Overcomplete Free Energy Functional for $D=1$ Particle Systems with Next Neighbor Interactions

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We deduce an overcomplete free energy functional for $D=1$ particle systems with next neighbor interactions, where the set of redundant variables are the local block densities ϱ_i of i interacting particles. The idea is to analyze the decomposition of a given pure system into blocks of i interacting particles by means of a mapping onto a hard rod mixture. This mapping uses the local activity of component i of the mixture to control the local association of i particles of the pure system. Thus it identifies the local particle density of component i of the mixture with the local block density ϱ_i of the given system. Consequently, our overcomplete free energy functional takes on the hard rod mixture form with the set of block densities ϱ_i representing the sequence of partition functions of the local aggregates of particle numbers i. The system of equations for the local particle density ϱ of the original system is closed via a subsidiary condition for the block densities in terms of ϱ. Analoguous to the uniform isothermal-isobaric technique, all our results are expressible in terms of effective pressures. We illustrate the theory with two standard examples, the adhesive interaction and the square-well potential. For the uniform case, our proof of such an overcomplete format is based on the exponential boundedness of the number of partitions of a positive integer (Hardy-Ramanujan formula) and on Varadhan's theorem on the asymptotics of a class of integrals.

1. INTRODUCTION

The era of the class of exactly solvable $D=1$ particle systems with next neighbor interactions in classical density functional theory (for an overview see, e.g., ref. 10) began in 1976, when Percus derived the free energy density functional for hard rods in an arbitrary external potential field.[8] Soon

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afterwards, he presented the inverse operator format.[9] This formalism not only allowed him to simplify the derivation of the hard rod functional, but also led him to the solution of the sticky core model, in which the interaction has a 0-range attractive component. Moreover, he showed that—analoguous to the uniform case—the adhesive interaction is the only potential with an attractive component, where an explicit solution is possible. The generalization of the pure hard core result to an additive mixture of hard rods was established by Vanderlick, Davis, and Percus in 1989.[14] Already a few years later, Brannock and Percus constructed along Wertheim's theory of local association (for a stringent review of Wertheim's approach see ref. 10) a free energy density functional for multicomponent systems with arbitrary next neighbor interactions.[2] One of the specific examples treated was the one-component case of the prototypical square-well interaction, called Herzfeld Goeppert-Mayer (HGM) system.[5] In abstracting from this Wertheim local association free energy density functional format, Percus invented in 1997 the overcompleteness technique.[11] In this paper, we present a particular realization of this strategy.

The essential idea of an overcomplete description[11] of thermodynamic functionals is to introduce a set of additional variables (over the basic local particle density ϱ) such that with respect to a direct evaluation the overcomplete format has a simpler formal structure and is physically more transparent. Thus, apart from the purely mathematical problem of deriving such a representation from first-principles, the second difficulty[11] is to give a physical interpretation for the redundant variables.

In our approach we use an observation of Kierlik and Rosinberg[7] to overcome the latter difficulty. Their idea, although stated originally only for nonuniform dimerizing hard rods (for the uniform case see, e.g., ref. 5), consists in interpreting a $D = 1$ particle system with next neighbor interactions as composed of blocks (clusters,[6] molecules,[5, 7] or superparticles[2]) of i interacting particles (monomers, dimers, trimers,...) and to use the corresponding local block densities ϱ_i as the set of additional variables. Here two particles are understood to interact, if in the standard decomposition of the Boltzmann factor into a reference hard core and an attractive part, (1.3), the interaction between the two particles is described by the latter one. Since the blocks of local aggregates interact by construction via hard core potentials, the free energy functional takes on the simple hard rod mixture form. In such an overcomplete description the physical significance of the redundant variables is given at the outset.

So our program is to analyze a given pure system with arbitrary next neighbor interactions by means of a mapping onto a hard rod mixture. This mapping uses the local activity of component i of the mixture to represent the local aggregates of i particles of the pure system and so it

identifies the local particle density of component i of the mixture with the local block density ϱ_i of the original system. Consequently, with the free energy of hard rod mixture form, the set of local block densities represents the sequence of partition functions of the local aggregates with particle numbers i. We close the system of equations for the local particle density via a relation between ϱ and the block densities inferred through a trivial identity of functional analysis.

Thus already implicitly formulated by Kierlik and Rosinberg,[7] they settled this general program only for the special case of dimerizing hard rods. They argued that, although this technique can be extended to the more general case of sticky cores, where blocks of any number of particles coexist, the possible difficulty of this method lies in the definition of blocks for arbitrary next neighbor interactions. So they proceeded with Wertheim's theory instead. They (i) showed that Wertheim's first-order thermodynamic perturbation theory (TPT1) is exact for dimerizing hard rods as well as for sticky cores and (ii) derived density functionals for these systems with the simple hard rod mixture form through TPT1. Later on, the exactness of the TPT1 also for sticky core mixtures was established by Brannock and Percus.[2]

Actually, already Brannock and Percus[2] used the block interpretation of Kierlik and Rosinberg[7] to construct an overcomplete free energy functional. But only formally, as a purely technical intermediate step in their proof, because their aim was to infer density functionals that take on the Wertheim local association form. However, in such an overcomplete description the remarkable hard rod mixture form of the free energy is obscured. As already stated, again Kierlik and Rosinberg[7] first revealed that at least for dimerizing hard rods and for sticky cores, functionals of the simple hard rod mixture form underly the Wertheim functionals.

Similarly, also with respect to the relative density format of Percus,[11] another earlier and formally alike equivalent overcomplete description, where the redundant variables are partition function densities, our realization has a simpler formal characterization (in terms of a functional of hard rod mixture form) and is physically more transparent (with the block densities as the elements of the theory). Moreover, all our main results possess higher dimensional analogues, so that our overcomplete description immediately suggests $D > 1$ models as well.

Formally, we start from the (configurational) isothermal measure (or the Gibbs measure thereof) for a particle system on the line $\mathbb{R}$ with next neighbor interactions, given by the density

$$\prod_{k=1}^{n-1} e(q_{k+1}, q_k) \prod_{k=1}^{n} \exp[-\beta U(q_k)] \tag{1.1}$$

with respect to the usual Lebesgue measure. Here, n denotes the number of particles, their positions being $q_k \in \mathbb{R}$, U is the external potential, and the translation-invariant interaction V is represented by the Boltzmann factor (at reciprocal temperature β)

$$e(y, x) = \begin{cases} \exp[-\beta V(y-x)] & \text{for} \quad y \geqslant x, \\ 0 & \text{for} \quad y < x. \end{cases} \tag{1.2}$$

We assume that V has a hard core of diameter $a > 0$. Hence if we restrict ourselves to the next neighbor case, the range of V is $2a$, i.e., $V(x) \equiv 0$, $x \geqslant 2a$. Furthermore, we introduce the standard decomposition (for a related analysis based on a different decomposition see, e.g., ref. 6)

$$e(y, x) = h_a(y-x) + f(y, x) \tag{1.3}$$

with h_a the Heaviside function shifted to the right by a and $f(y, x) = h_a(y-x)[e(y, x) - 1]$, known as the attractive part of the Boltzmann factor.

