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# Correlation correction algorithm for binary systems

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We develop a simple iterative algorithm for successive corrections of the correlation function and the free energy of a binary system. The main characteristics of the formalism are the use of an exact statistical-thermodynamic relations and the absence of the small parameters. The only approximation involved is the form of the configurational free energy which serves as a starting point for the iterative procedure. Two iterations within this algorithm for a dispersion-free and a microscopic model of fluctuations are presented starting with a one-site mean-field approximation. We obtain closed analytical expressions for the correlation function and thermodynamic potentials in each iteration. The algorithm can be widely applied, as in the calculation of phase diagrams, and segregation profiles at surfaces and thin films, and in **k**-space kinetic theories of atomic ordering and decomposition in alloys.

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## I. INTRODUCTION

The microscopic understanding of the atomic interactions in multicomponent systems and how they influence the properties of the system is a cornerstone in condensed matter physics and materials sciences. One ultimate goal is the prediction of the phase behavior of a given multicomponent system from the known interaction potentials. In order to tackle this difficult task, binary alloys have served as model systems for theoretical as well as experimental studies, since they are simple enough to be handled with current theoretical tools and include, on the other hand, essential features that emerge in such complex systems and thus need to be understood. In turn, much effort has been devoted in the last decades to the development of theories that are able to predict structural and thermodynamic properties of alloy systems (see the reviews Refs. 1–5).

Monte Carlo[6–8] (MC) and cluster variation methods[2,3,9–12] (CVM) are standard methods nowadays for statistical-thermodynamic simulations. Using the atomic interaction potentials (deduced from first principles[4,13–18] as well as from diffuse x-ray and neutron scattering data[5,11,19–21]) as input parameters, these methods allowed successful study of a wide range of metallic and semiconducting alloys. A common challenge for these theories is the long-ranging character of the interactions in alloys[8,22–24] which unavoidably originates from the atomic size mismatch and leads to strain fields exhibiting power-law decay,[1,2,5,25] and in addition from the presence of flat portions on the Fermi surface ("nesting effects").[2,5,26,27]

A further challenge in striving for the aforementioned goals is the proper introduction of the spatial correlations between the alloy constituents into the theory at hand. These local correlations are a direct consequence of the interatomic interactions and contribute to the free energy of the system. The key quantity that determines the accuracy of the statistical-thermodynamic approximation is the correlation function [which is also known as the set of short-range order parameters deduced from diffuse scattering data]. If this function is known, the configurational energy can be calculated[3] and the free energy is determined by the temperature dependence of the energy.[3,6] The **k**-space Krivoglaz-Clapp-Moss[19,28,29] (KCM) formula for the correlation function, which has no limitation for the radius of atomic interaction, has been used extensively over the past 40 years. More advanced **k**-space correlation functions are obtained in the spherical model[20–36] (SM), Tahir-Keli,[37,38] high-temperature,[3,39–43] Tokar-Masanskii-Grishchenko[36,44] and ring[25,45,46] approximations. The accuracy of these approximations in comparison with the results of MC simulations for model systems and real alloys has been discussed in Ref. 47. The common feature in all these analytical approximations that ultimately limits their applicability is the use of a small parameter, such as the inverse temperature or the inverse correlation length.

The aim of the present paper is to develop a correlation correction algorithm (CCA) that allows us to find successive corrections for both the correlation function and the configurational free energy of the alloy. This algorithm does not employ a small expansion parameter and is not challenged by the long-ranging character of the interatomic interactions. As we will show in what follows, the only approximation involved is the form of the configurational free energy, which is used as the starting point for the iteration algorithm. The basic principle of the CCA has been presented in a recent communication and successfully applied for the calculation of the chemical potential.[48] In this paper we present the details of this algorithm and apply it (i) to a dispersion-free model for the fluctuations and (ii) to a microscopic **k**-space theory of fluctuations.

This paper is organized as follows. In Sec. II, we introduce concentration fluctuations. The configurational Hamiltonian and the internal energy of the alloy are presented, assuming the atomic interactions to be pairwise. The calculation of the correlation function and the integration with respect to inverse temperature for the calculation of the free energy are described and the general scheme of the CCA is presented. In Sec. III, we apply two iterations of the CCA to a simple model of concentration fluctuations with no spatial dispersion. In Sec. IV, we apply the CCA to the microscopic theory of concentration fluctuations taking into account their spatial dispersion. Using some examples we demonstrate in Sec. V the convergence of the CCA and its applicability to ordered as well as disordered systems, before we discuss future applications and also limitations of this algorithm in Sec. VI.

## II. CORRELATION CORRECTION ALGORITHM

In the following the correlation correction algorithm, which has recently been introduced in Ref. 48 is presented in full detail within the lattice-gas model of binary alloys.[49]

### A. Concentration fluctuations in disordered alloys

Consider a macroscopically homogeneous disordered binary alloy ($A_cB_{1-c}$) on a simple Bravais lattice with $N$ sites. The distribution of the $A$ and $B$ atoms over the lattice sites is commonly described by a set of variables $c_{\mathbf{R}}=1$ (0), if an $A$ ($B$) atom occupies the lattice site with coordinate $\mathbf{R}$. For our purpose it is more convenient to introduce instead a set of continuous variables $\{0 \leqslant P_{\mathbf{R}} \leqslant 1\}$, which have been introduced by de Fontaine[2,50] as single-site averages of the $c_{\mathbf{R}}$ over the ensemble of supercells.[51]

$P_{\mathbf{R}}$ can be represented as

$$P_{\mathbf{R}} = c + \delta P_{\mathbf{R}}, \tag{1}$$

with

$$c = \frac{1}{N}\sum_{\mathbf{R}} P_{\mathbf{R}} \tag{2}$$

as the average concentration of $A$ atoms in the alloy and $\delta P_{\mathbf{R}}$ as the concentration fluctuation at site $\mathbf{R}$. (The sum over $\mathbf{R}$ is carried over all sites of the crystal lattice.)

The normalization requirements then imply

$$\frac{1}{N}\sum_{\mathbf{R}} P_{\mathbf{R}} = \frac{1}{N}\sum_{\mathbf{R}} P_{\mathbf{R}}^2 = c; \tag{3}$$

in turn,

$$\sum_{\mathbf{R}} \delta P_{\mathbf{R}} = 0 \tag{4}$$

and

$$\sum_{\mathbf{R}} \delta P_{\mathbf{R}}^2 = Nc(1-c). \tag{5}$$

The spatial distribution of the fluctuations $\{\delta P_{\mathbf{R}}\}$ can conveniently be described by a linear superposition of plane waves,[2,5,52]

$$P_{\mathbf{R}} = c + \sum_{\mathbf{k}} \delta P_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}}. \tag{6}$$

The summation is carried out over all the $\mathbf{k}$ vectors in the first Brillouin zone (applying periodic boundary conditions) except the vector $\mathbf{k}=\mathbf{0}$. The amplitudes $\delta P_{\mathbf{k}}$ are given by

$$\delta P_{\mathbf{k}} = N^{-1}\sum_{\mathbf{R}} \delta P_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}}. \tag{7}$$

Using Eq. (6), Eqs. (4) and (5) can be rewritten as

$$\delta P_{\mathbf{k}=\mathbf{0}} = 0, \tag{8}$$

$$\sum_{\mathbf{k}} \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}} = c(1-c). \tag{9}$$

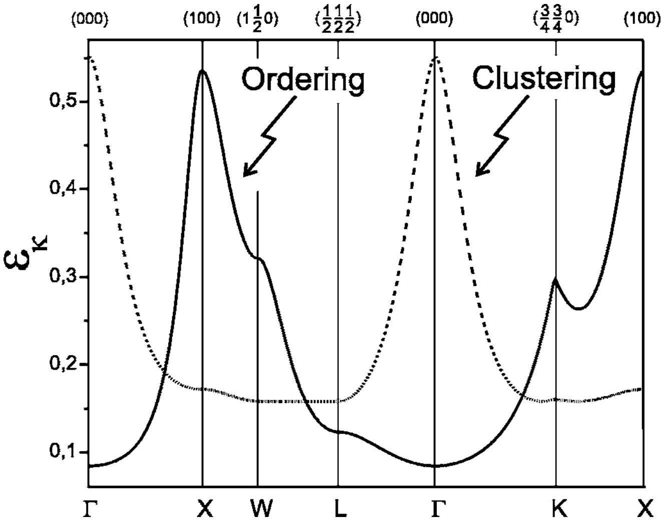

FIG. 1. The two generic dispersion relations $\varepsilon_{\mathbf{k}}$ in binary alloys, for the cases of ordering (full line) and clustering (dashed line). $\varepsilon_{\mathbf{k}}$ has been calculated for a model system $AB_3$ with nearest- and next-nearest-neighbor interactions $V_1$ and $V_2=-0.5V_1$ (ordering, $V_1>0$; clustering, $V_1<0$).

The presence of interactions between the alloy constituents manifests itself by characteristic spatial correlations between concentration fluctuations.[3,5,43] Key quantities in alloy theory are the socalled two-point correlation function

$$\varepsilon_{\mathbf{R}_1-\mathbf{R}_2} = \langle \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2} \rangle \tag{10}$$

and its Fourier transform

$$\varepsilon_{\mathbf{k}} = N\langle \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}} \rangle, \tag{11}$$

which describes the dispersion relation of the concentration fluctuations ($\langle \cdots \rangle$ denotes the statistical average over the Gibbs ensemble). The average over Eq. (9) is the normalization condition

$$N^{-1}\sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} = c(1-c). \tag{12}$$

The two generic dispersion relations $\varepsilon_{\mathbf{k}}$ are illustrated in Fig. 1 for a binary alloy with ordering and clustering fluctuations, respectively.

Atomic correlations are mediated by the internal interactions and contribute directly to the configurational energy and to the entropy of the system. The relevant corrections of the internal energy ($\Delta E$) and entropy ($\Delta S$) have thus to be accounted for as reliably as possible. The CCA presented here provides an analytical iteration algorithm for the correlation correction of the configurational Gibbs free energy ($\Delta F$).

### B. Configurational Hamiltonian and internal energy

Assuming pairwise atomic interactions the configurational Hamiltonian of the binary alloy can be presented in the form[2,53,54]

$$H = N\Phi c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} P_{\mathbf{R}_1} P_{\mathbf{R}_2}. \tag{13}$$

$\Phi$ is the injection energy of an $A$ atom into the crystal lattice and $V_{\mathbf{R}_1-\mathbf{R}_2}$ is the mixing energy of atomic species, which depends on the vector difference $\mathbf{R}_1-\mathbf{R}_2$ in macroscopically homogeneous alloys (note also that $V_{\mathbf{R}_1=\mathbf{R}_2}=0$).

Using Eq. (1) the Hamiltonian in Eq. (13) can be rewritten as

$$H = N\Phi c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} c^2 + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2}. \tag{14}$$

With the Fourier transforms

$$V_{\mathbf{k}} = \sum_{\mathbf{R}} V_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}} \tag{15}$$

and

$$V_{\mathbf{R}} = N^{-1}\sum_{\mathbf{k}} V_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} \tag{16}$$

Eq. (14) becomes

$$H = H_0 + N\Phi c + \frac{N}{2} V_{\mathbf{k}=\mathbf{0}} c^2 + \frac{N}{2}\sum_{\mathbf{k}} V_{\mathbf{k}} \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}. \tag{17}$$

The average of Eq. (17) over the Gibbs ensemble finally gives the configurational energy

$$E = E_0 + \Delta E, \tag{18}$$

where

$$E_0 = N\Phi c + \frac{N}{2} V_{\mathbf{k}=\mathbf{0}} c^2 \tag{19}$$

is the configurational energy of the disordered alloy in the absence of atomic correlations [“mean-field (MF) approximation”[1–3,9,31]] and

$$\Delta E = \frac{N}{2}\sum_{\mathbf{k}} V_{\mathbf{k}} \langle \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}} \rangle = \frac{1}{2}\sum_{\mathbf{k}} V_{\mathbf{k}} \varepsilon_{\mathbf{k}} \tag{20}$$

is the energy contribution from atomic correlations.

