

**Exact density functional for hard-rod mixtures derived from Markov chain approach**

Benaoumeur Bakhti, Stephan Schott, and Philipp Maass\*

*Fachbereich Physik, Universität Osnabrück, Barbarastraße 7, 49076 Osnabrück, Germany*

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Using a Markov chain approach we rederive the exact density functional for hard-rod mixtures on a one-dimensional lattice, which forms the basis of the lattice fundamental measure theory. The transition probability in the Markov chain depends on a set of occupation numbers, which reflects the property of a zero-dimensional cavity to hold at most one particle. For given mean occupation numbers (density profile), an exact expression for the equilibrium distribution of microstates is obtained, which means an expression for the unique external potential that generates the density profile in equilibrium. By considering the rod ends to fall onto lattice sites, the mixture is always additive.

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The extension of density functional theory from continuum to lattice fluids [1] has proven to be useful for treating problems like ordering transitions [1–3], properties of interfaces separating different phases [4–6], phase separation in mixtures [7], or polymer adsorption at solid-liquid interfaces [8]. Time-dependent density functional theory [9] furthermore allows one to describe the kinetics of lattice fluids [10], as emerging in phase ordering phenomena [11], relaxation processes [12], and particle transport in driven lattice gases [13–15].

In 2002 Lafuente and Cuesta extended Rosenfeld’s fundamental measure theory to lattice models based on a derivation of an exact density functional for hard-rod mixtures in one dimension [16,17]. This derivation was carried out following a procedure developed by Vanderlick *et al.* [18] for continuum fluids. Since the excess free energy part of the functional could be expressed in terms of differences between parts that agree in their functional form with the excess free energy functional of a zero-dimensional cavity, approximate functionals in higher dimensions were obtained by dimensional expansion of the corresponding difference operator. By construction these fundamental measure functionals have the property to become exact under dimensional reduction and their impressive power was first shown by determining phase diagrams of hard squares [17,19] and hard cube mixtures [16,17,20] with good quality. The fundamental measure functionals moreover allow one to apply the method of dimensional crossover and the merit of this was demonstrated by deriving functionals for lattice gases with nearest neighbor exclusion for different lattice types (square, triangular, and face- and body-centered cubic) from the functional for cubes in  $(d + 1)$  dimensions [21]. The structure of the corresponding results led to a suggestion how to construct fundamental measure functionals for hard-core lattice gases for any type of lattice, shape of the particles, and arbitrary dimension [22].

In this Brief Report we rederive the exact density functional for hard-rod mixtures in one dimension, which means the starting point of the fundamental measure theory for hard-core lattice gases, by applying the Markov chain approach developed by Buschle *et al.* [23]. This approach is conceptually different from the procedure of Vanderlick *et al.* [18] and we believe that it is useful and important for the following reasons:

(i) The derivation of the functional becomes surprisingly simple. Making use only of the constraints of mutual rod exclusions, the relevant transition probability in the Markov chain is determined almost without any calculation.

(ii) The transition probability is (conditionally) dependent on a spatial region, where at most one particle can be placed, i.e., that of a zero-dimensional cavity. In this respect it reflects a property which turned out to be decisive for the generalized construction of fundamental measure functionals by Lafuente and Cuesta [22].

(iii) The simplicity of the derivation suggests that it can be extended to hard-rod mixtures with additional (thermal) interactions.

(iv) The derivation yields also an explicit expression for the probability distribution of microstates for a given density profile. This means that in the present case an explicit expression for the “Mermin potential” is obtained, i.e., the unique external potential that would generate the given density profile in thermal equilibrium.

In addition to these points we show that it is not necessary to consider nonadditive mixtures when mixed parities of rod lengths are present (i.e., rods with both even and odd lengths in units of the lattice spacing).

The mixture is considered to consist of  $q$  types of hard rods with length  $l_\alpha$ ,  $\alpha = 1, \dots, q$ , in the presence of an external potential. It is convenient (although not necessary) to order the lengths according to  $l_1 \geq l_2 \geq \dots \geq l_q$ , where different types of rods could have the same lengths due to different coupling to the external potential. The rods are located on a one-dimensional lattice with  $L$  sites and the  $l_\alpha$  are integer multiples of the lattice spacing that sets our length unit, i.e.,  $l_\alpha \in \mathbb{N}$ . The lattice is defined in such a way that the ends of the rods coincide with lattice sites and we introduce occupation numbers  $n_j^\alpha$  ( $j = 1, \dots, L$ ;  $\alpha = 1, \dots, q$ ) to specify the microstate of the mixture. We note that this assignment is different from that in Refs. [16,17], where it was made with respect to the rod centers. If the left end of a rod of type  $\alpha$  is at site  $j$ , then  $n_j^\alpha = 1$ , else  $n_j^\alpha = 0$  (here and in the following, Greek superscripts refer to the type and must not be mixed up with exponents). The mutual exclusion of hard rods implies the constraint  $n_k^\alpha n_j^\beta = 0$  for  $j = k, \dots, k + l_\alpha - 1$  (and  $k = j, \dots, j + l_\beta - 1$ ) and all  $\alpha, \beta = 1, \dots, q$  [24].