First, we will treat for the sake of completeness the uniform case within our overcomplete description. This will also allow us to introduce the concept most clearly. Our account will be inductive. We are going to develop the theory along two standard examples, the sticky core model and the HGM system. Second, we will lift our overcomplete format to the general nonuniform case and illustrate the results with the two examples already examined for the uniform case.

2. UNIFORM CASE

In this section we introduce the concept of overcomplete description for the free energy of uniform systems with arbitrary next neighbor interactions. We derive such a representation from first-principles as $n \to \infty$ based on the exponential boundedness of the number of partitions of a positive integer n (Hardy-Ramanujan formula, see, e.g., ref. 1) and on Varadhan's theorem on the asymptotic behavior of a class of measures (see, e.g., ref. 4).

Formally, we assume $U(x) \equiv 0$, $x \in \mathbb{R}$. Then the total isothermal measure on $(0, l)^n$, under the condition that the particles be reflected elastically at the endpoints of the interval $(0, l)$ (the volume $|(0, l)| = l$ is called the length of the system), becomes

$$\exp[-n\beta f_n(l)] = \int_{(0, l)^n} \prod_{k=1}^{n-1} e(q_{k+1}, q_k) \, d(q_1, ..., q_n), \tag{2.1}$$

where we have introduced f_n known as the (configurational) n-particle free energy per particle.

For the sake of explicitness and to make contact with a previous paper,[7] we start our presentation with the sticky core model.

2.1. Adhesive Interaction

Adhesive particle systems are systems composed of hard rods with an additional attractive interaction on the boundary of the particles, which allows for local association. Thus an adhesive system may be represented as a limiting case of a HGM system. In such systems, the interaction is

$$V(x) = \begin{cases} +\infty & \text{for} \quad x \in [0, a), \\ -\mathscr{E}\chi_{[0,1)}(\frac{x-a}{d}) & \text{for} \quad x \in [a, \infty), \end{cases} \tag{2.2}$$

where d is the width of the well (note that we have restricted ourselves to $d \leqslant a$), $\mathscr{E}$ the interaction strength, and χ_A denotes the characteristic function of the set A. Then—on inserting (2.2) into (1.3) via (1.2)—adhesive systems are characterized by the limit

$$\lim_{\substack{\mathscr{E} \to \infty \\ d \to 0}} f(y, x)|_{de^{\beta\mathscr{E}} \to \lambda} = \lambda\, \delta_a(y-x) \tag{2.3}$$

with $\delta_a = h'_a$, $\lambda = \gamma a$, and $\gamma \in \mathbb{R}_+$ being the stickiness parameter of the interaction.

Hence, due to the 0-range attractive component (2.3), our overcomplete description for the n-particle sticky core model translates to the decomposition into blocks (monomers, dimers, trimers,..., n-mers) of pure hard core particles with diameters $(a_1,...,a_n)$, $a_i = ia$, and to the introduction of the n block densities as the set of redundant variables. Therefore f_n is defined on an enlarged space with n additional dimensions. Consequently, the free energy is calculated by means of a minimum principle, (2.14).

Formally, upon substituting (2.3) into (2.1) via (1.3), f_n can be interpreted as a sum over a binary tree with 2^{n-1} branches. Consider the contribution of an arbitrary branch, i.e., an arbitrary convolution sequence of h_a and $\lambda \delta_a$, to this sum. For $y, x \in (0, l)$ denote by a block (or cluster,[6] molecule,[5,7] or superparticle[2]) b_i of $i \in \{1,...,n\}$ interacting particles the convolution sequence

$$b_i(y, x) = \begin{cases} h_a(y-x) & \text{for} \quad i = 1, \\ b_{i-1} * \lambda\, \delta_a(y-x) & \text{for} \quad 1 < i \leqslant n \end{cases} \tag{2.4}$$

with $a * b(y, x) = \int_0^l a(y-z) \, b(z-x) \, dz$. Let k_i be the number of times b_i (modulo h_a at the right boundary) appears in such a branch. For each $n \geqslant 2$ define the set

$$A_n = \left\{ k = (k_1,\ldots, k_n) : k_i \in \{0,\ldots,n\} \wedge \sum_{i=1}^{n} i k_i = n \right\}. \qquad (2.5)$$

Fix $k \in A_n$. Then, on using the commutativity of the convolution (for another application of this elementary property see, e.g., ref. 6), we conclude that each of the

$$C(n, k) = \frac{(\sum_{i=1}^{n} k_i)!}{k_1! \cdots k_n!} \qquad (2.6)$$

branches characterized by the vector k contributes the same value to f_n. Again through the commutativity of the convolution, we can rearrange the blocks according to their length, starting with the group of k_1 particles of length a next to the origin, so that the total isothermal measure reduces to

$$\exp[-n\beta f_n(l)] = \sum_{k \in A_n} C(n, k) \, \lambda^{\sum_{i=1}^{n} (i-1) k_i} \exp[-n\beta f_{n,k}(l)] \qquad (2.7)$$

with

$$\begin{aligned}
\mathscr{L}\{\exp[-n\beta f_{n,k}(l)]\}(s) &= \frac{1}{s} \exp(as) \, s \prod_{i=1}^{n} \left[\frac{\exp(-ias)}{s} \right]^{k_i} \frac{1}{s} \\
&= \frac{1}{s} \frac{\exp[-(\sum_{i=1}^{n} i k_i - 1) \, as]}{s^{\sum_{i=1}^{n} k_i - 1}} \frac{1}{s}, \quad k \in A_n, \qquad (2.8)
\end{aligned}$$

where $\mathscr{L}\{\exp[-n\beta f_{n,k}(l)]\}(s)$ is the Laplace transform of $\exp[-n\beta f_{n,k}(l)]$ with respect to l and we used the relative positions

$$x_0 = q_1, \quad x_k = q_{k+1} - q_k \qquad \text{for} \quad 1 \leqslant k < n, \quad x_n = l - q_n \qquad (2.9)$$

as well as (2.4). On transforming back, we infer

$$\begin{aligned}
\exp[-n\beta f_n(l)] = h_{(n-1)a}(l) \sum_{k \in A_n} C(n, k) \, \lambda^{\sum_{i=1}^{n} (i-1) k_i} \\
\times \frac{[l - (\sum_{i=1}^{n} i k_i - 1) \, a]^{\sum_{i=1}^{n} k_i}}{(\sum_{i=1}^{n} k_i)!}. \qquad (2.10)
\end{aligned}$$

Finally, let us analyze the leading order asymptotic behavior of f_n for the nontrivial case $l > (n-1) \, a$. Denote by $\pi(n)$ the number of partitions of

a positive integer n. Since $|A_n| = \pi(n)$, it follows by the leading term of the asymptotic series of the Hardy-Ramanujan formula (see, e.g., ref. 1) that as $n \to \infty$

$$|A_n| \asymp \frac{1}{2\pi\sqrt{2}} \frac{d}{dn} \left[\frac{\exp\left(\frac{2\pi}{\sqrt{6}}\sqrt{n-\frac{1}{24}}\right)}{\sqrt{n-\frac{1}{24}}} \right]. \tag{2.11}$$