### C. General scheme of the correlation correction algorithm

Consider the case of a known functional $\widetilde{F}$ for the free energy. Assuming the fluctuations to be small, we expand $\widetilde{F}$ with respect to the fluctuations and take into account only quadratic terms. We obtain[1,2,5,42,43,50,52,55–58]

$$\widetilde{F} = \bar{F}(c)|_{\{\delta P_{\mathbf{R}}\}=0} + F_{fl}(\{\delta P_{\mathbf{R}}\}) \tag{21}$$

where $\bar{F}$ is the part of the free energy that does not depend on the fluctuations, and

$$\begin{aligned} F_{fl} &= \frac{1}{2}\sum_{\mathbf{R}_1\mathbf{R}_2} \frac{\partial^2 F_{fl}}{\partial \delta P_{\mathbf{R}_1} \partial \delta P_{\mathbf{R}_2}} \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2} \\ &= \frac{N}{2}\sum_{\mathbf{k}} \frac{\partial^2 F_{fl}}{\partial \delta P_{\mathbf{k}} \partial \delta P_{-\mathbf{k}}} \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}} \end{aligned} \tag{22}$$

is the nonequilibrium part of the free energy as caused by fluctuations. Note that the form of the fluctuation part $F_{fl}$ depends on the initial approximation for the free energy.

The derivative in Eq. (22) is taken at $\{\delta P_{\mathbf{R}}=0\,\forall\,\mathbf{R}\}$. The dispersion law for the correlation function is then obtained by the Landau relation[2,3,5,43,51,55]

$$\varepsilon_{\mathbf{k}} = k_B T N \left( \frac{\partial^2 F_{fl}}{\partial \delta P_{\mathbf{k}} \partial \delta P_{-\mathbf{k}}} \right)^{-1}_{\{\delta P_{\mathbf{k}}\}=0}, \tag{23}$$

where $k_B$ is the Boltzmann constant and $T$ the absolute temperature. Equation (23) holds if the fluctuations follow a Gaussian distribution. In this case, Eq. (23) is exact[5,51] and any uncertainty in $\varepsilon_{\mathbf{k}}$ is only caused by the approximations made for the initial free energy.

The configurational free energy of the system follows from the exact relation[3,6,48]

$$F = k_B T \int_0^{1/k_B T} E(T') d(1/k_B T') - T S_0 \tag{24}$$

with $S_0$ being the configurational entropy as taken in the high-temperature limit and $E$ is the internal configurational energy of the alloy.

Equation (24) can be rewritten using Eq. (18),

$$F = F_0 + k_B T \int_0^{1/k_B T} \Delta E(T') d(1/k_B T'), \tag{25}$$

where $F_0 = E_0 - T S_0$, and $\Delta E$ is determined by Eq. (20). Notice here that not only $E_0$ but also $S_0$ and $F_0$ correspond to the MF approximation, because it is asymptotically exact in the high-temperature limit.[1,59]

Substitution of Eq. (20) into Eq. (25) gives the contribution of the atomic correlations to the free energy,

$$\Delta F = F - F_0 = \frac{k_B T}{2}\sum_{\mathbf{k}} V_{\mathbf{k}} \int_0^{1/k_B T} \varepsilon_{\mathbf{k}}(T') d(1/k_B T'), \tag{26}$$

where we assume that the value $V_{\mathbf{k}}$ does not explicitly depend on temperature.

Equation (26) allows one to calculate the free energy of the alloy, provided that the temperature dependence of the correlation function $\varepsilon_{\mathbf{k}}(T)$ is known.

With the relation Eq. (20), which provides a precise recipe for calculating the energy corrections as caused by the atomic correlations, and with the exact integration for the free energy defined in Eq. (24) we have the elements at hand to set up a convenient and effective iterative algorithm for correcting the Gibbs free energy of a disordered alloy to account for the fluctuation dispersion relation $\varepsilon_{\mathbf{k}}$.

This iteration scheme, denoted the correlation correction algorithm in what follows, is illustrated in Fig. 2. We start with the known functional for the free energy $\widetilde{F}(V,T;\{P_{\mathbf{R}}\})$.

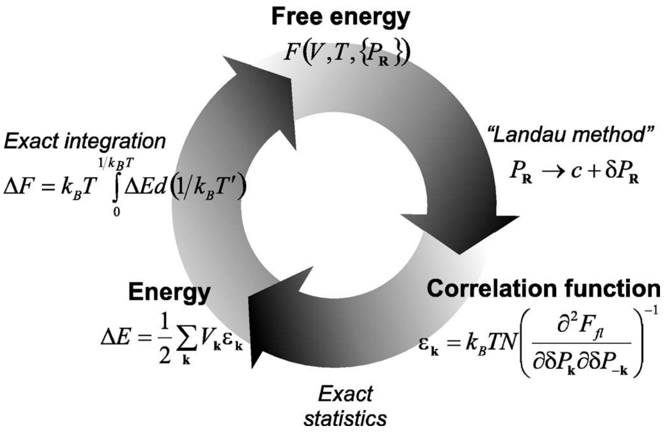

FIG. 2. Correlation correction algorithm.

Introducing fluctuations as defined in Eq. (1) we obtain the relation for the correlation function Eq. (23). In turn, the correlation function allows us to calculate the energy corrections caused by fluctuations. As a result, following Eq. (25), we derive a new expression for the Gibbs free energy. This corrected free energy in terms of probabilities $\{P_{\mathbf{R}}\}$ can again be expanded with respect to fluctuations and used as a starting point to find successive corrections to the correlation function and the free energy.

We show in the subsequent sections that this iteration can be performed twice in a fully analytical way. For almost all practical cases the accuracy of the second iteration is already sufficient. However, the assumption of a Gaussian distribution for fluctuation amplitudes in the Landau relation Eq. (23) may not be justified upon approaching a phase transformation temperature. In what follows we apply this algorithm for "macroscopic" (dispersion-free) fluctuations and for microscopic fluctuations taking into account the full dispersion relation $\varepsilon_{\mathbf{k}}$.

## III. THERMODYNAMIC (DISPERSION-FREE) APPROACH

We consider a volume element $V'$ that is small compared to the volume $V$ ($V' \ll V$) of the crystal but large compared to the unit cell. Let the concentration of $A$ atoms within $V'$ be given by $c+\delta c$, whereby the "local" fluctuations $\delta c$ are governed by the Boltzmann factor $\exp(-\mathfrak{R}/k_B T)$ with $\mathfrak{R}$ as the minimum work associated with the concentration excitation $\delta c$.[55]

In harmonic approximation, $\mathfrak{R}$ is given[5] by

$$\mathfrak{R} = \frac{1}{2} V' \frac{d^2 f}{dc^2} (\delta c)^2, \tag{27}$$

where $d^2 f/dc^2$ is the second derivative of the specific (relative to $V'$) configurational free energy of the volume $V'$ with respect to the concentration $c$, calculated for a fixed temperature and volume.

Inserting Eq. (27) into the Boltzmann factor finally leads to

$$\langle (\delta c)^2 \rangle = \frac{k_B T}{V'} \left( \frac{d^2 f}{dc^2} \right)^{-1}. \tag{28}$$

Note that $\langle (\delta c)^2 \rangle$ decreases with increasing local volume $V'$.

### A. First iteration of the CCA

At high temperatures, the specific free energy of the volume element $V'$ can be written as[5]

$$f^{(0)} = f_0 + e - Ts = f_0 + \rho e_1 c + \frac{1}{2} \rho e_2 c^2 + \rho k_B T [c \ln c + (1-c) \ln (1-c)], \tag{29}$$

where $f_0$ denotes the specific free energy of the pure component $B$,

$$e = \rho e_1 c + \frac{1}{2} \rho e_2 c^2 \tag{30}$$

the specific internal energy with $e_1 = \rho^{-1} e_c$, $e_2 = \rho^{-1} e_{cc}$, and

$$s = -\rho k_B [c \ln c + (1-c) \ln (1-c)] \tag{31}$$

the specific entropy of the volume element $V'$.

The parameters $e_c = \frac{\partial e}{\partial c}\big|_{c=0}$, $e_{cc} = \frac{\partial^2 e}{\partial c^2}\big|_{c=0}$, $\rho = \frac{N'}{V'}$ ($N'$ is the number of lattice sites in the volume element $V'$) do not explicitly depend on concentration and temperature. Note further that Eq. (29) is also obtained within the single-site MF approximation (assuming pairwise interactions).

From Eqs. (28) and (29) we find

$$\langle (\delta c)^2 \rangle^{(1)} = \frac{k_B T}{V'} \frac{1}{f_{cc}^{(1)}} = \frac{c(1-c)}{\rho V' \left( 1 + \frac{e_2}{k_B T} c(1-c) \right)} \tag{32}$$

with

$$f_{cc}^{(1)} = \frac{\partial^2 f}{\partial c^2} = \frac{k_B T \rho}{c(1-c)} \left[ 1 + \frac{e_2}{k_B T} c(1-c) \right]. \tag{33}$$

The superscript index (1) in Eqs. (32) and (33) denotes the iteration number of the CCA.

A local fluctuation of the concentration in the volume $V'$ is necessarily accompanied by a change $\Delta e$ of the specific internal energy defined in Eq. (30),

$$\Delta e^{(1)} = \frac{1}{2} \rho e_2 \langle (\delta c)^2 \rangle^{(1)} = \frac{1}{2V'} \frac{e_2 c(1-c)}{\left( 1 + \frac{e_2}{k_B T} c(1-c) \right)}, \tag{34}$$

and, in turn, by a change of the free energy,

$$\Delta f = k_B T \int_0^{1/k_B T} \Delta e(T') d(1/k_B T'). \tag{35}$$

Thus, the specific free energy decomposes into two terms,

$$f = f^{(0)} + \Delta f^{(1)}, \tag{36}$$

with

$$\Delta f^{(1)} = \frac{1}{2V'} k_B T \ln \left( 1 + \frac{c(1-c) e_2}{k_B T} \right), \tag{37}$$

which follows after substituting Eq. (34) into Eq. (35) and performing the integration with respect to the inverse temperature. We obtain in this way the specific free energy $\Delta f^{(1)}$ within the first iteration of the CCA,

$$f^{(1)} = f^{(0)} + \Delta f^{(1)} = f_0 + \rho e_1 c + \frac{1}{2}\rho e_2 c^2 + \rho k_B T[c \ln c + (1-c)\ln(1-c)] + \frac{1}{2V'} k_B T \ln\left(1 + \frac{c(1-c)e_2}{k_B T}\right). \tag{38}$$

### B. Second iteration of the CCA

Inserting $f^{(1)}$ defined in Eq. (38) into Eq. (28) starts the second iteration process and gives

$$\langle(\delta c)^2\rangle^{(2)} = \frac{c(1-c)}{\dfrac{c(1-c)}{k_B T} V' f_{cc}^{(1)} - \dfrac{e_{cc}}{f_{cc}^{(1)}} - \dfrac{(1-2c)^2}{2c(1-c)}\left(\dfrac{e_{cc}}{f_{cc}^{(1)}}\right)^2}, \tag{39}$$

where $f_{cc}^{(1)}$ is given by Eq. (33) and

$$\frac{e_{cc}}{f_{cc}^{(1)}} = \frac{e_2 c(1-c)}{k_B T\left(1 + \dfrac{e_2}{k_B T} c(1-c)\right)}. \tag{40}$$

Note that even for high temperature the correlation function $\langle(\delta c)^2\rangle^{(2)}$ cannot be simply replaced by $\langle(\delta c)^2\rangle^{(1)}$ neglecting second-order terms with respect to inverse temperature. Nevertheless, both correlation functions approach asymptotically $\frac{c(1-c)}{N'}$ in the high-temperature limit.

