Apparently, the density expansion is applicable not only to the intrinsic Helmholtz energy but also to other quantities with a similar mathematic form, for example, the excess free energy and the exchange-correlation energy.

## The Ornstein-Zernike (OZ) Equation

Recalling that the vertex function is inversely related to the density–density correlation function  $\chi(\mathbf{r}_1, \mathbf{r}_2)$ , which is also related to the total correlation function  $h(\mathbf{r}_1, \mathbf{r}_2)$

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2) + \rho(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (108)$$

For classical systems, the Helmholtz energy of a non-interacting system is exactly known.

$$F^{ID} = k_B T \int \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r}) \Lambda^3] - 1 \} d\mathbf{r}. \quad (109)$$

Subsequently, we may express the vertex function in terms of the direct correlation function (DCF)

$$\beta K(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 \beta F}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\rho(\mathbf{r})} - c(\mathbf{r}, \mathbf{r}') \quad (110)$$

where  $c(\mathbf{r}, \mathbf{r}')$  corresponds to the second-order functional derivatives of the excess Helmholtz energy  $F^{\text{ex}} \equiv F - F^{\text{ID}}$

$$c(\mathbf{r}, \mathbf{r}') \equiv -\frac{\delta^2 \beta F^{\text{ex}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (111)$$

Because

$$\int d\mathbf{r}_2 \chi(\mathbf{r}_1, \mathbf{r}_2) \beta K(\mathbf{r}_3, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_3), \quad (112)$$

substituting Eqs. (110) and (108) into (111) leads to the Ornstein-Zernike (OZ) equation

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int \rho(\mathbf{r}_3) h(\mathbf{r}_1, \mathbf{r}_3) c(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \quad (113)$$

For uniform systems, the OZ equation can be simplified as

$$h(r) = c(r) + \rho_0 \int h(|\mathbf{r}_1 - \mathbf{r}_3|) c(|\mathbf{r}_2 - \mathbf{r}_3|) d\mathbf{r}_3 \quad (114)$$

or in the Fourier space

$$[1 + \rho_0 h_0(q)][1 - \rho_0 c_0(q)] = 1. \quad (115)$$

## Corrections to the Local Density Approximation (LDA)

Local density approximation (LDA) assumes that the free energy density of an inhomogeneous system is the same as that of a uniform system at the local density. According to LDA, the intrinsic Helmholtz energy functional is given by

$$F^{\text{LDA}}[\rho(\mathbf{r})] = \int f_0[\rho(\mathbf{r})] d\mathbf{r} \quad (116)$$

where  $f_0 = F_0/V$  corresponds to the intrinsic free energy density (per volume) of a uniform system. LDA ignores the spatial correlation effect.

Because LDA assumes  $f_0$  as a **function** of  $\rho(\mathbf{r})$ , we may express it as a regular Taylor expansion with respect to that of a uniform system

$$f_0[\rho(\mathbf{r})] = f_0(\rho_0) + \frac{\partial f_0}{\partial \rho_0} \Delta \rho(\mathbf{r}) + \frac{1}{2} \frac{\partial^2 f_0}{\partial \rho_0^2} [\Delta \rho(\mathbf{r})]^2 + \dots \quad (117)$$

Substituting Eq. (117) into (116), we have:

$$F^{\text{LDA}}[\rho(\mathbf{r})] = F_0 + \int \frac{\partial f_0}{\partial \rho_0} \Delta \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\partial^2 f_0}{\partial \rho_0^2} [\Delta \rho(\mathbf{r})]^2 d\mathbf{r} + \dots \quad (118)$$

Comparing Eq. (118) with the functional expansion form, i.e., Eq. (90), we have:

$$\begin{aligned} F[\rho(\mathbf{r})] &= F^{\text{LDA}}[\rho(\mathbf{r})] \\ &+ \frac{1}{2} \int \int [K_0(|\mathbf{r} - \mathbf{r}'|) - \left( \frac{\partial \mu}{\partial \rho_0} \right)_T \delta(\mathbf{r} - \mathbf{r}')] \Delta \rho(\mathbf{r}) \Delta \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \end{aligned} \quad (119)$$