Hence the number of terms in the sum (2.10) is exponentially bounded. Thus one may determine the asymptotic behavior of f_n by the asymptotic behavior of the largest summand in (2.10). This is a standard argument of large deviation theory (see, e.g., ref. 4). Therefore, if we use a weak form of Stirling's formula, $\ln(n!) = n \ln n - n + O(\ln n)$, we find as $n \to \infty$

$$\frac{1}{n} \ln C(n, k) = \sum_{i=1}^{n} \frac{k_i}{n} \ln\left(\sum_{j=1}^{n} \frac{k_j}{n}\right) - \sum_{i=1}^{n} \frac{k_i}{n} \ln \frac{k_i}{n} + O\left(\frac{\ln n}{n}\right), \tag{2.12}$$

and so, on introducing the particle density $\rho^{-1} = l/n$ with $\rho < a^{-1}$ as $n \to \infty$ by $l > (n-1)\,a$, via (2.11) that

$$\lim_{n \to \infty} \beta f_n(\rho) = \lim_{n \to \infty} \min_{k \in A_n} \left\{ \sum_{i=1}^{n} \frac{k_i}{n} \left[\ln \frac{k_i}{n} - 1 - \ln \lambda^{i-1} - \ln\left(\rho^{-1} - a \sum_{i=1}^{n} i \frac{k_i}{n}\right) \right] \right\}. \tag{2.13}$$

By the properties of the sets $\{A_n\}_{n \geqslant 2}$, of the set $A = \{t = (t_1,\ldots) : t_i \geqslant 0 \wedge \sum_{i=1}^{\infty} i t_i = 1\}$, and of the function on the right hand side (RHS) of (2.13), we finally infer

$$\lim_{n \to \infty} \beta f_n(\rho) \equiv \beta f_\infty(\rho) = \min_{c \in A} \left\{ \sum_{i=1}^{\infty} c_i \left[\ln \frac{c_i}{\lambda^{i-1}} - 1 - \ln(\rho^{-1} - a) \right] \right\}, \tag{2.14}$$

where f_∞ is the free energy per particle. This proves (4.2)–(4.4) of ref. 7.

Fix $\gamma, a \in \mathbb{R}_+$, $\rho \in (0, a^{-1})$. The function appearing on the RHS of (2.14) is convex. Hence it attains its minimum at the unique value $c = (c_1,\ldots)$ with

$$c_i = \begin{cases} \dfrac{1}{(1 + \lambda\theta)^2} & \text{for} \quad i = 1, \\[4mm] \dfrac{c_1}{\left(\left(1 + \dfrac{1}{\lambda\theta}\right)\right)^{i-1}} & \text{for} \quad i > 1. \end{cases} \tag{2.15}$$

Here, while it is possible to write c directly as a function of ρ, we preferred to introduce for later reference the pressure p via the thermodynamic relation

$$\beta p(\rho) = \rho^2 \frac{\partial}{\partial \rho} \beta f_\infty(\rho) \qquad (2.16)$$

with $\theta \equiv \beta p(\rho)$. Thus we have by

$$\sum_{i=1}^{\infty} c_i = \frac{1}{1 + \lambda \theta} \qquad (2.17)$$

that

$$\theta(1 + \lambda \theta) = \frac{1}{\rho^{-1} - a}, \qquad (2.18)$$

or explicitly

$$\theta = \frac{1}{2\lambda} \left(-1 + \sqrt{1 + \frac{4\lambda}{\rho^{-1} - a}} \right). \qquad (2.19)$$

Therefore f_∞ simplifies to

$$\beta f_\infty(\rho) = -\ln(1 + \lambda \theta) - \theta(\rho^{-1} - a) + \ln \theta, \qquad (2.20)$$

which is the known result. Formula (2.15) is equivalent to the findings (4.5) and (4.7) of ref. 7.

As will be shown in Section 3, the remarkable hard rod mixture form of f_∞ as given by (2.14), is an instance of a general result that even holds true in the context of nonuniformity.

2.2. Arbitrary Next Neighbor Interactions

So far, we treated particle systems with adhesive interactions. Essentially, the full and explicit analysis was possible because of the contact nature of the adhesive potential. When arbitrary next neighbor interactions are present, only the minimum of the length of a block b_i of i interacting particles is ia. The purpose of the present subsection is to establish our overcompleteness technique for the general uniform case.

Formally, our proof of such an overcomplete description for uniform systems with arbitrary next neighbor interactions as $n \to \infty$ is based on the Hardy-Ramanujan formula, (2.11), and on an application of Varadhan's theorem on the asymptotic behavior of a class of measures (see, e.g., ref. 4).

Consider first the prototypical HGM system. Then, upon substituting (2.2) into (1.3) via (1.2), the total isothermal measure on $(0, l)^n$ is completely characterized by

$$f(y, x) = \lambda \, h_{a, d}(y - x) \tag{2.21}$$

with $h_{a, d} = h_a - h_{a+d}$ and $\lambda = e^{\beta \mathcal{E}} - 1$. Hence, as in the deduction of our overcomplete description for the adhesive interaction, we start the proof by analyzing an arbitrary branch of the binary tree associated with f_n. Let us again decompose such a branch into k_i (modulo h_a at the right boundary) blocks b_i of $i \in \{1, ..., n\}$ interacting particles, now defined by the convolution sequence [cf. (2.4)]

$$b_i(y, x) = \begin{cases} h_a(y - x) & \text{for} \quad i = 1, \\ b_{i-1} * \lambda \, h_{a, d}(y - x) & \text{for} \quad 1 < i \leqslant n. \end{cases} \tag{2.22}$$

Then, via (2.9) as well as (2.22) and on using the commutativity of the convolution, we conclude that

$$\exp[-n\beta f_n(l)] = \sum_{k \in A_n} C(n, k) \, \lambda^{\sum_{i=1}^{n}(i-1) k_i} \exp[-n\beta f_{n, k}(l)] \tag{2.23}$$

with

$$\begin{aligned} \mathcal{L}\{\exp[-n\beta f_{n, k}(l)]\}(s) &= \frac{1}{s} \exp(as) \, s \prod_{i=1}^{n} \left\{ \frac{\exp(-ias)}{s} \left[\frac{1 - \exp(-ds)}{s} \right]^{i-1} \right\}^{k_i} \frac{1}{s} \\ &= \frac{1}{s} \left[\frac{\exp(-as)}{s} \right]^{n-1} [1 - \exp(-ds)]^{\sum_{i=1}^{n}(i-1) k_i} \frac{1}{s}. \end{aligned} \tag{2.24}$$

Next, let as usual $l = n\rho^{-1}$, and consider the asymptotic behavior of f_n for the nontrivial case $\rho^{-1} > a$. Since $|A_n|$ is exponentially bounded as $n \to \infty$ by the Hardy-Ramanujan formula, (2.11), the asymptotics of f_n is governed by the asymptotic behavior of the largest summand in (2.23). Thus, by the formal structure of (2.23), the analysis of f_n as $n \to \infty$ reduces to an asymptotic evaluation of $f_{n, k}$. If we combine such an evaluation of

$f_{n,k}$ as $n \to \infty$ by means of Varadhan's theorem (see, e.g., ref. 4) with (2.12), we finally infer for $\beta \in (0, \infty)$

$$\beta f_{\infty}(\rho) = \min_{c \in A} \left(\sum_{i=1}^{\infty} c_i \ln \frac{c_i}{\lambda^{i-1} \sum_{j=1}^{\infty} c_j} \right.$$
$$\left. - \min_{\theta \in \mathbb{R}_+} \left\{ \theta(\rho^{-1} - a) - \ln \theta + \left(1 - \sum_{i=1}^{\infty} c_i \right) \ln[1 - \exp(-\theta d)] \right\} \right). \tag{2.25}$$

The case $\beta = \infty$ has to be treated separately (see, e.g., ref. 6).