In the second iteration the change of the specific internal energy is given by

$$\Delta e^{(2)} = \frac{1}{2}\rho e_2 \langle(\delta c)^2\rangle^{(2)} = \frac{1}{2}\frac{\rho e_2 c(1-c)}{\dfrac{c(1-c)}{k_B T} V' f_{cc}^{(1)} - \dfrac{e_{cc}}{f_{cc}^{(1)}} - \dfrac{(1-2c)^2}{2c(1-c)}\left(\dfrac{e_{cc}}{f_{cc}^{(1)}}\right)^2} \tag{41}$$

Substituting Eq. (41) into Eq. (35) gives the specific free energy within the second iteration of the CCA,

$$f^{(2)} = f_0 + \rho e_1 c + \frac{1}{2}\rho e_2 c^2 + \rho k_B T[c \ln c + (1-c)\ln(1-c)] + \frac{1}{2}\rho e_2 k_B T c(1-c)\int_0^{1/k_B T}\left\{\frac{c(1-c)}{k_B T} V' f_{cc}^{(1)} - \frac{e_{cc}}{f_{cc}^{(1)}} - \frac{(1-2c)^2}{2c(1-c)}\left[\frac{e_{cc}}{f_{cc}^{(1)}}\right]^2\right\}^{-1} d\left(\frac{1}{k_B T'}\right).$$

Hence, using general thermodynamical expressions within the CCA, we successively derived two corrections to the Gibbs free energy caused by the concentration fluctuations. The approach we have outlined in this section can be easily implemented numerically, allowing one to include correlation corrections, e.g., in CALPHAD calculations, in a computationally very efficient way.

## IV. MICROSCOPIC APPROACH

### A. First iteration of the CCA

#### *1. Calculation of the correlation function*

In order to introduce interactions between individual atoms and to describe their distribution over the lattice sites, a microscopic model is mandatory. We start the first iteration of the CCA from the known expression for the free energy functional of an alloy in terms of nonequilibrium variables $P_{\mathbf{R}}$ within the one-site MF approximation[1,2,9,3]

$$\tilde{F} = \tilde{E} - T\tilde{S}, \tag{42}$$

with the configurational internal energy

$$\tilde{E} = N\Phi c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} P_{\mathbf{R}_1} P_{\mathbf{R}_2} \tag{43}$$

and the configurational entropy

$$\tilde{S} = -k_B \sum_{\mathbf{R}} [P_{\mathbf{R}} \ln P_{\mathbf{R}} + (1-P_{\mathbf{R}})\ln(1-P_{\mathbf{R}})]. \tag{44}$$

Using Eq. (1) the energy can be rewritten as

$$\tilde{E} = N\Phi c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} c^2 + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2}. \tag{45}$$

The products $\delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2}$ in Eq. (45) are not independent, but related by the sum rule given in Eq. (5). It is convenient to introduce this relation directly into the internal energy functional by a Lagrangian multiplier $\lambda$; then we obtain

$$\begin{aligned}\tilde{E} &= N\Phi c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} c^2 + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2} + \frac{1}{2}\lambda\left(\sum_{\mathbf{R}_1,\mathbf{R}_2} \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2} \delta_{\mathbf{R}_1,\mathbf{R}_2} - c(1-c)\right)\\ &= N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}\left(V_{\mathbf{R}_1-\mathbf{R}_2} + \lambda\right)c^2 + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}\left(V_{\mathbf{R}_1-\mathbf{R}_2} + \lambda\,\delta_{\mathbf{R}_1,\mathbf{R}_2}\right)\delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2}\end{aligned} \tag{46}$$

($\delta_{\mathbf{R}_1,\mathbf{R}_2}$ is the Kronecker symbol).

Inserting Eqs. (6), (7), and (16) into Eq. (46) we arrive at

$$\begin{aligned}\tilde{E} &= N\Phi c + \frac{N}{2} V_{\mathbf{k}=\mathbf{0}} c^2 + \frac{N}{2}\sum_{\mathbf{k}} V_{\mathbf{k}} \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}} + \frac{N}{2}\lambda\left(\sum_{\mathbf{k}} \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}} - c(1-c)\right)\\ &= N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{N}{2}(V_{\mathbf{k}=\mathbf{0}} + \lambda)c^2 + \frac{N}{2}\sum_{\mathbf{k}} (V_{\mathbf{k}} + \lambda)\,\delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}.\end{aligned} \tag{47}$$

Note that the interaction energy parameters $\{V_{\mathbf{k}}\}$ are replaced by the parameters $\{V_{\mathbf{k}}+\lambda\}$, this results in a higher accuracy of the correlation function calculations.[47]

Expanding Eq. (44) with respect to the fluctuations and taking only quadratic terms into account we find, after inserting Eqs. (6) and (7), the expression

$$\tilde{S} = S_0 - \frac{k_B N}{2}\sum_{\mathbf{k}} \frac{\delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}}{c(1-c)} \qquad (48)$$

for the entropy $\tilde{S}$ with

$$S_0 = -k_B N[c \ln c + (1-c)\ln(1-c)] \qquad (49)$$

as the high-temperature limit.

Substitution of Eq. (47) into Eq. (42) gives then the expression for the free energy in harmonic approximation with respect to fluctuations,

$$\tilde{F} = \bar{F}^{(0)}(c) + F_{fl}^{(1)}(\{\delta P_{\mathbf{k}}\}), \qquad (50)$$

where

$$\bar{F}^{(0)}(c) = F_0 - N\frac{\lambda}{2}c(1-c) = N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{N}{2}(V_{\mathbf{k}=\mathbf{0}}+\lambda)c^2 + k_B T N[c \ln c + (1-c)\ln(1-c)], \qquad (51)$$

and the contribution of the fluctuations to the free energy is

$$F_{fl}^{(1)}(\{\delta P_{\mathbf{k}}\}) = \frac{N}{2}\sum_{\mathbf{k}}\left(V_{\mathbf{k}} + \lambda + \frac{k_B T}{c(1-c)}\right)\delta P_{\mathbf{k}}\delta P_{-\mathbf{k}}. \qquad (52)$$

In order to derive the correlation function we calculate the second derivative of Eq. (52) with respect to $\delta P_{\mathbf{k}}$:

$$\frac{\partial^2 F_{fl}^{(1)}}{\partial \delta P_{\mathbf{k}} \partial \delta P_{-\mathbf{k}}} = N\left(V_{\mathbf{k}} + \lambda + \frac{k_B T}{c(1-c)}\right). \qquad (53)$$

Applying Eq. (23) the correlation function is now given by

$$\varepsilon_{\mathbf{k}}^{(1)} = N\langle \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}\rangle = \frac{c(1-c)}{1 + \dfrac{c(1-c)}{k_B T}(V_{\mathbf{k}}+\lambda)}. \qquad (54)$$

For $\lambda=0$ we recover the well-known KCM formula.[19,28,29,43] We note here that an equivalent formulation has also been derived for magnetic systems[60] within the so-called random phase approximation. Notice further that $\lambda \neq 0$ in Eq. (54) corresponds to the spherical model.[29–36] (The same expression was also derived within the first approximation of the thermodynamical perturbation theory.[45])

The actual value of the Lagrangian multiplier $\lambda$ is obtained numerically by the normalization condition Eq. (12)

$$\frac{1}{N}\sum_{\mathbf{k}} \frac{1}{1 + \dfrac{c(1-c)}{k_B T}(V_{\mathbf{k}}+\lambda)} = 1. \qquad (55)$$

Since by definition $\varepsilon_{\mathbf{k}} = N\langle \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}\rangle > 0$, the denominator in Eq. (54) must be positive. This corresponds to the disordered state of the alloy.[1–3,20] The spinodal temperature of the alloy corresponds to a vanishing denominator; then the system becomes unstable with respect to arbitarily small fluctuations.

### 2. Calculation of thermodynamical potentials

Using the correlation function $\varepsilon_{\mathbf{k}}$ we calculate the corrections to the thermodynamic potentials, i.e., the internal energy ($\Delta E$), the Gibbs free energy ($\Delta F$), and the grand canonical potential ($\Delta\Omega$).

Substituting Eq. (54) into Eq. (20) allows us to calculate the energy contribution from the concentration correlations:

$$\Delta E = \frac{c(1-c)}{2}\sum_{\mathbf{k}} \frac{V_{\mathbf{k}}}{1 + \dfrac{c(1-c)}{k_B T}(V_{\mathbf{k}}+\lambda)}, \qquad (56)$$

which according to Eq. (A1) is proportional to the Lagrangian multiplier $\lambda$ (see Appendix A):

$$\Delta E = -\frac{c(1-c)}{2}\lambda N. \qquad (57)$$

Performing the exact integration of Eq. (26) the contribution of the correlations to the free energy of the disordered alloy is given by

$$\Delta F = \frac{k_B T}{2}\sum_{\mathbf{k}} \ln\left[1 + \frac{c(1-c)}{k_B T}(V_{\mathbf{k}}+\lambda)\right] - \frac{c(1-c)}{2}\lambda N. \qquad (58)$$

The contribution $\Delta S$ to the entropy caused by correlations reads as $\Delta S = T^{-1}(\Delta E - \Delta F)$. Inserting Eqs. (57) and (58) we find[61]

$$\Delta S = -\frac{k_B}{2}\sum_{\mathbf{k}} \ln\left(1 + \frac{c(1-c)(V_{\mathbf{k}}+\lambda)}{k_B T}\right). \qquad (59)$$

All the other important thermodynamic configurational potentials of the alloy can be calculated in a similar way. For instance, the chemical potential $\mu = \mu_A - \mu_B$ ($\mu_A$ and $\mu_B$ are the chemical potentials of the alloy components) reads

$$\mu = \mu_0 + \Delta\mu, \qquad (60)$$

where

$$\mu_0 = \frac{1}{N}\frac{\partial F_0}{\partial c} = \Phi + V_{\mathbf{k}=\mathbf{0}}c + k_B T \ln\frac{c}{1-c} \qquad (61)$$

is the chemical potential of alloy within the MF approximation.[3] The contribution of the concentration fluctuations to the chemical potential is given by

$$\Delta\mu = \frac{1}{N}\frac{\partial \Delta F}{\partial c} = \frac{1-2c}{2N}\sum_{\mathbf{k}} \frac{V_{\mathbf{k}}}{1 + \dfrac{c(1-c)}{k_B T}(V_{\mathbf{k}}+\lambda)}. \qquad (62)$$

Using Eqs. (54), (20), and (57), this can be rewritten as

$$\Delta\mu = \frac{1-2c}{2Nc(1-c)}\sum_{\mathbf{k}} V_{\mathbf{k}}\varepsilon_{\mathbf{k}} = \frac{1-2c}{Nc(1-c)}\Delta E = -\frac{1-2c}{2}\lambda. \qquad (63)$$

The grand canonical potential is given by

$$\Omega = \Omega_0 + \Delta\Omega, \tag{64}$$

with $\Omega_0 = F_0 - N\mu_0 c$ as the MF approximation and

$$\Delta\Omega = \Delta F - N\Delta\mu c \tag{65}$$

as the correlation correction.