In writing the above equation, we have used the thermodynamic relation

$$\mu = (\partial f_0 / \partial \rho_0)_T \quad (120)$$

and the mathematic identity

$$\int \frac{\partial^2 f_0}{\partial \rho_0^2} [\Delta \rho(\mathbf{r})]^2 d\mathbf{r} = \int \left( \frac{\partial \mu}{\partial \rho_0} \right)_T \Delta \rho(\mathbf{r}) \Delta \rho(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (121)$$

In Eq. (119), the terms after  $F^{\text{LDA}}$  can be regarded as spatial correlation effects neglected by LDA.

Now let  $F_2$  represent the second term on right side of Eq. (119). Using the Fourier transform, we can express  $F_2$  as

$$F_2 = \frac{1}{2(2\pi)^3} \int [\tilde{K}_0(q) - \left( \frac{\partial \mu}{\partial \rho_0} \right)_T] [\Delta \tilde{\rho}(\mathbf{q})]^2 d\mathbf{q} \quad (122)$$

According to Eqs. (102) and (107), we have

$$\beta \tilde{K}_0(q) = \frac{1}{\rho_0^2 \tilde{h}_0(q) + \rho_0} \quad (123)$$

In addition, the compressibility equation gives

$$\left( \frac{\partial \rho_0}{\partial \beta \mu} \right)_T = \rho_0 + \rho_0^2 \int h_0(r) d\mathbf{r} = \rho_0 + \rho_0^2 \tilde{h}_0(q=0) = \frac{1}{\beta \tilde{K}_0(0)}. \quad (124)$$

Accordingly, Eq. (122) can be rewritten in a more compact form:

$$F_2 = \frac{1}{16\pi^3} \int [\tilde{K}_0(q) - \tilde{K}_0(0)] [\Delta \tilde{\rho}(\mathbf{q})]^2 d\mathbf{q} \quad (125)$$

With Eq. (125), we formulate the additional correlation term beyond LDA. Similar to the functional expansion, such procedure can be extended to other quantities.

To connect Eq. (125) with the square-gradient expansion, we recall that

$$\tilde{K}_0(q) = \tilde{K}_0(\mathbf{q}) \equiv \int K_0(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \int \frac{\sin(qr)}{qr} K_0(r) d\mathbf{r} \quad (126)$$

Using the Taylor series

$$\frac{\sin(qr)}{qr} = 1 - \frac{(qr)^2}{3!} + \dots \quad (127)$$

we have

$$\begin{aligned} \tilde{K}_0(q) &= \int \left[ 1 - \frac{(qr)^2}{3!} \right] K_0(r) d\mathbf{r} \\ &= \tilde{K}_0(0) - \frac{q^2}{3!} \int r^2 K_0(r) d\mathbf{r} \end{aligned} \quad (128)$$

Substituting Eq. (128) into (127) gives

$$F_2 = -\frac{\kappa}{16\pi^3} \int q^2 [\Delta \tilde{\rho}(\mathbf{q})]^2 d\mathbf{q} \quad (129)$$

where  $\kappa$  is the influence parameter defined as

$$\kappa \equiv -\frac{1}{3!} \int r^2 K_0(r) d\mathbf{r} = \frac{1}{3} \lim_{q \rightarrow 0} [K_0(q) - K_0(0)]/q^2 \quad (130)$$

Note

$$\int \nabla \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = -i\mathbf{q} \Delta \tilde{\rho}(\mathbf{q}) \quad (131)$$

and

$$\frac{1}{(2\pi)^3} \int q^2 [\Delta \tilde{\rho}(\mathbf{q})]^2 d\mathbf{q} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \nabla \rho(\mathbf{r}_1) \nabla \rho(\mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (132)$$

we arrive the square-gradient correction to the LDA

$$F_2 = \frac{\kappa}{2} \int d\mathbf{r} [\nabla \rho(\mathbf{r})]^2. \quad (133)$$