Fix $a, \rho^{-1}, \mathscr{E}, d, \beta \in \mathbb{R}_+$ such that $d \leq a$ and $\rho^{-1} > a$. Then the function appearing on the RHS of (2.25) is convex. Hence the minimum is attained at the unique value $c = (c_1, \dots)$ with

$$c_i = \begin{cases} \dfrac{1}{\{1 + \lambda[1 - \exp(-\theta d)]\}^2} & \text{for} \quad i = 1, \\[4mm] \dfrac{c_1}{\left\{ 1 + \dfrac{1}{\lambda[1 - \exp(-\theta d)]} \right\}^{i-1}} & \text{for} \quad i > 1, \end{cases} \tag{2.26}$$

and thus

$$\sum_{i=1}^{\infty} c_i = \frac{1}{1 + \lambda[1 - \exp(-\theta d)]}. \tag{2.27}$$

Therefore f_{∞} simplifies for $\beta \in (0, \infty)$ to

$$\beta f_{\infty}(\rho) = -\ln\{1 + \lambda[1 - \exp(-\theta d)]\} - \theta(\rho^{-1} - a) + \ln \theta, \tag{2.28}$$

which is the known result. In the sticky limit $\mathscr{E} \to \infty \wedge d \to 0$ such that $d e^{\beta \mathscr{E}} \to \gamma a$, expressions (2.28) respective (2.26) reduce to (2.20) respective (2.15). An approximation of (2.26) was given by Herzfeld and Goeppert-Mayer already in 1934.[5]

Moreover, through (2.16) and (2.25), we have the interpretation

$$\theta \equiv \beta p(\rho), \tag{2.29}$$

and so, upon using (2.26) in (2.25), that the pressure for $\beta \in (0, \infty)$ is uniquely determined by

$$\rho^{-1} - a = \frac{1}{\beta p} - \frac{d}{\exp(\beta p d)\left(1 + \dfrac{1}{\lambda}\right) - 1}. \tag{2.30}$$

Hence, p is a differentiable function with range $\mathbb{R}_+$. In particular, we have $\frac{\partial p}{\partial \rho} > 0$.

Finally, since Varadhan's theorem allows us to analyze the asymptotic behavior of a large class of total measures $f_{n,k}$, our scheme of proof for the HGM system extends directly to (in this sense) arbitrary next neighbor interactions. This completes our presentation of the uniform case.

3. NONUNIFORM CASE

We now generalize the ideas of Section 2 to the nonuniform case. Our approach is formal. We assume that for a sufficiently large class of pair interactions V and external potentials U the corresponding free energy density functional exists and is convex. In fact, Chayes and Chayes[3] showed, that for our domain of interest of $D = 1$ particle systems with stable (see, e.g., ref. 13) hard core next neighbor interactions, the set of external potentials for which a convex free energy density functional exists is nonempty. Thus, our calculus solves indeed a well-posed inverse problem for (in this sense) arbitrary next neighbor interactions.

We construct our overcomplete free energy functional through a reduction of the original problem to a readily solvable multicomponent inverse problem. The blocks of i interacting particles [cf. for the uniform case the instances (2.4) respective (2.22)] are controlled by an effective local activity of component i of the mixture. Hence, since the blocks interact by definition via hard core potentials, the interaction between components i and j of the mixture is represented by an effective pure hard core Boltzmann factor. Thus, we reduce the inverse problem for arbitrary next neighbor interactions to a type of polydisperse hard rod mixture problem. Consequently, we first extend the technique of proof of Vanderlick, Davis, and Percus[14] for an additive mixture of pure hard cores in an external field to our case of polydispersity. Results for the local block densities are given next. Finally, the isomorphism between the original and our overcomplete description is established via a trivial identity of functional analysis.

The presentation of the nonuniform case closes with the two examples already treated at the uniform level. The especially suggestive formal structure of these results provides evidence for our conjecture on a direct nonuniform isothermal-isobaric representation.

3.1. Overcomplete Free Energy Functional Format

We start with the standard description of nonuniform systems in direct form. So consider first the Gibbs measure (see, e.g., ref. 13) of (1.1) at chemical potential μ (implicitly including the momentum contributions). Denote the local activity by $z(x) = \exp\{\beta[\mu - U(x)]\}$. Then the total Gibbs measure becomes[9] [in Dirac notation $ab \equiv ab(y, x) = \int_{\mathbb{R}} a(y, z) \, b(z, x) \, dz$]

$$\Xi = 1 + Iz(\mathbb{I} - ez)^{-1} I, \tag{3.1}$$

where $\mathbb{I}$ is the identity, I represents the constant $I(x) = 1$, z refers to the matrix with elements $z(y, x) = z(x) \, \delta(y - x)$, and e is given by (1.2). If $\lim_{x \to \pm\infty} z(x) = 0$ sufficiently rapidly, then Ξ exists. Hence, on following Percus,[9, 11] the local particle density ϱ can be written as

$$\varrho(x) = \frac{\delta \ln \Xi}{\delta \ln z(x)} = \frac{1}{\Xi} \, \Xi_i^+(x) \, z(x) \, \Xi^-(x) \tag{3.2}$$

with

$$\Xi^- = (\mathbb{I} - ez)^{-1} I, \qquad \Xi^+ = I(\mathbb{I} - ze)^{-1}, \tag{3.3}$$

and thus we have by (1.2) as well as $\lim_{x \to \pm\infty} z(x) = 0$ the boundary conditions

$$\lim_{x \to -\infty} \Xi^-(x) = \lim_{x \to +\infty} \Xi^+(x) = 1, \tag{3.4a}$$

$$\lim_{x \to +\infty} \Xi^-(x) = \lim_{x \to -\infty} \Xi^+(x) = \Xi, \tag{3.4b}$$

$$\lim_{x \to \pm\infty} \varrho(x) = 0. \tag{3.4c}$$

The strategy is to determine z as a functional of ϱ for (in the above sense) arbitrary V. The main stage to settle this inverse problem is the concept of overcomplete description, formulated next.