Combining Eqs. (58) and (63) we obtain

$$\Delta\Omega = \frac{k_B T}{2}\sum_{\mathbf{k}} \ln\left(1 + \frac{c(1-c)}{k_B T}(V_{\mathbf{k}} + \lambda)\right) - \frac{\lambda N c^2}{2}. \tag{66}$$

Thus, as a result of the first iteration of the CCA, the configurational internal energy of a disordered alloy can be found by combining Eqs. (18), (19), and (57):

$$E^{(1)} = N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{N}{2}(V_{\mathbf{k=0}} + \lambda)c^2. \tag{67}$$

Equations (49) and (59) define the configurational entropy

$$S^{(1)} = S_0 + \Delta S = -k_B N[c \ln c + (1-c)\ln(1-c)] - \frac{k_B}{2}\sum_{\mathbf{k}} \ln\left(1 + \frac{c(1-c)(V_{\mathbf{k}} + \lambda)}{k_B T}\right). \tag{68}$$

Accordingly, the configurational free energy of a disordered alloy $F = E_0 - TS_0 + \Delta F$ is calculated from Eqs. (19), (49), and (58):

$$F^{(1)} = N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{N}{2}(V_{\mathbf{k=0}} + \lambda)c^2 + k_B T N[c \ln c + (1-c)\ln(1-c)] + \frac{k_B T}{2}\sum_{\mathbf{k}} \ln\left(1 + \frac{c(1-c)(V_{\mathbf{k}} + \lambda)}{k_B T}\right). \tag{69}$$

Using Eqs. (60), (61), and (63) the chemical potential is finally given by

$$\mu^{(1)} = \Phi - \frac{\lambda}{2} + (V_{\mathbf{k=0}} + \lambda)c + k_B T \ln\frac{c}{1-c}, \tag{70}$$

and the grand canonical potential reads

$$\Omega^{(1)} = F^{(1)} - N\mu^{(1)}c, \tag{71}$$

where $F^{(1)}$ and $\mu^{(1)}$ are defined in Eqs. (69) and (70).

### B. Second iteration of the CCA

The starting point for the second iteration of the CCA is the free energy functional in terms of the variables $\{P_{\mathbf{R}}\}$, which has been derived in the first iteration of the CCA (see Appendix B):

$$\tilde{F}(\{P_{\mathbf{R}}\}) = N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}(V_{\mathbf{R}_1-\mathbf{R}_2} + \lambda\delta_{\mathbf{R}_1,\mathbf{R}_2})P_{\mathbf{R}_1}P_{\mathbf{R}_2} + k_B T\sum_{\mathbf{R}}[P_{\mathbf{R}}\ln P_{\mathbf{R}} + (1-P_{\mathbf{R}})\ln(1-P_{\mathbf{R}})] + \frac{k_B T}{2}\ln\det\left\|\delta_{\mathbf{R}_1,\mathbf{R}_2} + \frac{\sqrt{P_{\mathbf{R}_1}(1-P_{\mathbf{R}_1})}(V_{\mathbf{R}_1-\mathbf{R}_2} + \lambda\delta_{\mathbf{R}_1,\mathbf{R}_2})\sqrt{P_{\mathbf{R}_2}(1-P_{\mathbf{R}_2})}}{k_B T}\right\|. \tag{72}$$

Expanding this functional with respect to fluctuations, we obtain

$$\tilde{F} = \bar{F}^{(0)}(c) + F_{fl}(\{\delta P_{\mathbf{k}}\}), \tag{73}$$

where $\bar{F}^{(0)}(c)$ is given by Eq. (51) and the fluctuation part is defined by $F_{fl}(\{\delta P_{\mathbf{k}}\}) = F_{fl}^{(1)}(\{\delta P_{\mathbf{k}}\}) + F_{fl}^{(2)}(\{\delta P_{\mathbf{k}}\})$ with $F_{fl}^{(1)}(\{\delta P_{\mathbf{k}}\})$ determined by Eq. (52) and $F_{fl}^{(2)}(\{\delta P_{\mathbf{k}}\})$ given by Eq. (C27) (see Appendix C).

Thus, after the second iteration of the CCA, the total correlation correction of the configurational free energy in Eq. (73) reads

$$F_{fl}(\{\delta P_{\mathbf{k}}\}) = \frac{N k_B T}{2c(1-c)}\sum_{\mathbf{k}}\left(\Psi_{\mathbf{k}}^{(1)} + \frac{1}{N}\sum_{\mathbf{q}}\frac{(1-\Psi_{\mathbf{q}}^{(1)})}{\Psi_{\mathbf{q}}^{(1)}} - \frac{(1-2c)^2}{2Nc(1-c)}\sum_{\mathbf{q}}\frac{(1-\Psi_{\mathbf{q}}^{(1)})(1-\Psi_{\mathbf{k-q}}^{(1)})}{\Psi_{\mathbf{q}}^{(1)}\Psi_{\mathbf{k-q}}^{(1)}}\right)|\delta P_{\mathbf{k}}|^2, \tag{74}$$

where

$$\Psi_{\mathbf{k}}^{(1)} = 1 + \frac{c(1-c)}{k_B T}(V_{\mathbf{k}} + \lambda). \tag{75}$$

The second derivative of Eq. (74) with respect to variables $\delta P_{\mathbf{k}}$ is

$$\frac{\partial^2 F_{fl}}{\partial \delta P_{\mathbf{k}} \partial \delta P_{-\mathbf{k}}} = \frac{N k_B T}{c(1-c)} \left( \Psi_{\mathbf{k}}^{(1)} + \frac{1}{N} \sum_{\mathbf{q}} \frac{(1-\Psi_{\mathbf{q}}^{(1)})}{\Psi_{\mathbf{q}}^{(1)}} - \frac{(1-2c)^2}{2Nc(1-c)} \sum_{\mathbf{q}} \frac{(1-\Psi_{\mathbf{q}}^{(1)})(1-\Psi_{\mathbf{k}-\mathbf{q}}^{(1)})}{\Psi_{\mathbf{q}}^{(1)} \Psi_{\mathbf{k}-\mathbf{q}}^{(1)}} \right). \tag{76}$$

According to Eq. (23) the expression for correlation function is defined as

$$\varepsilon_{\mathbf{k}}^{(2)} = \frac{c(1-c)}{\Psi_{\mathbf{k}}^{(2)}}, \tag{77}$$

with

$$\Psi_{\mathbf{k}}^{(2)} = \Psi_{\mathbf{k}}^{(1)} + \frac{1}{N} \sum_{\mathbf{q}} \frac{(1-\Psi_{\mathbf{q}}^{(1)})}{\Psi_{\mathbf{q}}^{(1)}} - \frac{1}{2N} \frac{(1-2c)^2}{c(1-c)} \sum_{\mathbf{q}} \frac{(1-\Psi_{\mathbf{q}}^{(1)})(1-\Psi_{\mathbf{k}-\mathbf{q}}^{(1)})}{\Psi_{\mathbf{q}}^{(1)} \Psi_{\mathbf{k}-\mathbf{q}}^{(1)}}. \tag{78}$$

The Lagrangian multiplier $\lambda$ is again obtained from the normalization condition Eq. (12) applied to the correlation function $\varepsilon_{\mathbf{k}}^{(2)}$ Eq. (77). $\varepsilon_{\mathbf{k}}^{(1)} = \frac{c(1-c)}{\Psi_{\mathbf{k}}^{(1)}}$ is represented in the same form as $\varepsilon_{\mathbf{k}}^{(2)}$ with $\Psi_{\mathbf{k}}^{(1)}$ replaced by $\Psi_{\mathbf{k}}^{(2)}$. The second-order correlation contributions to the internal and Gibbs free energy as well as other thermodynamical potentials are calculated using Eqs. (77) and (78) and the relations given by Eqs. (20) and (26), the first relation of Eq. (62), and Eq. (65). However, this can be done only numerically.

Equations (77) and (78) have been obtained before in Ref. 25 by the use of ring diagrams within the thermodynamic perturbation theory.[1,29–31,39,56,62,63]

### C. Concentration fluctuations in alloys with many-body atomic interactions

With many-body interactions present in the system, the configurational Hamiltonian reads[53,64]

$$H = H_0 + N\Phi c + \frac{1}{2!} \sum_{\mathbf{R}_1 \mathbf{R}_2} V^{(2)}_{\mathbf{R}_1,\mathbf{R}_2} P_{\mathbf{R}_1} P_{\mathbf{R}_2} + \frac{1}{3!} \sum_{\mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3} V^{(3)}_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3} P_{\mathbf{R}_1} P_{\mathbf{R}_2} P_{\mathbf{R}_3} + \frac{1}{4!} \sum_{\mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 \mathbf{R}_4} V^{(4)}_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4} P_{\mathbf{R}_1} P_{\mathbf{R}_2} P_{\mathbf{R}_3} P_{\mathbf{R}_4} + \cdots. \tag{79}$$

Here $V^{(3)}_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3}$ and $V^{(4)}_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4}$ are the three- and four-body mixing energies of atoms.

Expanding Eq. (79) with respect to fluctuations using Eq. (1) and performing the Fourier transform defined in Eq. (6) allows us to calculate the configurational energy of the alloy in a form similar to Eq. (47):

$$\tilde{E} = N\left(\tilde{\Phi} - \frac{\lambda}{2}\right)c + \frac{N}{2}(\tilde{V}_{\mathbf{k}=\mathbf{0}} + \lambda)c^2 + \frac{N}{2} \sum_{\mathbf{k}} (\tilde{V}_{\mathbf{k}} + \lambda)\, \delta P_{\mathbf{k}} \delta P_{-\mathbf{k}}, \tag{80}$$

with the effective mixing energy

$$\tilde{V}_{\mathbf{k}} = V^{(2)}_{\mathbf{k}} + c V^{(3)}_{\mathbf{k},0} + \frac{c^2}{2} V^{(4)}_{\mathbf{k},0,0} + \cdots, \tag{81}$$

including now many-body contributions.

The Fourier transformations are performed by applying the identities[53]

$$V^{(n)}_{\mathbf{k}_1,\mathbf{k}_2,\ldots,\mathbf{k}_{n-1}} = \sum_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{n-1}} V^{(n)}_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{n-1},\mathbf{0}} \exp\left( - i \sum_{l=1}^{n-1} \mathbf{k}_l \mathbf{R}_l \right),$$

$$\begin{aligned} V^{(n)}_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_n} &= V^{(n)}_{\mathbf{0},\mathbf{R}_2-\mathbf{R}_1,\mathbf{R}_3-\mathbf{R}_1,\ldots,\mathbf{R}_n-\mathbf{R}_1} \\ &= N^{-(n-1)} \sum_{\mathbf{k}_2,\mathbf{k}_3,\ldots,\mathbf{k}_n} V^{(n)}_{\mathbf{k}_2,\mathbf{k}_3,\ldots,\mathbf{k}_n} \\ &\quad \times \exp\left( i \sum_{l=2}^{n} \mathbf{k}_l (\mathbf{R}_l - \mathbf{R}_1) \right). \end{aligned} \tag{82}$$

Since Eq. (80) is similar to Eq. (47), the first iteration of the CCA leads to analogous expressions for the correlation function and correlation contributions to the internal and free energies. They are given by Eqs. (54), (56), and (58) where the concentration-independent mixing energy $V_{\mathbf{k}}$ is substituted by the explicitly concentration-dependent parameter $\tilde{V}_{\mathbf{k}}$ given by Eq. (81).

The expression for the chemical potential determined by Eqs. (60) is then given by

$$\mu = \mu_0 - \frac{(1-2c)}{2}\lambda + \frac{c(1-c)}{2N} \sum_{\mathbf{k}} \frac{V^{(3)}_{\mathbf{k},\mathbf{0}} + c V^{(4)}_{\mathbf{k},\mathbf{0},\mathbf{0}}}{1 + \frac{c(1-c)}{k_B T}(\tilde{V}_{\mathbf{k}} + \lambda)}, \tag{83}$$

with

$$\mu_0 = \Phi + c\tilde{V}_{\mathbf{k}=\mathbf{0}} + \frac{c^2}{2}(V^{(3)}_{\mathbf{k},\mathbf{0}} + c V^{(4)}_{\mathbf{k},\mathbf{0},\mathbf{0}}) + k_B T \ln \frac{c}{1-c}. \tag{84}$$

Equation (83) is the generalization of the expression for the configurational chemical potential[48] for the case of many-body interactions.