To set up the Markov chain approach following Ref. [23] it is useful to introduce the multicomponent state variables

\*philipp.maass@uni-osnabrueck.de

$\hat{n}_j = (n_j^1, \dots, n_j^q)$  that can assume  $(q + 1)$  states  $\hat{e}_0, \dots, \hat{e}_q$ , where  $\hat{e}_0$  refers to an empty site, i.e.,  $\hat{e}_0 = (0, \dots, 0)$ , while  $\hat{e}_\alpha$ ,  $\alpha = 1, \dots, q$ , refer to a site occupied by rods of type  $\alpha$ , i.e.,  $\hat{e}_\alpha = (0, \dots, 1, \dots, 0)$  with the 1 at the  $(\alpha + 1)$ th entry. The probability  $\chi(\hat{n}_1, \dots, \hat{n}_L)$  of microstates can be decomposed as

$$\chi(\hat{n}_1, \dots, \hat{n}_L) = \prod_{k=1}^L \psi(\hat{n}_k | \hat{n}_{k-1}, \dots, \hat{n}_1), \quad (1)$$

where  $\psi(\dots)$  denote the corresponding conditional probabilities. To keep the notation simple, we have labeled the starting of the chain, i.e.,  $\psi(\hat{n}_1)\psi(\hat{n}_2|\hat{n}_1)\psi(\hat{n}_3|\hat{n}_2, \hat{n}_1)\dots$ , by the same symbol “ $\psi$ ” (meaning in particular that  $\psi(\hat{n}_1)$  is not a conditional probability). By using the Boltzmann expression for the probability of microstates in the grand-canonical equilibrium ensemble, i.e.,  $\chi \propto \exp[-\beta \sum_{i,\alpha} (u_i^\alpha - \mu_\alpha) n_i^\alpha]$ , where  $\beta = 1/k_B T$  is the inverse thermal energy,  $u_i^\alpha$  the external, and  $\mu_\alpha$  the chemical potential, it can be proven [25] that the conditional probabilities satisfy the Markov property

$$\psi(\hat{n}_k | \hat{n}_{k-1}, \dots, \hat{n}_1) = \psi(\hat{n}_k | \{n_j^\alpha\}_{k-1}), \quad (2)$$

where  $\{n_j^\alpha\}_{k-1} = \{n_j^\alpha | 1 \leq \alpha \leq q, k - l_\alpha + 1 \leq j \leq k - 1\}$  denotes the set of occupation variables, which have an influence on the occupation of site  $k$  (see Fig. 1).

In the set  $\{n_j^\alpha\}_k = \{n_j^\alpha | 1 \leq \alpha \leq q, k - l_\alpha + 1 \leq j \leq k\}$ , i.e., all occupation variables involved in Fig. 1, there can be at most one occupation variable  $n_j^\alpha = 1$  due to the hard-rod constraints, which reflects the corresponding property of a zero-dimensional cavity. In fact this set corresponds exactly to the zero-dimensional cavity for a mixture introduced in Ref. [17] as a collection of sets for each rod type. The property to have at most one occupation variable  $n_j^\alpha = 1$  in  $\{n_j^\alpha\}_k$  can be utilized to determine the conditional probabilities by simple probabilistic considerations. First let us write for  $\alpha = 0, \dots, q$

$$\psi(\hat{n}_k = \hat{e}_\alpha | \{n_j^\beta\}_{k-1}) = \frac{\text{Prob}(\hat{n}_k = \hat{e}_\alpha, \{n_j^\beta\}_{k-1})}{\text{Prob}(\{n_j^\beta\}_{k-1})}, \quad (3)$$

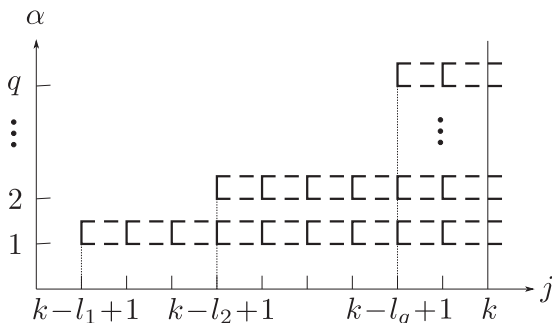


FIG. 1. Illustration of the set of occupation numbers affecting the occupation of site  $k$ . Any placement of the left end of a rod of type  $\alpha$  at the sites  $j$  with  $k - l_\alpha + 1 \leq j \leq k$  means that site  $k$  is covered by a part of this rod. This implies (i) that if a left rod end is at site  $k$ , all occupation numbers in the set  $\{n_j^\alpha\}_{k-1} = \{n_j^\alpha | 1 \leq \alpha \leq q, k - l_\alpha + 1 \leq j \leq k - 1\}$  must be zero, and (ii) that in the set  $\{n_j^\alpha\}_k = \{n_j^\alpha | 1 \leq \alpha \leq q, k - l_\alpha + 1 \leq j \leq k\}$  there can be at most one occupation number with value 1.