Consider the Gibbs measure for a nonuniform multicomponent system on the line $\mathbb{R}$,[14, 11] where the local activity of component i is given by [henceforth a bar signifies a quantity within the overcomplete description]

$$\bar{w}_i(x, l) = z(fz)^{i-1} \left(x + \tfrac{l}{2}, x - \tfrac{l}{2}\right). \tag{3.5}$$

Here, x is the position of the block of i interacting particles, $l+a$ its diameter with l being the distance between the boundary particles, and f is brought in via (1.3). Hence definition (3.5), as the total isothermal measure of a i particle system in a box $(x-\frac{l}{2}, x+\frac{l}{2})$ with fixed boundary particles and Boltzmann factor f, controls the local aggregates. So the block description [cf. for the uniform case the examples (2.4) respective (2.22)] is completed by the pure hard core Boltzmann factor between components i and j, given within the present parameterization by

$$\bar{e}_{ij}(x, x', l, l') = h_{\frac{l+l'}{2}+a}(x-x'). \tag{3.6}$$

Then, on assuming that the indices of the blocks are determined statistically,[14, 11] the total Gibbs measure for such a mixture can be written as (cf. refs. 14 and 11)

$$\bar{\bar{\Xi}} = 1 + \bar{I}^T \bar{w} (\mathbb{I} - \bar{e}\bar{w})^{-1} \bar{I}, \tag{3.7}$$

where $\bar{e}$ is the matrix whose elements are $\bar{e}_{ij}(x, x', l, l')$, $\bar{w}$ represents the matrix $\bar{w}_{ij}(x, x', l, l') = \bar{w}_i(x, l) \, \delta(x-x') \, \delta(l-l') \, \delta_{ij}$, $\bar{I}_i(x) = 1$ is the constant vector, and we used the Dirac-Einstein notation $ab \equiv a_{ik}b_{kj}(y, x)$ $= \sum_{k=1}^{\infty} \int_{\mathbb{R}} a_{ik}(y, z) \, b_{kj}(z, x) \, dz$. A term by term analysis of the sums (3.1) and (3.7) shows $\bar{\bar{\Xi}} \equiv \Xi$. Hence we conclude

$$\Xi = 1 + \bar{I}^T \bar{w} (\mathbb{I} - \bar{e}\bar{w})^{-1} \bar{I}, \tag{3.8}$$

which is the desired overcomplete description in direct form. Similarly, upon using $\sum_{i=1}^{\infty} (fz)^{i-1} = (\mathbb{I} - fz)^{-1}$, the equivalence of (3.7) with the Brannock-Percus format[2] can be formally established. Finally, the local block densities are found to be

$$\varrho_i(x, l) = \frac{\delta \ln \Xi}{\delta \ln \bar{w}_i(x, l)} = \frac{1}{\Xi} \bar{\Xi}^+(x, l) \, \bar{w}_i(x, l) \, \bar{\Xi}^-(x, l) \tag{3.9}$$

with

$$\bar{\Xi}^- = (\mathbb{I} - \bar{e}\bar{w})^{-1} \bar{I}, \qquad \bar{\Xi}^+ = \bar{I}^T(\mathbb{I} - \bar{w}\bar{e})^{-1}. \tag{3.10}$$

Therefore by (3.6) and again $\lim_{x \to \pm\infty} z(x) = 0$ we have for $l \in \mathbb{R}$

$$\lim_{x \to -\infty} \bar{\Xi}^-(x, l) = \lim_{x \to +\infty} \bar{\Xi}^+(x, l) = 1, \tag{3.11a}$$

$$\lim_{x \to +\infty} \bar{\Xi}^-(x, l) = \lim_{x \to -\infty} \bar{\Xi}^+(x, l) = \Xi, \tag{3.11b}$$

$$\lim_{x \to \pm\infty} \varrho_i(x, l) = 0. \tag{3.11c}$$

Now, what makes the overcomplete description (3.8) more handy than the original formulation (3.1) is, that as for an additive hard rod mixture $\bar{e}$ is of rank 1 on index space (cf. ref. 11), and hence can be immediately written as

$$\bar{e}_{ij} = h_{\frac{l+a}{2}}\delta_{\frac{l'+a}{2}} = \delta_{\frac{l+a}{2}}h_{\frac{l'+a}{2}}. \tag{3.12}$$

Correspondingly, the technique of proof of ref. 14 for the free energy functional of additive mixtures of hard rods goes indeed through, with only minor modifications, for the case of our overcomplete free energy functional for arbitrary next neighbor interactions.

The details are as follows. Introduce the one-dimensional auxiliary functions (cf. ref. 14)

$$\bar{A}^-(x) = \sum_{i=1}^{\infty} \int_{\mathbb{R}^2} \delta_{\frac{l+a}{2}}(x-x')\,\bar{w}_i(x',l')\,\bar{\Xi}^-(x',l')\,d(x',l'), \tag{3.13a}$$

$$\bar{A}^+(x) = \sum_{i=1}^{\infty} \int_{\mathbb{R}^2} \bar{\Xi}^+(x',l')\,\bar{w}_i(x',l')\,\delta_{\frac{l'+a}{2}}(x'-x)\,d(x',l'), \tag{3.13b}$$

as well as

$$\bar{\Xi}^-(x) = 1 + \int_{-\infty}^{x} \bar{A}^-(y)\,dy, \qquad \bar{\Xi}^+(x) = 1 + \int_{x}^{+\infty} \bar{A}^+(y)\,dy. \tag{3.14}$$

Then we find by (3.12) and (3.10) the reduction (cf. refs. 14 and 2)

$$\bar{\Xi}^{\pm}(x,l) = \bar{\Xi}^{\pm}(x\pm\tfrac{l+a}{2}), \tag{3.15}$$

and via (3.9) that

$$\frac{\bar{A}^-(x)}{\Xi} = \frac{\varrho^-(x)}{\bar{\Xi}^+(x)}, \qquad \frac{\bar{A}^+(x)}{\Xi} = \frac{\varrho^+(x)}{\bar{\Xi}^-(x)} \tag{3.16}$$

with the densities at the boundaries of the blocks of i interacting particles

$$\varrho_i^{\pm}(x) = \int_{\mathbb{R}} \varrho_i(x\pm\tfrac{l+a}{2},l)\,dl \tag{3.17}$$

and

$$\varrho^{\pm}(x) = \sum_{i=1}^{\infty} \varrho_i^{\pm}(x). \tag{3.18}$$

Hence, on using the boundary conditions (3.11), we infer that (cf. ref. 14)

$$\frac{\bar{\Xi}^+(x)}{\Xi}\frac{d\bar{\Xi}^-(x)}{dx}=\varrho^-(x), \qquad -\frac{\bar{\Xi}^-(x)}{\Xi}\frac{d\bar{\Xi}^+(x)}{dx}=\varrho^+(x). \qquad (3.19)$$

If we substract these two equations, then we obtain

$$\frac{1}{\Xi}\frac{d[\bar{\Xi}^-(x)\,\bar{\Xi}^+(x)]}{dx}=\varrho^-(x)-\varrho^+(x), \qquad (3.20)$$

which integrates upon using the boundary conditions (3.11) via (3.15) to

$$\frac{\bar{\Xi}^-(x)\,\bar{\Xi}^+(x)}{\Xi}=1+\int_{-\infty}^{x}\left[\varrho^-(y)-\varrho^+(y)\right]dy\equiv\omega(x). \qquad (3.21)$$

Thus we deduce from (3.11), (3.15), (3.19), and (3.21) that (cf. refs. 14 and 2)

$$\ln\bar{\Xi}^-(x)=\int_{-\infty}^{x}\frac{\varrho^-(y)}{\omega(y)}\,dy, \qquad \ln\frac{\bar{\Xi}^+(x)}{\Xi}=-\int_{-\infty}^{x}\frac{\varrho^+(y)}{\omega(y)}\,dy, \qquad (3.22)$$

and so we conclude by (3.11) via (3.15) that

$$\ln\Xi=\int_{\mathbb{R}}\frac{\varrho^-(y)}{\omega(y)}\,dy=\int_{\mathbb{R}}\frac{\varrho^+(y)}{\omega(y)}\,dy, \qquad (3.23)$$

or more symmetrically

$$\ln\Xi=\frac{1}{2}\int_{\mathbb{R}}\frac{\varrho^-(y)+\varrho^+(y)}{\omega(y)}\,dy, \qquad (3.24)$$

which generalizes the results (3.10) respective (4.30) of ref. 7 for dimerizing hard rods respective sticky cores to systems with arbitrary V.