## V. APPLICATION TO MODEL SYSTEMS

### A. Disordered fcc $AB_3$ alloy

In the following we apply the CCA to a disordered model $AB_3$ fcc system with $c=0.25$ and nearest- and next- nearest-neighbor interactions $V_1$ and $V_2=-0.5V_1$, respectively. As a benchmark we are using results from MC simulations[47] in the first four coordination shells in real space. In Fig. 3 we show the results of calculations of the correlation function at two different temperatures, $k_B T/V_1=1.15$ close to the phase

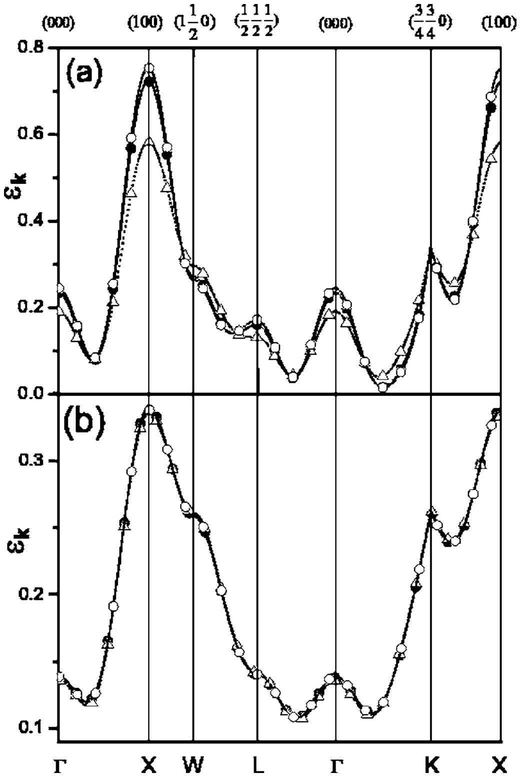

FIG. 3. Correlation function $\varepsilon_k$ in the disordered state for two different temperatures (a) close to ($k_BT/V_1=1.15$) and (b) far above ($k_BT/V_1=2.25$) the phase transition temperature. MC results (filled circles) first iteration (triangles), and second iteration (open circles).

transition and $k_BT/V_1=2.25$ far above the phase transition, which is located at $k_BT_0/V_1=1.09$. For high temperatures the results of the first and the second iteration are almost identical with only minor deviations from the MC results [see Fig. 3(b)]. As expected the correlations are more pronounced close to the phase transition [see Fig. 3(a)]. In this regime we find significant differences between the first and second iterations of the CCA. While the results of the first iteration deviate significantly from the correct MC result, the results of the second iteration are practically identical to the MC results. This demonstrates the excellent convergence of the CCA even at temperatures close to phase transitions where the fluctuations within the disordered system are more pronounced.

Using Eqs. (20) and (26) we have calculated the fluctuation-induced corrections $\Delta E$ and $\Delta F$ to the configurational energy and the free energy, respectively. We have then determined the correction to the configuational entropy from the relation $T\Delta S=\Delta E-\Delta F$. The results are summarized in Fig. 4. While the first iteration of the CCA shows deviations from the MC results which are more pronounced upon approaching the phase transition temperature, the second iteration shows excellent agreement with the MC results for all temperatures, demonstrating again the excellent convergence of the CCA. Interestingly, the corrections for the configurational energy [see Fig. 4(a)] and the configurational entropy [see Fig. 4(c)] are both systematically too large in the first iteration. This is compensated in the free energy, which therefore provides good results already in the first iteration

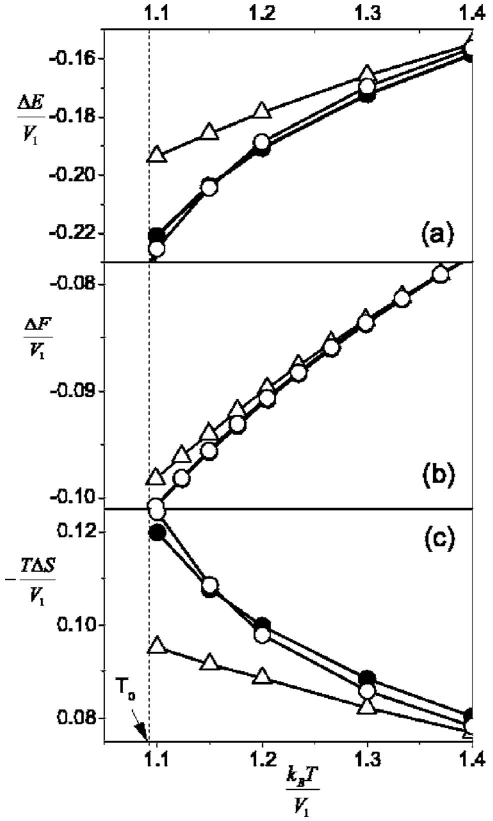

FIG. 4. Correlation-correction-induced $\Delta E$, $\Delta F$, and $\Delta S$ as functions of temperature from MC results (filled circles) and after the first (triangles) and second (open circles) iterations of the CCA. The phase transition temperature is indicated by the dashed vertical line.

[see Fig. 4(b)]. The results clearly demonstrate that the CCA is a highly efficient method to calculate thermodynamic properties in the entire temperature and concentration range.

### B. $L1_2$ and $L1_0$ ordering

In the following we demonstrate that the CCA is more efficient in characterizing the phase transition itself. We consider a system that undergoes a phase transformation at a temperature $T_0$. As a result the values $\langle P_{\mathbf{R}}\rangle$ will be different in certain lattice sites defining $l$ different crystallographically equivalent sublattices. The probabilities $\langle P_{m,\mathbf{r}}\rangle=P_m$ are equal on all sites of the sublattice $m$, where $\mathbf{r}$ denotes the coordinate within the sublattice. Similarly to Eq. (1) we introduce

$$P_{m,\mathbf{r}}=P_m+\delta P_{m,\mathbf{r}} \tag{85}$$

and define the matrix $\|V^{mn}_{\mathbf{r}_m-\mathbf{r}_n}\|$ of interaction parameters instead of the interactions $V_{\mathbf{R}_m-\mathbf{R}_n}$. Following a procedure developed by Bugaev and Ryzhkov[65] (see also Appendix B) we obtain the first iteration of the free energy of the alloy in the ordered state

$$F_{ord}^{(1)} = N\Phi c + k_B T N_0 \sum_m [P_m \ln P_m + (1-P_m)\ln(1-P_m)] + \frac{N_0}{2}\sum_{m,n} V_{\mathbf{k=0}}^{mn} P_m P_n - \frac{N_0}{2}\sum_m \lambda_m P_m (1-P_m) + \frac{k_B T}{2}\sum_{\mathbf{k}} \ln \det M_{\mathbf{k}}, \tag{86}$$

where $N_0$ is the number of sites in each sublattice and the matrix $M_{\mathbf{k}}$ is given by

$$M_{\mathbf{k}} = \left\| \delta_{m,n} + \frac{\sqrt{P_m(1-P_m)}(V_{\mathbf{k}}^{mn} + \lambda_m \delta_{mn})\sqrt{P_n(1-P_n)}}{k_B T} \right\|. \tag{87}$$

The Fourier components $V_{\mathbf{k}}^{mn}$ are defined by

$$V_{\mathbf{k}}^{mn} = \sum_{\mathbf{r}_{mn}} V_{\mathbf{r}_{mn}}^{mn} e^{-i\mathbf{k}\mathbf{r}_{mn}}, \quad \mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n \tag{88}$$

with $\mathbf{r}_{mn}=\mathbf{r}_m-\mathbf{r}_n$. The summations over $m$ and $n$ are performed over all sublattices $m=1,2,\ldots,l$ while the summation over the wave vector $\mathbf{k}$ is performed over the first Brillouin zone of the reciprocal space determined by one sublattice. The Lagrangian multipliers $\lambda_m$ for each sublattice are determined by

$$N_0^{-1}\sum_{\mathbf{k}} \|M_{\mathbf{k}}^{-1}\|_{mm} = 1 \tag{89}$$

for $m=1,2,\ldots,l$. Equations (86) and (89) were obtained within the ring approximation using the thermodynamic perturbation method.[46]

The equilibrium values of $P_m$ are determined by the minimum of the free energy [Eq. (86)]. In order to test the accuracy of Eq. (86) we consider $L1_2$ and $L1_0$ ordering, which exhibit, according to the Lifshitz theorem,[1] phase transformations of first order. Both structures are described by the superstructure wave vector $\mathbf{k}_0=(1,0,0)$ in the Brillouin zone of the disordered phase defining[1] four different sublattices $m=1,2,3,4$. In the $L1_2$ structure the $P_m$ are given by

$$P_1 = P_2 = P_3 = c - \frac{\eta}{4}, \quad P_4 = c + \frac{3}{4}\eta, \tag{90}$$

where $\eta$ is the long-range order parameter of the system with $\eta=1(0)$ in the perfectly ordered (disordered) state. For the $L1_0$ structure the $P_m$ are given by

$$P_1 = P_2 = c - \frac{\eta}{2}, \quad P_3 = P_4 = c + \frac{\eta}{2}. \tag{91}$$

Substituting Eqs. (90) and (91), into Eq. (86) and neglegting interactions in all coordination shells larger than the next-nearest-neighbor shell, we can now minimize the free energy as a function of $\eta$ at fixed temperature and concentration, taking into account the normalization condition defined in Eq. (89). In the following we show results for systems with nearest- and next-nearest-neighbor interactions $V_1$ and $V_2=-0.5V_1$, at a concentration of $c=0.25$ ($L1_2$) and 0.5 ($L1_0$).

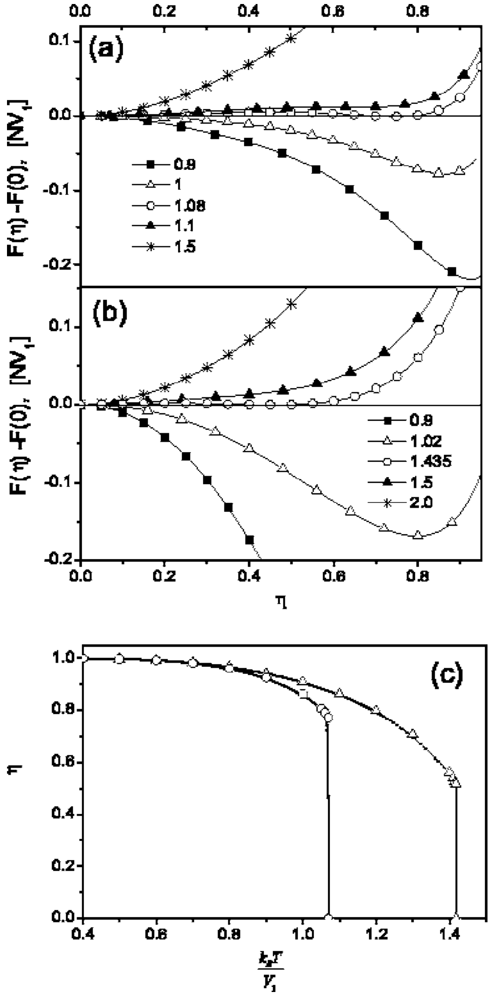

FIG. 5. Free energy of an $L1_2$ model system calculated (a) with the first iteration of the CCA and (b) within the MF approximation for various temperatures in units of $k_BT/V_1$. (c) Long-range order parameter extracted from the free energy calculations (open circles, CCA; triangles, MF).