In some applications, we use the static structure factor  $\tilde{S}_0(q) = \tilde{\chi}_0(q)/\rho_0$  instead of the vertex function. In that case,

$$\tilde{K}_0(q) = [\beta \rho_0 \tilde{S}_0(q)]^{-1}. \quad (134)$$

thus the influence parameter is given by

$$\kappa = -\frac{1}{3!} \int r^2 K_0(r) \mathbf{dr} = \frac{1}{3\beta\rho_0} \lim_{q \rightarrow 0} [\tilde{S}_0^{-1}(q) - \tilde{S}_0^{-1}(0)]/q^2. \quad (135)$$

## Intra-Chain Correlation Function of a Gaussian Chain

In a polymer blend A and B, the intra-chain correlation for polymer A as an ideal chain is given by

$$\chi_{0,AA}(|\mathbf{r} - \mathbf{r}'|) = \frac{1}{v_0^2} \langle \delta \hat{\phi}_A(\mathbf{r}) \delta \hat{\phi}_A(\mathbf{r}') \rangle = \frac{\phi_{0,A}}{v_0^2} P_A(|\mathbf{r} - \mathbf{r}'|) \quad (136)$$

where  $P_A$  represents the probability to find a segment at position  $\mathbf{r}$  given that another segment from the same polymer chain is located at  $\mathbf{r}'$ . A similar expression can be written for polymer B.

For a non-interacting polymer,  $P_A$  corresponds to a Gaussian average of all segment pairs separated by distance  $r$

$$P_A(r) = \frac{1}{N_A V} \sum_{i \neq j}^{N_A} \int d\mathbf{r}_i \int d\mathbf{r}_j p_{ij}(\mathbf{r}) \delta[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \quad (137)$$

where  $\mathbf{r}_i$  and  $\mathbf{r}_j$  represent the position of segment  $i$  and  $j$  from the same polymer chain, respectively. In Eq. (137), the Gaussian distribution function is given by the random walk model [20]

$$p_{ij}(\mathbf{r}) = \left( \frac{3}{2\pi|i-j|l_A^2} \right)^{3/2} \exp \left( -\frac{3r^2}{2|i-j|l_A^2} \right) \quad (138)$$

where  $l_A$  stands for step length or the polymer bond length. Applying the 3-D Fourier transform to both side of Eq. (136) yields

$$\tilde{P}_A(q) = \frac{1}{N_A} \sum_{i \neq j}^{N_A} \exp \left( -\frac{q^2|i-j|l_A^2}{6} \right) \quad (139)$$

For a long polymer chain,  $N_A \gg 1$ , the double summations in Eq. (139) can be replaced by integrations

$$\begin{aligned} \tilde{P}_A(q) &= \frac{1}{N_A} \int_0^{N_A} dx \int_0^{N_A} dy \exp \left( -\frac{q^2|x-y|l_A^2}{6} \right) \\ &= N_A D(qR_A) \end{aligned} \quad (140)$$



where  $R_A \equiv N_A l_A^2/6$  is the radius of gyration for an ideal polymer chain (Gaussian chain), and

$$D(x) = \frac{2}{x^4} \left( e^{-x^2} + x^2 - 1 \right) \quad (141)$$

is known as the Debye function. For small  $x$ ,  $D(x) \approx 1 - x^2/3$ , we can derive from Eq. (136) the intra-chain correlation in the Fourier space

$$\tilde{\chi}_{0,AA}(q) = \frac{\phi_{0,A}}{v_0^2} \tilde{P}_A(q) \approx \frac{N_A \phi_{0,A}}{v_0^2} \left( 1 - \frac{q^2 R_A^2}{3} \right). \quad (142)$$

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