Next, let us analyze the one-dimensional marginals $\varrho_i^\pm$ of ϱ_i. According to (3.17) and (3.9), we have by (3.10) and (3.6)

$$\varrho_i^-(x+\tfrac{a}{2})=\frac{1}{\Xi}\bar{\Xi}^+(x,0)\cdot\int_{\mathbb{R}}z(fz)^{i-1}(x,x-l)\,\bar{\Xi}^-(x-\tfrac{l}{2},l)\,dl, \qquad (3.25a)$$

$$\varrho_i^+(x-\tfrac{a}{2})=\frac{1}{\Xi}\int_{\mathbb{R}}\bar{\Xi}^+(x+\tfrac{l}{2},l)\,z(fz)^{i-1}(x+l,x)\,dl\cdot\bar{\Xi}^-(x,0). \qquad (3.25b)$$

Hence, on using the reparameterizations

$$\int_{\mathbb{R}} z(fz)^{i-1}(x, x-l)\, \bar{\bar{\Xi}}^-(x-\tfrac{l}{2}, l)\, dl = \int_{\mathbb{R}} z(fz)^{i-1}(x, y)\, \bar{\bar{\Xi}}^-(y, 0)\, dy, \tag{3.26a}$$

$$\int_{\mathbb{R}} \bar{\bar{\Xi}}^+(x+\tfrac{l}{2}, l)\, z(fz)^{i-1}(x+l, x)\, dl = \int_{\mathbb{R}} \bar{\bar{\Xi}}^+(y, 0)\,(zf)^{i-1}\, z(y, x)\, dy, \tag{3.26b}$$

as well as (3.15), we infer the block densities equations

$$\varrho_i^-(x) = \frac{1}{\Xi}\, \bar{\bar{\Xi}}^+(x)\cdot z(x-\tfrac{a}{2})\cdot \int_{\mathbb{R}} (fz)^{i-1}(x-\tfrac{a}{2}, y)\, \bar{\bar{\Xi}}^-(y-\tfrac{a}{2})\, dy, \tag{3.27a}$$

$$\varrho_i^+(x) = \frac{1}{\Xi}\int_{\mathbb{R}} \bar{\bar{\Xi}}^+(y+\tfrac{a}{2})\,(zf)^{i-1}(y, x+\tfrac{a}{2})\, dy\cdot z(x+\tfrac{a}{2})\cdot \bar{\bar{\Xi}}^-(x). \tag{3.27b}$$

In particular, we find for $i = 1$ the profile equation (cf. ref. 2)

$$\varrho_1(x) = \varrho_1^\pm(x \mp \tfrac{a}{2}) = \frac{1}{\Xi}\, \bar{\bar{\Xi}}^+(x+\tfrac{a}{2})\, z(x)\, \bar{\bar{\Xi}}^-(x-\tfrac{a}{2}) \equiv z(x)\, \psi(x+\tfrac{a}{2}, x-\tfrac{a}{2}), \tag{3.28}$$

where the two-dimensional weight function ψ (cf. refs. 2 and 11) evaluates by (3.21) and (3.22) for $y \geqslant x$ to (cf. ref. 2)

$$\psi(y, x) = \omega(y)\exp\left[-\int_x^y \frac{\varrho^-(z)}{\omega(z)}\, dz\right] = \omega(x)\exp\left[-\int_x^y \frac{\varrho^+(z)}{\omega(z)}\, dz\right] \tag{3.29}$$

or

$$\psi(y, x) = \sqrt{\omega(y)\,\omega(x)}\exp\left[-\frac{1}{2}\int_x^y \frac{\varrho^-(z)+\varrho^+(z)}{\omega(z)}\, dz\right]. \tag{3.30}$$

Thus, upon substituting (3.28) into (3.27), and since ϱ_1 is the density of the monomers, result (3.27) characterizes blocks as conformations of monomers correlated by the attractive part of the interaction. This proposition, as the foregoing hard rod mixture form density functional (3.24), indicates a general pattern of transition from $D = 1$ to $D > 1$ (cf. Section 4).

Finally, to close the system of equations for the local particle density, we derive a subsidiary condition for the marginals $\varrho_i^{\pm}$ in terms of ϱ. Let us first rewrite (3.2) in the form

$$\varrho(x) = \frac{\delta \ln \varXi}{\delta \ln z(x)} = \sum_{i=1}^{\infty} \int_{\mathbb{R}^2} \frac{\delta \ln \varXi}{\delta \ln \bar{w}_i(y, l)} \frac{\delta \ln \bar{w}_i(y, l)}{\delta \ln z(x)} d(y, l)$$

$$= \int_{\mathbb{R}^2} \frac{\delta \ln \varXi}{\delta \ln[\sum_{i=1}^{\infty} \bar{w}_i(y, l)]} \frac{\delta \ln[\sum_{i=1}^{\infty} \bar{w}_i(y, l)]}{\delta \ln z(x)} d(y, l). \quad (3.31)$$

This yields

$$\varrho(x) = \frac{1}{\varXi} \int_{\mathbb{R}^2} \bar{\varXi}^+(y, l)\, (\mathbb{I} - zf)^{-1}\, (y + \tfrac{l}{2}, x)\, z(x)$$

$$\times (\mathbb{I} - fz)^{-1}\, (x, y - \tfrac{l}{2})\, \bar{\varXi}^-(y, l)\, d(y, l) \quad (3.32)$$

via (3.8), (3.9), and (3.5). Accordingly, we have through a reparameterization of the integral and by (3.2) as well as (3.15) that[2]

$$\bar{\varXi}^-(x - \tfrac{a}{2}) = \int_{\mathbb{R}} (\mathbb{I} - fz)(x, y)\, \varXi^-(y)\, dy, \quad (3.33a)$$

$$\bar{\varXi}^+(x + \tfrac{a}{2}) = \int_{\mathbb{R}} \varXi^+(y)(\mathbb{I} - zf)(y, x)\, dy, \quad (3.33b)$$

or that

$$\varXi^-(x) = \int_{\mathbb{R}} (\mathbb{I} - fz)^{-1}\, (x, y)\, \bar{\varXi}^-(y - \tfrac{a}{2})\, dy, \quad (3.34a)$$

$$\varXi^+(x) = \int_{\mathbb{R}} \bar{\varXi}^+(y + \tfrac{a}{2})\, (\mathbb{I} - zf)^{-1}\, (y, x)\, dy. \quad (3.34b)$$