Figure 5 shows the free energy in Eq. (86) calculated as a function of $\eta$ for the $L1_2$ system in the MF approximation [Fig. 5(b)] and after the first iteration of the CCA [Fig. 5(a)] for selected temperatures. This allows us to extract the long-range order parameter as a function of temperature [see Fig. 5(c)]. In particular, we can determine the phase transformation temperature $T_0$, which coincides for the CCA extremely well with the value determined in MC simulations[47] ($k_BT_0^{\mathrm{MC}}/V_1=1.09$). Here the first iteration is accurate enough for our purposes as we have already demonstrated in Fig. 4(b). The CCA correctly predicts a first-order phase transition at $k_BT_0^{\mathrm{CCA}}/V_1=1.08$, while the MF approximation results in large errors ($k_BT_0^{\mathrm{MF}}/V_1=1.44$) as expected.[3]

Similar results for the $L1_0$ system are shown in Fig. 6. The free energy is calculated in the MF approximation [Fig. 6(b)] and after the first iteration of the CCA [Fig. 6(a)] for selected temperatures. The long-range order parameter as a function of temperature is shown in Fig. 6(c). In this case the MF approximation gives qualitatively wrong results with a second-order phase transformation at high temperature ($k_BT_0^{\mathrm{MF}}/V_1=1.75$). In the CCA we find again a first-order

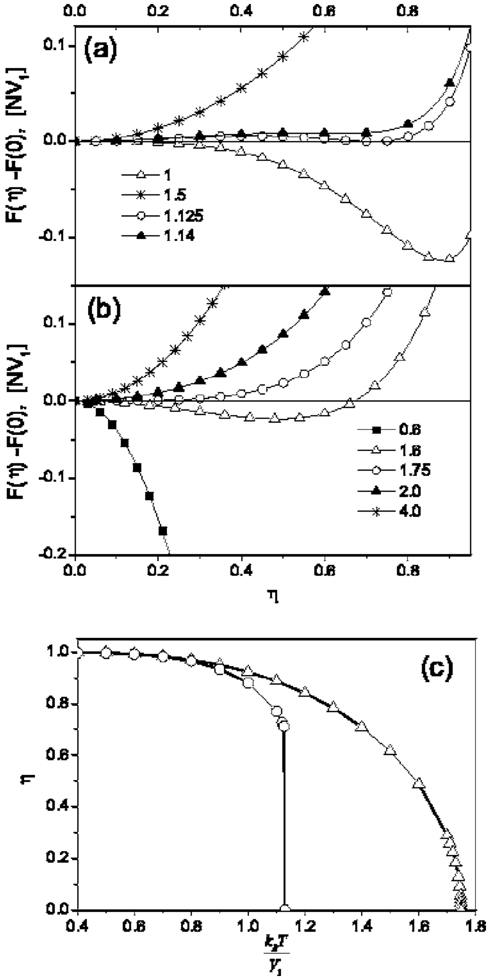

FIG. 6. Free energy of a $L1_0$ model system calculated (a) with the first iteration of the CCA and (b) within the MF approximation for various temperatures in units of $k_BT/V_1$. (c) Long-range order parameter extracted from the free energy calculations (open circles, CCA; triangles, MF).

phase transition at $k_BT_0^{\mathrm{CCA}}/V_1=1.125$ which coincides very well with the MC result[47] $k_BT_0^{\mathrm{MC}}/V_1=1.15$.

The results presented in this section were obtained in only a few seconds of CPU time on a conventional desktop computer. The examples demonstrate the applicability and fast convergence of the CCA in systems exhibiting first-order phase transformations. In the CCA we assume only that the fluctuations follow a Gaussian distribution. Recently, it has been shown experimentally that even in a system with a second-order phase transformation close to the critical point, the fluctuations follow such a Gaussian distribution.[66] Therefore, we speculate that the CCA should be applicable also to second-order phase transformation in the critical regime.

## VI. CONCLUSIONS

In this work we presented a straightforward iterative algorithm (CCA) to calculate the contribution of atomic correlations to the free energy of a binary alloy system. The accuracy of the results is determined by the initial approximation for the free energy and by the assumption about the Gaussian distribution for the fluctuation amplitudes. This assumption may be violated upon approaching a phase transformation of the system.

We have performed two iterations of the CCA assuming the atomic interactions to be pairwise. We also have shown the first iteration result for a system governed by many-body interactions. Closed analytical expressions for the correlation function and thermodynamic potentials were obtained in each iteration. Starting from the MF approximation for the free energy we successively arrive at the SM (Refs. 29–36) and the ring[25,45] approximations for the correlation function. Comparing with MC simulations it was already shown[47] that the ring approximation is much more accurate than the SM. This confirms the rapid convergence of the CCA. We obtain the same rapid convergence in our calculations of thermodynamic potentials, long-range order parameters, and phase transformation temperatures in Sec. V. Our results support the qualitative hypothesis by Brout[31] on the dominating contribution of the ring diagrams to cumulant expansion series, which was used in the initial derivation of the ring approximation.[25,45]

One important advantage of the presented algorithm is the absence of *a priori* limitations on the radius of the effective interaction due to the use of a **k**-space approach. Thus, within the presented formalism the long-ranging strain-induced interaction[1,2] caused by atomic size-mismatch as well as electronic effects[2,5,26,27] can be naturally implemented. The CCA can be generalized for the case of multicomponent alloys and systems with magnetic interactions. Due to the simplicity of the CCA, it can be conveniently applied for the investigation of surface segregation in amorphous and fluid systems as as well in thin films.

The numerical implementation of the formalism outlined in this work is straightforward. In particular, calculations including the dispersion-free case outlined in Sec. III are very efficient. Including the effects of fluctuations even in a simplified (dispersion-free) model in thermodynamic calculations such as CALPHAD could therefore significantly improve such calculations.

We finally note that our results can be used directly in the linear kinetic theory of atomic ordering and decomposition in alloys in order to calculate the influence of correlations on the relaxation behavior of the concentration wave amplitudes which approach their equilibrium values as[1,2]

$$\tau_{\mathbf{k}}=-k_BTN\left(c(1-c)L_{\mathbf{k}}\frac{\partial^2F_{fl}}{\partial\delta P_{\mathbf{k}}\partial\delta P_{-\mathbf{k}}}\right)^{-1}, \tag{92}$$

with the new correlation corrected quantity $\frac{\partial^2F_{fl}}{\partial\delta P_{\mathbf{k}}\partial\delta P_{-\mathbf{k}}}$ as defined by Eq. (76).

## ACKNOWLEDGMENT

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## APPENDIX A: CONFIGURATIONAL ENERGY AND LAGRANGIAN MULTIPLIER

Equation (56) can be simplified if we employ the normalization condition Eq. (55):

$$\Delta E = \frac{c(1-c)}{2}\sum_{\mathbf{k}} \frac{V_{\mathbf{k}}}{1+\frac{c(1-c)}{k_BT}(V_{\mathbf{k}}+\lambda)} = \frac{c(1-c)}{2}\frac{k_BT}{c(1-c)} \times \sum_{\mathbf{k}} \frac{\frac{c(1-c)}{k_BT}V_{\mathbf{k}}+1-1+\frac{c(1-c)}{k_BT}\lambda-\frac{c(1-c)}{k_BT}\lambda}{1+\frac{c(1-c)}{k_BT}(V_{\mathbf{k}}+\lambda)} = -\frac{c(1-c)}{2}\lambda N. \tag{A1}$$

From Eqs. (A1) and (20) it follows that

$$\lambda = -\frac{2\Delta E}{Nc(1-c)} = -\frac{1}{Nc(1-c)}\sum_{\mathbf{k}} V_{\mathbf{k}}\varepsilon_{\mathbf{k}}. \tag{A2}$$

Thus, the Lagrangian multiplier is proportional to the energy correlation contribution per atom [see Eq. (56)].

## APPENDIX B: First iteration of the CCA in terms of variables $\{P_{\mathbf{R}}\}$

### 1. Correlation function for fluctuation modes

Consider the fluctuation part of the configurational free energy as the harmonic series

$$F_{fl} = \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} \left.\frac{\partial^2\tilde{F}}{\partial\delta P'_{\mathbf{R}_1}\partial\delta P'_{\mathbf{R}_2}}\right|_{\{P_{\mathbf{R}}\}} \delta P'_{\mathbf{R}_1}\delta P'_{\mathbf{R}_2}. \tag{B1}$$

The derivative in Eq. (B1) is taken in a state of the system with $\{\delta P'_{\mathbf{R}}=0\,\forall\mathbf{R}\}$. In such a state the system is described by the set of variables $\{P_{\mathbf{R}}\}$ and the fluctuations

$$\delta P'_{\mathbf{R}} = P'_{\mathbf{R}} - P_{\mathbf{R}}. \tag{B2}$$

Note that such a definition of the fluctuations is different from the one used in Sec. III, where the reference state for the fluctuations is kept at thermodynamic equilibrium with $P_{\mathbf{R}}=c\,\forall\mathbf{R}$. We will show in the following, that the atomic correlations for the fluctuations defined by Eq. (B2) are described in terms of fluctuation modes, but not in terms of the fluctuations in Eq. (23).

We start with the following expression for the free energy functional:

$$\tilde{F} = N\left(\Phi - \frac{\lambda}{2}\right)c + \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}(V_{\mathbf{R}_1-\mathbf{R}_2}+\lambda\delta_{\mathbf{R}_1,\mathbf{R}_2})P_{\mathbf{R}_1}P_{\mathbf{R}_2} + k_BT\sum_{\mathbf{R}}[P_{\mathbf{R}}\ln P_{\mathbf{R}} + (1-P_{\mathbf{R}})\ln(1-P_{\mathbf{R}})], \tag{B3}$$

which is obtained from Eqs. (42)–(44) taking into account the conservation law defined in Eq. (3) via the Lagrangian multiplier $\lambda$.

Equation (B3) is valid for both the variables $P_{\mathbf{R}}$ and $P'_{\mathbf{R}}$ since the latter variables correspond by definition to one and the same macroscopically homogeneous sample. The difference consists in different sets of supercells[50] used for the averaging during the calculation of $\{P_{\mathbf{R}}\}$ and $\{P'_{\mathbf{R}}\}$. Substituting $P'_{\mathbf{R}}=P_{\mathbf{R}}+\delta P'_{\mathbf{R}}$ in Eq. (B3) and calculating the second derivative defined in Eq. (B1), we derive the contribution of the atomic correlations to the configurational free energy

$$F_{fl}^{(1)} = \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}\left(V_{\mathbf{R}_1-\mathbf{R}_2}+\lambda\delta_{\mathbf{R}_1,\mathbf{R}_2}+\frac{k_BT\delta_{\mathbf{R}_1,\mathbf{R}_2}}{P_{\mathbf{R}_1}(1-P_{\mathbf{R}_1})}\right)\delta P'_{\mathbf{R}_1}\delta P'_{\mathbf{R}_2}. \tag{B4}$$

Using the following transformation of the variables:[64]

$$\delta\tilde{P}_{\mathbf{R}} = [P_{\mathbf{R}}(1-P_{\mathbf{R}})]^{-1/2}\delta P'_{\mathbf{R}}, \tag{B5}$$

the quadratic form with respect to the values $\delta\tilde{P}_{\mathbf{R}}$ can be represented as

$$F_{fl}^{(1)} = \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}(W_{\mathbf{R}_1-\mathbf{R}_2}+k_BT\delta_{\mathbf{R}_1,\mathbf{R}_2})\delta\tilde{P}_{\mathbf{R}_1}\delta\tilde{P}_{\mathbf{R}_2}, \tag{B6}$$

where

$$W_{\mathbf{R}_1-\mathbf{R}_2} = \sqrt{P_{\mathbf{R}_1}(1-P_{\mathbf{R}_1})}(V_{\mathbf{R}_1-\mathbf{R}_2}+\lambda\delta_{\mathbf{R}_1,\mathbf{R}_2})\sqrt{P_{\mathbf{R}_2}(1-P_{\mathbf{R}_2})}. \tag{B7}$$

The matrix $\|W_{\mathbf{R}_1,\mathbf{R}_2}\|$ can be diagonalized by means of a linear nonsingular similarity transformation to new variables (normal modes)

$$\delta\tilde{P}_{\mathbf{R}} = \sum_{\omega} t_{\omega\mathbf{R}}Q_{\omega} \tag{B8}$$

with $t_{\omega\mathbf{R}}$ as the eigenfunctions of the matrix $\|W_{\mathbf{R}_1,\mathbf{R}_2}\|$. The secular equation reads

$$\sum_{\mathbf{R}_2} W_{\mathbf{R}_1-\mathbf{R}_2}t_{\omega\mathbf{R}_2} = \Lambda_{\omega}t_{\omega\mathbf{R}_1}, \tag{B9}$$

where $\Lambda_{\omega}$ are the eigenvalues of the matrix $\|W_{\mathbf{R}_1,\mathbf{R}_2}\|$. Note that the eigenfunctions and eigenvalues are real numbers, because of the symmetry of $\|W_{\mathbf{R}_1,\mathbf{R}_2}\|$.