Hence, on combining (3.34) with the block densities equations (3.27), we obtain[2]

$$\varrho^-(x + \tfrac{a}{2}) = \frac{1}{\varXi} \bar{\varXi}^+(x + \tfrac{a}{2})\, z(x)\, \varXi^-(x), \quad (3.35a)$$

$$\varrho^+(x - \tfrac{a}{2}) = \frac{1}{\varXi} \varXi^+(x)\, z(x)\, \bar{\varXi}^-(x - \tfrac{a}{2}), \quad (3.35b)$$

and so we conclude via (3.2), (3.35), and (3.28) that (cf. ref. 2)

$$\varrho(x) = \frac{\varrho^+(x-\frac{a}{2})\,\varrho^-(x+\frac{a}{2})}{\varrho_1(x)}, \tag{3.36}$$

which is the desired closure relation. On starting from (3.31), the very simple formal structure of (3.36) is certainly due to the $D=1$ next neighbor nature of our problem. Therefore, the form (3.31) has a higher dimensional analogue [as the result (3.27) respective (3.24)], whereas (3.36) has not. Proposition (3.36) completes the deduction of the nonuniform case.

In passing, we point out that the main results of our analysis are completely characterized by the pressure-like quantities, termed effective pressures, $p^\pm$, defined as[8, 15]

$$\beta p^\pm(x) = \frac{\varrho^\pm(x)}{\omega(x)} \tag{3.37}$$

with the $\varrho^\pm$ brought in via (3.18) and ω by (3.21). We also introduce

$$\beta\pi^\pm(y, x) = \int_x^y \beta p^\pm(z)\,dz. \tag{3.38}$$

Upon using definition (3.37) and the corresponding results in the form derived so far, one can show that our overcomplete format free energy F for $D=1$ particle systems with next neighbor interactions is given by

$$\beta F[U] = \min_{\varrho\,\in\,D_n} \left\{ \int_{\mathbb{R}} \varrho(x)[\beta U(x) + \ln z(x)]\,dx - \ln \varXi \right\} \tag{3.39}$$

with $D_n = \{t \in L^1(\mathbb{R}) : t(x) \geqslant 0 \wedge \int_{\mathbb{R}} t(x)\,dx = n\}$, n fixed, the profile equation

$$\beta[\mu - U(x)] = \ln \varrho_1(x) - \tfrac{1}{2}\ln[\psi^+(x)\,\psi^-(x)], \tag{3.40}$$

where $\psi^\pm(x) = \omega(x\mp\frac{a}{2})\exp[-\beta\pi^\pm(x+\frac{a}{2}, x-\frac{a}{2})]$, $\psi^- \equiv \psi^+$ by (3.29), and the total Gibbs measure of hard rod mixture form (cf. ref. 15)

$$\ln \varXi = \tfrac{1}{2}\int_{\mathbb{R}} [\beta p^-(y) + \beta p^+(y)]\,dy. \tag{3.41}$$

One further finds that the block densities equations transcribe to

$$\varrho_i^-(x) = \varrho_1^-(x) \cdot \int_{\mathbb{R}} \left(f \frac{\varrho_1}{\psi^-} \right)^{i-1} (x - \tfrac{a}{2}, y + \tfrac{a}{2}) \exp[-\beta \pi^-(x - a, y)] \, dy, \tag{3.42a}$$

$$\varrho_i^+(x) = \int_{\mathbb{R}} \exp[-\beta \pi^+(y, x + a)] \left(\frac{\varrho_1}{\psi^+} f \right)^{i-1} (y - \tfrac{a}{2}, x + \tfrac{a}{2}) \, dy \cdot \varrho_1^+(x) \tag{3.42b}$$

with the subsidiary condition (3.36). These results extend—indirectly—the well-known (see, e.g., ref. 13) isothermal-isobaric technique from the uniform to the nonuniform case. So we are led to conjecture that a direct nonuniform isothermal-isobaric approach should be possible as well.

3.2. Examples

We apply the theory to the adhesive respective HGM system. This allows us to make contact with the associated results for the uniform case, Section 2, and to provide detailed evidence for our conjecture on the nonuniform isothermal-isobaric format.

To present the examples most adequately, we give first closed expressions for the sums $\varrho^{\pm}$. Again, these simplifications are only possible for the $D = 1$ next neighbor case. Namely, if we start with (3.35), and use (3.33) as well as (3.28), we end up with

$$\frac{\varrho(x - \tfrac{a}{2})}{\varrho^-(x)} = 1 + \int_{\mathbb{R}} f(y + a - x) \, \beta p^+(y) \exp[-\beta \pi^+(y, x)] \, dy, \tag{3.43a}$$

$$\frac{\varrho(x + \tfrac{a}{2})}{\varrho^+(x)} = 1 + \int_{\mathbb{R}} f(x + a - y) \, \beta p^-(y) \exp[-\beta \pi^-(x, y)] \, dy \tag{3.43b}$$

via the subsidiary condition (3.36), (3.19), and through definition (3.37). This result is equivalent to the one-component case of formula (3.12) of ref. 2.

3.2.1. Adhesive Interaction

Due to the contact nature of (2.3), we find by (3.43)

$$\frac{\varrho(x - \tfrac{a}{2})}{\varrho^-(x)} = 1 + \lambda \beta p^+(x), \tag{3.44a}$$

$$\frac{\varrho(x + \tfrac{a}{2})}{\varrho^+(x)} = 1 + \lambda \beta p^-(x), \tag{3.44b}$$

which are the generalizations of (2.17) to the nonuniform case. Consequently, we have that

$$\omega(x) = 1 - \int_{x-\frac{a}{2}}^{x+\frac{a}{2}} \varrho(y)\, dy \equiv 1 - \tau(x), \tag{3.45}$$

and by (3.36) also the case $i = 1$ of (2.15) at the nonuniform level,

$$\varrho_1(x) = \frac{\varrho(x)}{[1 + \lambda\beta p^-(x-\frac{a}{2})][1 + \lambda\beta p^+(x+\frac{a}{2})]}. \tag{3.46}$$

Moreover, rewriting (3.44) via (3.37) and (3.45) as

$$\frac{\varrho(x-\frac{a}{2})}{1-\tau(x)} = \beta p^-(x)[1 + \lambda\beta p^+(x)], \tag{3.47a}$$

$$\frac{\varrho(x+\frac{a}{2})}{1-\tau(x)} = \beta p^+(x)[1 + \lambda\beta p^-(x)] \tag{3.47b}$$

gives

$$\beta p^\pm(x) = \frac{1}{2\lambda}\left\{ -1 \pm \frac{\tau'(x)}{1-\tau(x)} + \sqrt{1 + \frac{4\lambda\sigma(x)}{1-\tau(x)} + \left[\frac{\lambda\tau'(x)}{1-\tau(x)}\right]^2} \right\} \tag{3.48}$$

with $\sigma(x) = \frac{1}{2}[\varrho(x+\frac{a}{2}) + \varrho(x-\frac{a}{2})]$. Hence, on substituting (3.48) into (3.41), we arrive at formula (5.17) respective (6.16) of ref. 9. In the uniform limit, we recover (2.18) respective (2.19).

Finally, if we specialize (3.42) to (2.3), then we obtain via (3.45) that

$$\varrho_i^-(x) = \varrho_1^-(x)\, \lambda^{i-1} \prod_{j=1}^{i-1} \frac{\varrho_1^-(x-ja)}{1-\tau(x-ja)}, \tag{3.49a}$$

$$\varrho_i^+(x) = \varrho_1^+(x)\, \lambda^{i-1} \prod_{j=1}^{i-1} \frac{\varrho_1^+(x+ja)}{1-\tau(x+ja)}, \tag{3.49b}$$

which correspond immediately to (2.15) for $i > 1$ through (3.46) and (3.47).

3.2.2. HGM System

For an interaction characterized by (2.21), the block densities equations (3.42) are no longer analytically tractable. Thus, upon substituting (2.21) into (3.43), we are left with

$$\frac{\varrho(x - \frac{a}{2})}{\varrho^-(x)} = 1 + \lambda\{1 - \exp[-\beta\pi^+(x+d, x)]\}, \qquad (3.50a)$$

$$\frac{\varrho(x + \frac{a}{2})}{\varrho^+(x)} = 1 + \lambda\{1 - \exp[-\beta\pi^-(x, x-d)]\}, \qquad (3.50b)$$

and so we have by (3.36) that

$$\frac{\varrho(x)}{\varrho_1(x)} = (1 + \lambda\{1 - \exp[-\beta\pi^-(x - \tfrac{a}{2}, x - \tfrac{a}{2} - d)]\})$$
$$\times (1 + \lambda\{1 - \exp[-\beta\pi^+(x + \tfrac{a}{2} + d, x + \tfrac{a}{2})]\}). \qquad (3.51)$$

These results generalize (2.27) respective (2.26) for $i = 1$ to the nonuniform case.

Furthermore, on substituting (3.43) into (3.21), we find through (2.21), (3.29), as well as definitions (3.37) respective (3.38)

$$\omega(x) = 1 - \tau(x) - \lambda \int_x^{x+d} \varrho^+(y) \left\{ \int_{y-d}^x \beta p^-(z) \exp[-\beta\pi^-(y, z)]\, dz \right\} dy, \qquad (3.52)$$

yielding via definition (3.38), (3.50), (3.29), and definition (3.37)

$$\omega(x) = 1 - \tau(x) + \int_x^{x+d} \frac{\varrho(y + \frac{a}{2})}{\exp[\beta\pi^-(y, y-d)]\left(1 + \dfrac{1}{\lambda}\right) - 1}\, dy$$
$$- \lambda \int_x^{x+d} \beta p^+(y)\, \omega(x) \exp[-\beta\pi^+(y, x)]\, dy, \qquad (3.53)$$

and so we conclude on using again proposition (3.50) that the effective pressure p^- is determined by [cf. for the uniform case (2.30)]

$$1 - \tau(x) = \frac{\varrho(x - \frac{a}{2})}{\beta p^-(x)} - \int_x^{x+d} \frac{\varrho(y + \frac{a}{2})}{\exp[\beta\pi^-(y, y-d)]\left(1 + \dfrac{1}{\lambda}\right) - 1}\, dy, \quad (3.54a)$$

and likewise p^+ by

$$1 - \tau(x) = \frac{\varrho(x + \frac{a}{2})}{\beta p^+(x)} - \int_{x-d}^x \frac{\varrho(y - \frac{a}{2})}{\exp[\beta\pi^+(y+d, y)]\left(1 + \dfrac{1}{\lambda}\right) - 1}\, dy, \quad (3.54b)$$

which is equivalent to formula (6.15) of ref. 2. This completes our discussion of the nonuniform HGM system within the $p^{\pm}$ representation.

In summary, the examples demonstrate in detail that a suggestive formal correspondence between the usual uniform isothermal-isobaric method and the nonuniform effective pressures format exists. This supports the idea of an isothermal-isobaric representation for arbitrary nonuniform $D = 1$ particle systems.

4. CONCLUSION

We presented a realization of the overcompleteness strategy for $D = 1$ systems with next neighbor interactions, where the supplementary variables are the local block densities ϱ_i of i associated particles. The corresponding free energy density functional is of the simple additive hard rod mixture type. The isomorphism between our overcomplete format and the standard description was established through a trivial identity of functional analysis. The first results on this class of density functionals have been derived by Kierlik and Rosinberg[7] for the special case of dimerizing hard rods. So we lifted their approach to particle systems with arbitrary next neighbor interactions. Moreover, we showed that all our main results are completely characterized by the effective pressures $p^{\pm}$. This proposition in conjunction with the detailed results for the adhesive interaction and the HGM system support the idea of a nonuniform isothermal-isobaric representation (analoguous to the well-known uniform isothermal-isobaric method) for arbitrary nonuniform $D = 1$ systems.

To introduce our concept of overcomplete description most concisely, we started with the uniform case. We treated first the two examples of adhesive systems and HGM systems. These results formed also the basis for our conjecture on a nonuniform isothermal-isobaric representation. We deduced our overcomplete description for arbitrary next neighbor interactions by means of an application of large deviation techniques, accompanied by the Hardy-Ramanujan formula on the number of partitions of a positive integer.

What we can learn from the $D = 1$ case is the logic of the problem for $D > 1$ systems with finite range interactions. In abstracting from the block densities equations (3.42), (i) we decompose a given $D > 1$ system into blocks of i monomers correlated by the attractive part of the interaction. (ii) Hence, on interpreting the blocks as components of a mixture, where the interaction between the components is given by construction by a hard core potential, we arrive at the extension of the hard rod mixture form density functional (3.41). (iii) Finally, we establish the isomorphism

between our overcomplete description and the standard formalism by an application of an identity of functional analysis as in (3.31).

Of course, it is the peculiarity of the $D = 1$ case that space can be disconnected by a point—see (1.2). This together with the fact that the geometry of the blocks is known a priori allows a successful application of our strategy. Somewhat more challenging is the question of control of the conformations in $D > 1$, where the shape functions of the blocks are no longer defined by a single real parameter l. Focusing on the first-principles approach (i)–(iii), it may therefore be convenient to start by going over to discrete systems (see, e.g., ref. 13). Then a natural extension of the $D = 1$ case to higher dimensions are interacting systems with next neighbor forces on a Cayley tree (for an overview see, e.g., ref. 10). Although such a lattice is actually infinite-dimensional, it may still serve as a suitable starting point for a systematic analysis of our overcomplete description in $D > 1$ due to its simply connectedness (cf. ref. 12). Progress in this direction will be the subject of a future communication.

Complementary to the reduction of the geometry of the phase space, another possibility when trying to apply mathematical techniques is to restrict the class of interactions. For the prominent example of systems with strong, short range interactions, free energy models can be constructed along these lines. We begin with the physical observation, that in such, e.g., $D = 3$ systems the blocks take on predominantly elementary sphere-like or cube-like conformations. Thus, the available analytic expressions for the hard sphere respective hard cube mixture free energy functional can be used to model the hard core interaction between the blocks [cf. (ii)]. Modelling of the internal block free energy [cf. (i)] and the incorporation of the subsidiary condition [cf. (iii)] requires a more incisive approach, but may still be amenable via the strong, short range character of the interaction. Also the implementation of this program will be reported in the future.

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