The orthonormalization requirement for the eigenfunctions $t_{\omega\mathbf{R}}$ is set as

$$\sum_{\mathbf{R}} t^*_{\omega_1\mathbf{R}}t_{\omega_2\mathbf{R}} = \delta_{\omega_1\omega_2}, \qquad \sum_{\omega} t^*_{\mathbf{R}_1\omega}t_{\mathbf{R}_2\omega} = \delta_{\mathbf{R}_1\mathbf{R}_2}. \tag{B10}$$

We multiply both parts of the secular equation (B9) by $t^*_{\omega\mathbf{R}_1}$ and perform the summation over $\mathbf{R}_1$. Considering the requirement Eq. (B10) the eigenvalues $\Lambda_{\omega}$ can be written in the form

$$\Lambda_{\omega} = \sum_{\mathbf{R}_1\mathbf{R}_2} t^*_{\omega\mathbf{R}_1}W_{\mathbf{R}_1-\mathbf{R}_2}t_{\omega\mathbf{R}_2}. \tag{B11}$$

With the linear transformations defined in Eq. (B8), the secular equation (B9), and the orthonormalization requirement Eq. (B10), the correlation contribution to the free energy Eq. (B6) can be written in diagonal form

$$F_{fl}^{(1)} = \frac{1}{2}\sum_{\omega} (\Lambda_\omega + k_BT)|Q_\omega|^2. \tag{B12}$$

We then assume a Boltzmann probability for the normal modes

$$W \sim \exp\left(-\frac{F_{fl}^{(1)}}{k_BT}\right). \tag{B13}$$

Inserting Eq. (B12) into Eq. (B13) leads to the Gaussian distribution for the normal modes,

$$W \sim \exp\left(-\frac{1}{2k_BT}\sum_{\omega}(\Lambda_\omega + k_BT)|Q_\omega|^2\right) = \prod_{\omega}\exp\left(-\frac{|Q_\omega|^2}{2k_BT/(\Lambda_\omega + k_BT)}\right). \tag{B14}$$

Finally the correlation function for the normal modes is given by

$$\langle|Q_\omega|^2\rangle = \frac{1}{1 + \Lambda_\omega/k_BT}. \tag{B15}$$

### B. The free energy functional

The fluctuation contribution to the internal energy

$$\Delta E = \frac{1}{2}\sum_{\mathbf{R}_1\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2}\langle\delta P'_{\mathbf{R}_1}\delta P'_{\mathbf{R}_2}\rangle \tag{B16}$$

can be rewritten as

$$\Delta E = \frac{1}{2}\sum_{\omega}\Lambda_\omega\langle|Q_\omega|^2\rangle - \frac{N}{2}\lambda c(1-c). \tag{B17}$$

The equilibrium correlation contribution to the free energy is then given by

$$\Delta F = k_BT\int_0^{1/k_BT}\Delta E^{(1)}d(1/k_BT') = \frac{k_BT}{2}\sum_{\omega}\Lambda_\omega\int_0^{1/k_BT}\langle|Q_\omega|^2\rangle d(1/k_BT') - \frac{N}{2}\lambda c(1-c). \tag{B18}$$

Performing the integration after inserting Eq. (B15) we derive

$$\Delta F = \frac{k_BT}{2}\sum_{\omega}\ln\left(1 + \frac{\Lambda_\omega}{k_BT}\right) - \frac{N}{2}\lambda c(1-c) = \frac{k_BT}{2}\ln\prod_{\omega}\left(1 + \frac{\Lambda_\omega}{k_BT}\right) - \frac{N}{2}\lambda c(1-c). \tag{B19}$$

There is a product of the eigenvalues under the logarithm sign in Eq. (B19). This product is equal to the determinant of the matrix $\|1+\frac{W_{\mathbf{R}_1\mathbf{R}_2}}{k_BT}\|$. Thus, the equilibrium correlation contribution to the free energy reads

$$\Delta F = \frac{k_BT}{2}\ln\det\|M_{\mathbf{R}_1,\mathbf{R}_2}\| - \frac{N}{2}\lambda c(1-c), \tag{B20}$$

with

$$\|M_{\mathbf{R}_1,\mathbf{R}_1}\| = \delta_{\mathbf{R}_1,\mathbf{R}_1} + \frac{\sqrt{P_{\mathbf{R}_1}(1-P_{\mathbf{R}_1})}(V_{\mathbf{R}_1-\mathbf{R}_2} + \lambda\delta_{\mathbf{R}_1,\mathbf{R}_2})\sqrt{P_{\mathbf{R}_2}(1-P_{\mathbf{R}_2})}}{k_BT}. \tag{B21}$$

## APPENDIX C: FLUCTUATIONS IN THE SECOND ITERATION OF THE CCA

The correlation contribution $F_{fl}^{(2)}(\{\delta P_{\mathbf{R}}\})$ to the free energy Eq. (73) in the second iteration of the CCA can be calculated using Eq. (22).

The first term in Eq. (B19)

$$-T\Delta S = \frac{k_BT}{2}\sum_{\omega}\ln\left(1 + \frac{\Lambda_\omega}{k_BT}\right) \tag{C1}$$

can be represented as

$$-T\Delta S = -\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{1}{n}\sum_{\omega}\left(-\frac{\Lambda_\omega}{k_BT}\right)^n, \tag{C2}$$

where the eigenvalues $\Lambda_\omega$ are determined by Eq. (B11). In the following we use in Eq. (B8) the Fourier transformation as the similarity transformation $t_{\mathbf{R}\omega}=t_{\mathbf{R}\mathbf{k}}=e^{i\mathbf{k}\mathbf{R}}/N$. Then Eq. (B11) takes the form

$$\Lambda_\omega = \Lambda_{\mathbf{k}} = \sum_{\mathbf{R}_1,\mathbf{R}_2}\frac{e^{-i\mathbf{k}\mathbf{R}_1}}{N}W_{\mathbf{R}_1-\mathbf{R}_2}\frac{e^{i\mathbf{k}\mathbf{R}_2}}{N} = W_{\mathbf{k}}, \tag{C3}$$

with $W_{\mathbf{k}}$ as the Fourier transform of $W_{\mathbf{R}_1-\mathbf{R}_2}$ defined in Eq. (B7).

Substituting Eq. (C3) into Eq. (C2) gives

$$-T\Delta S = -\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{1}{n}\sum_{\mathbf{k}}\left(-\frac{W_{\mathbf{k}}}{k_BT}\right)^n. \tag{C4}$$

Performing the series of identity transformations we obtain

$$
\begin{aligned}
-T\Delta S &= -\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{1}{n}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\left(-\frac{W_{\mathbf{k}_1}}{k_BT}\right)\left(-\frac{W_{\mathbf{k}_2}}{k_BT}\right)\cdots\left(-\frac{W_{\mathbf{k}_n}}{k_BT}\right)\delta_{\mathbf{k}_1-\mathbf{k}_n}\delta_{\mathbf{k}_2-\mathbf{k}_1}\delta_{\mathbf{k}_3-\mathbf{k}_2}\cdots\delta_{\mathbf{k}_n-\mathbf{k}_{n-1}} \\
&= -\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{1}{n}\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}\frac{1}{N^n}\sum_{\mathbf{k}_1}\left(-\frac{W_{\mathbf{k}_1}}{k_BT}\right)e^{i\mathbf{k}_1(\mathbf{R}_1-\mathbf{R}_2)}\sum_{\mathbf{k}_2}\left(-\frac{W_{\mathbf{k}_2}}{k_BT}\right)e^{i\mathbf{k}_2(\mathbf{R}_2-\mathbf{R}_3)}\times\cdots\times\sum_{\mathbf{k}_n}\left(-\frac{W_{\mathbf{k}_n}}{k_BT}\right)e^{i\mathbf{k}_n(\mathbf{R}_n-\mathbf{R}_1)} \\
&= -\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{1}{n}\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}\left(-\frac{W_{\mathbf{R}_1-\mathbf{R}_2}}{k_BT}\right)\left(-\frac{W_{\mathbf{R}_2-\mathbf{R}_3}}{k_BT}\right)\cdots\left(-\frac{W_{\mathbf{R}_n-\mathbf{R}_1}}{k_BT}\right),
\end{aligned}
\tag{C5}
$$

where the delta function $\delta_{\mathbf{k}_m,\mathbf{k}_n}$ is defined as

$$
\delta_{\mathbf{k}_m,\mathbf{k}_n}=\frac{1}{N}\sum_{\mathbf{R}}e^{-i(\mathbf{k}_m-\mathbf{k}_n,\mathbf{R})}. \tag{C6}
$$

Taking into account the definition given in Eq. (B7), Eq. (C5) can be represented as

$$
\begin{aligned}
-T\Delta S = -\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}\prod_{i=1}^{n}P_{\mathbf{R}_i} \\
\times(1-P_{\mathbf{R}_i})v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1},
\end{aligned}
\tag{C7}
$$

where

$$
v_{\mathbf{R}_1-\mathbf{R}_2}=\frac{V_{\mathbf{R}_1-\mathbf{R}_2}+\lambda\delta_{\mathbf{R}_1,\mathbf{R}_2}}{k_BT}, \tag{C8}
$$

and its Fourier transformation is given by

$$
v_{\mathbf{k}}=\frac{V_{\mathbf{k}}+\lambda}{k_BT}. \tag{C9}
$$

Using the definition $P_{\mathbf{R}}=c+\delta P_{\mathbf{R}}$ Eq. (C7) can be rewritten as

$$
-T\Delta S=-\frac{k_BT}{2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}\xi v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}, \tag{C10}
$$

with

$$
\begin{aligned}
\xi = [c(1-c)]^n-[c(1-c)]^{n-1}(1-2c)\sum_{i=1}^{n}\delta P_{\mathbf{R}_i}+[c(1 \\
-c)]^{n-2}(1-2c)^2\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{n}\delta P_{\mathbf{R}_i}\delta P_{\mathbf{R}_j}-[c(1-c)]^{n-1}\sum_{i=1}^{n}\delta P^2_{\mathbf{R}_i}.
\end{aligned}
\tag{C11}
$$

We now split Eq. (C10) in to a sum of the following terms:

$$
\begin{aligned}
-T\Delta S = \frac{k_BT}{2}A_1+\frac{k_BT(1-2c)}{2c(1-c)}A_2+\frac{k_BT(1-2c)^2}{4[c(1-c)]^2}A_3 \\
+\frac{k_BT}{2c(1-c)}A_4,
\end{aligned}
\tag{C12}
$$

with

$$
A_1=-\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}, \tag{C13}
$$

$$
A_2=\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\sum_{i=1}^{n}\delta P_{\mathbf{R}_i}, \tag{C14}
$$

$$
A_3=-\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{n}\delta P_{\mathbf{R}_i}\delta P_{\mathbf{R}_j}, \tag{C15}
$$

$$
A_4=\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\sum_{i=1}^{n}\delta P^2_{\mathbf{R}_i}. \tag{C16}
$$

In the following we calculate explicit forms for the terms $A_i$. Using the Fourier transformation defined in Eq. (16), the $\delta$ function defined in Eq. (C6), the definition Eq. (C9), and the representation $\ln(1+x)=-\sum_{n=1}^{\infty}\frac{1}{n}(-x)^n$ we find

$$
A_1=-\sum_{\mathbf{k}}\sum_{n=1}^{\infty}\frac{1}{n}[-c(1-c)v_{\mathbf{k}}]^n=\sum_{\mathbf{k}}\ln[1+c(1-c)v_{\mathbf{k}}]. \tag{C17}
$$

Equation (4) implies that $A_2=0$.

Using the Fourier transformations defined by Eqs. (6) and (16) in Eq. (C15) we perform the following transformations:

$$\begin{aligned}
A_3 &= -\sum_{n=1}^{\infty}\frac{(-1)^n}{n}[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\sum_{\substack{i,j\\ i\neq j}}^{n}\delta P_{\mathbf{R}_i}\delta P_{\mathbf{R}_j}\\
&= -\sum_{n=1}^{\infty}(-1)^n[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\sum_{j=2}^{n}\delta P_{\mathbf{R}_j} = -\sum_{n=1}^{\infty}\frac{(-1)^n[c(1-c)]^n}{N^n}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\sum_{\mathbf{k}',\mathbf{k}''}v_{\mathbf{k}_1}v_{\mathbf{k}_2}\cdots v_{\mathbf{k}_n}\delta P_{\mathbf{k}'}\delta P_{\mathbf{k}''}\\
&\quad\times\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}e^{i\mathbf{k}_1(\mathbf{R}_1-\mathbf{R}_2)}\ldots e^{i\mathbf{k}_n(\mathbf{R}_n-\mathbf{R}_1)}e^{i\mathbf{k}'\mathbf{R}_1}\sum_{j=2}^{n}e^{i\mathbf{k}''\mathbf{R}_j} = -\sum_{n=1}^{\infty}\frac{(-1)^n[c(1-c)]^n}{N^n}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\sum_{\mathbf{k}',\mathbf{k}''}v_{\mathbf{k}_1}v_{\mathbf{k}_2}\cdots v_{\mathbf{k}_n}\delta P_{\mathbf{k}'}\delta P_{\mathbf{k}''}\\
&\quad\times\Bigg(\sum_{\mathbf{R}_1}e^{i\mathbf{R}_1(\mathbf{k}'+\mathbf{k}_1-\mathbf{k}_n)}\sum_{\mathbf{R}_2}e^{i\mathbf{R}_2(\mathbf{k}''-\mathbf{k}_1+\mathbf{k}_2)}\sum_{\mathbf{R}_3}e^{i\mathbf{R}_3(\mathbf{k}_3-\mathbf{k}_2)}\ldots\sum_{\mathbf{R}_n}e^{i\mathbf{R}_n(\mathbf{k}_n-\mathbf{k}_{n-1})}\\
&\quad+\sum_{\mathbf{R}_1}e^{i\mathbf{R}_1(\mathbf{k}'+\mathbf{k}_1-\mathbf{k}_n)}\sum_{\mathbf{R}_2}e^{i\mathbf{R}_2(\mathbf{k}_2-\mathbf{k}_1)}\sum_{\mathbf{R}_3}e^{i\mathbf{R}_2(\mathbf{k}''-\mathbf{k}_2+\mathbf{k}_3)}\ldots\sum_{\mathbf{R}_n}e^{i\mathbf{R}_n(\mathbf{k}_n-\mathbf{k}_{n-1})}+\cdots\\
&\quad+\sum_{\mathbf{R}_1}e^{i\mathbf{R}_1(\mathbf{k}'+\mathbf{k}_1-\mathbf{k}_n)}\sum_{\mathbf{R}_2}e^{i\mathbf{R}_2(\mathbf{k}_2-\mathbf{k}_1)}\sum_{\mathbf{R}_3}e^{i\mathbf{R}_3(\mathbf{k}_3-\mathbf{k}_2)}\ldots\sum_{\mathbf{R}_n}e^{i\mathbf{R}_n(\mathbf{k}_n-\mathbf{k}_{n-1}+\mathbf{k}'')}\Bigg).
\end{aligned}\tag{C18}$$

The term in large parentheses is a sum of the $\delta$ function [Eq. (C6)] products. Performing simple but cumbersome transformations Eq. (C18) can be simplified to

$$A_3=-\sum_{\mathbf{k},\mathbf{q}}\sum_{n=2}^{\infty}\sum_{i=1}^{n-1}[-c(1-c)v_{\mathbf{q}}]^i[-c(1-c)v_{\mathbf{k}-\mathbf{q}}]^{n-i}|\delta P_{\mathbf{k}}|^2.\tag{C19}$$

Taking into account the algebraic relation

$$\sum_{n=2}^{\infty}\sum_{i=1}^{n-1}(-x)^i(-y)^{n-i}=\frac{xy}{(x+1)(y+1)},\tag{C20}$$

$A_3$ can then be written as

$$A_3=-[c(1-c)]^2\sum_{\mathbf{k},\mathbf{q}}\frac{v_{\mathbf{q}}v_{\mathbf{k}-\mathbf{q}}}{[1+c(1-c)v_{\mathbf{q}}][1+c(1-c)v_{\mathbf{k}-\mathbf{q}}]}|\delta P_{\mathbf{k}}|^2.\tag{C21}$$

Performing the Fourier transformations defined in Eqs. (6) and (16) $A_4$ reads

$$\begin{aligned}
A_4 &= \sum_{n=1}\frac{(-1)^n}{n}[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\sum_{i=1}^{n}\delta P^2_{\mathbf{R}_i} = \sum_{n=1}(-1)^n[c(1-c)]^n\sum_{\mathbf{R}_1,\ldots,\mathbf{R}_n}v_{\mathbf{R}_1-\mathbf{R}_2}v_{\mathbf{R}_2-\mathbf{R}_3}\cdots v_{\mathbf{R}_n-\mathbf{R}_1}\delta P^2_{\mathbf{R}_1}\\
&= \sum_{n=1}\frac{(-1)^n[c(1-c)]^n}{N^n}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}v_{\mathbf{k}_1}v_{\mathbf{k}_2}\cdots v_{\mathbf{k_n}}\sum_{\mathbf{k}',\mathbf{k}''}\delta P_{\mathbf{k}'}\delta P_{\mathbf{k}''}\times\Bigg(\sum_{\mathbf{R}_1}e^{i\mathbf{R}_1(\mathbf{k}'+\mathbf{k}''+\mathbf{k}_1-\mathbf{k}_n)}\sum_{\mathbf{R}_2}e^{i\mathbf{R}_2(\mathbf{k}_2-\mathbf{k}_1)}\ldots\sum_{\mathbf{R}_n}e^{i\mathbf{R}_n(\mathbf{k}_n-\mathbf{k}_{n-1})}\Bigg).
\end{aligned}\tag{C22}$$

Using the $\delta$ function defined in Eq. (C6) and the geometrical series

$$\frac{1}{1+x}=\sum_{n=1}^{\infty}(-x)^{n-1},\tag{C23}$$

we can rewrite Eq. (C22) in the simple form

$$\begin{aligned}
A_4 &= \sum_{\mathbf{k},\mathbf{q}}[-c(1-c)v_{\mathbf{q}}]\sum_{n=1}^{\infty}[-c(1-c)v_{\mathbf{q}}]^{n-1}|\delta P_{\mathbf{k}}|^2\\
&= -c(1-c)\sum_{\mathbf{k},\mathbf{q}}\frac{v_{\mathbf{q}}}{[1+c(1-c)v_{\mathbf{q}}]}|\delta P_{\mathbf{k}}|^2.
\end{aligned}\tag{C24}$$

Substituting expressions for $A_1$, $A_2$, $A_3$, and $A_4$ in Eq. (C12) and using the definition Eq. (C9) results in

$$-T\Delta S=\frac{k_BT}{2}\sum_{\mathbf{k}}\ln\left(1+\frac{c(1-c)(V_{\mathbf{k}}+\lambda)}{k_BT}\right)-\frac{1}{2}\sum_{\mathbf{k},\mathbf{q}}\frac{(V_{\mathbf{q}}+\lambda)}{\left(1+\frac{c(1-c)(V_{\mathbf{q}}+\lambda)}{k_BT}\right)}|\delta P_{\mathbf{k}}|^2 -\frac{(1-2c)^2}{4k_BT}\sum_{\mathbf{k},\mathbf{q}}\frac{(V_{\mathbf{q}}+\lambda)(V_{\mathbf{k}-\mathbf{q}}+\lambda)}{\left(1+\frac{c(1-c)(V_{\mathbf{k}}+\lambda)}{k_BT}\right)\left(1+\frac{c(1-c)(V_{\mathbf{k}-\mathbf{q}}+\lambda)}{k_BT}\right)}|\delta P_{\mathbf{k}}|^2. \tag{C25}$$

Thus,

$$-T\Delta S=\Delta F+N\frac{\lambda}{2}c(1-c)+F_{fl}^{(2)}=\frac{k_BT}{2}\sum_{\mathbf{k}}\ln\left(1+\frac{c(1-c)(V_{\mathbf{k}}+\lambda)}{k_BT}\right)+F_{fl}^{(2)}, \tag{C26}$$

with $\Delta F$ determined by Eq. (58) and

$$F_{fl}^{(2)}=\left(-\frac{1}{2}\sum_{\mathbf{k},\mathbf{q}}\frac{(V_{\mathbf{q}}+\lambda)}{\left(1+\frac{c(1-c)(V_{\mathbf{q}}+\lambda)}{k_BT}\right)}-\frac{(1-2c)^2}{4k_BT}\sum_{\mathbf{k},\mathbf{q}}\frac{(V_{\mathbf{q}}+\lambda)(V_{\mathbf{k}-\mathbf{q}}+\lambda)}{\left(1+\frac{c(1-c)(V_{\mathbf{q}}+\lambda)}{k_BT}\right)\left(1+\frac{c(1-c)(V_{\mathbf{k}-\mathbf{q}}+\lambda)}{k_BT}\right)}\right)|\delta P_{\mathbf{k}}|^2. \tag{C27}$$

Finally, the derivative of the correlation contribution into the Gibbs free energy in the second iteration of the CCA reads

$$\frac{\partial^2F_{fl}^{(2)}}{\partial\delta P_{\mathbf{k}}\partial\delta P_{-\mathbf{k}}}=-\sum_{\mathbf{q}}\frac{(V_{\mathbf{q}}+\lambda)}{\left(1+\frac{c(1-c)(V_{\mathbf{q}}+\lambda)}{k_BT}\right)}-\frac{(1-2c)^2}{2k_BT}\sum_{\mathbf{q}}\frac{(V_{\mathbf{q}}+\lambda)(V_{\mathbf{k}-\mathbf{q}}+\lambda)}{\left(1+\frac{c(1-c)(V_{\mathbf{q}}+\lambda)}{k_BT}\right)\left(1+\frac{c(1-c)(V_{\mathbf{k}-\mathbf{q}}+\lambda)}{k_BT}\right)}. \tag{C28}$$

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