where  $\text{Prob}(\dots)$  denote joint probabilities. If  $\alpha \neq 0$ , then all  $n_j^\beta$  in the set  $\{n_j^\beta\}_{k-1}$  must be zero. This implies  $\text{Prob}(\hat{n}_k = \hat{e}_\alpha, \{n_j^\beta\}_{k-1}) = \text{Prob}(\hat{n}_k = \hat{e}_\alpha, \{n_j^\beta = 0\}_{k-1}) = p_k^\alpha$ , where  $p_k^\alpha = \langle n_\alpha \rangle$  is the mean occupation of site  $k$  [ $\langle \dots \rangle$  denotes an average over the microstate distribution  $\chi(\hat{n}_1, \dots, \hat{n}_L)$ ]. Since with the same reasoning  $\text{Prob}(\{n_j^\beta = 1, \text{all other } n_j^\gamma = 0\}_{k-1}) = p_j^\beta$ , we further have

$$\text{Prob}(\{n_j^\alpha = 0\}_{k-1}) + \sum_{\beta=1}^q \sum_{j=k-l_\beta+1}^{k-1} p_j^\beta = 1 \quad (4)$$

due to normalization. Accordingly, we obtain for  $\alpha \neq 0$

$$\psi(\hat{n}_k = \hat{e}_\alpha | \{n_j^\beta\}_{k-1}) = \frac{p_k^\alpha}{1 - S_k^{(0)}}, \quad (5)$$

where we used one of the weighted densities (weighted mean occupations) [26]

$$S_k^{(m)} = \sum_{\alpha=1}^q \sum_{j=1-m}^{l_\alpha-1} p_{k-j}^\alpha, \quad m = 0, 1, \quad (6)$$

appearing in the lattice fundamental measure theory [16]. If  $\hat{n}_k = \hat{e}_0$  there are two possibilities: either one element in  $\{n_j^\beta\}_{k-1}$  is one, or all elements are zero. In the first case,  $\hat{n}_k$  must be equal to  $\hat{e}_0$ , implying that the corresponding conditional probability is 1. In the second case we need  $\text{Prob}(\hat{n}_k = \hat{e}_0, \{n_j^\beta = 0\}_{k-1}) = \text{Prob}(\{n_j^\beta = 0\}_k)$  in Eq. (3), which by utilizing normalization as in Eq. (4) (now with inclusion of site  $k$ ) is given by  $\text{Prob}(\{n_j^\beta = 0\}_k) = 1 - \sum_{\beta=1}^q \sum_{j=k-l_\beta+1}^k p_j^\beta = 1 - S_k^{(1)}$ . In summary,

$$\psi(\hat{n}_k = \hat{e}_0 | \{n_j^\beta\}_{k-1}) = \begin{cases} 1, & \text{one } n_j^\beta = 1 \text{ in } \{n_j^\beta\}_{k-1}, \\ \frac{1 - S_k^{(1)}}{1 - S_k^{(0)}}, & \text{all } n_j^\beta = 0 \text{ in } \{n_j^\beta\}_{k-1}. \end{cases} \quad (7)$$

Combining Eqs. (5) and (7), we can write

$$\psi(\hat{n}_k | \{n_j^\beta\}_{k-1}) = \left( \frac{1 - S_k^{(1)}}{1 - S_k^{(0)}} \right)^{1 - \sum_{\beta=1}^q \sum_{j=0}^{k-1} n_j^\beta} \times \prod_{\alpha=1}^q \left( \frac{p_k^\alpha}{1 - S_k^{(0)}} \right)^{n_k^\alpha}, \quad (8)$$

where the distinction between the possible configurations in the set  $\{n_j^\beta\}_k$  is taken into account by the exponents.

Inserting Eq. (8) into Eqs. (2) and (1), the probability distribution of microstates is given by the product of  $\psi(\hat{n}_k | \{n_j^\beta\}_{k-1})$  from Eq. (8) over all lattice sites; i.e., an explicit expression for  $\chi(\mathbf{n})$  as a function of the set  $\mathbf{n} = \{n_i^\alpha | 1 \leq \alpha \leq q, 1 \leq i \leq L\}$  of occupation numbers is obtained [we define  $\chi(\mathbf{n}) = 0$  for all microstates  $\mathbf{n}$  violating the hard-rod constraints]. This means that, for a given density profile  $\mathbf{p} = \{p_k^\alpha | 1 \leq \alpha \leq q, 1 \leq k \leq L\}$ , the distribution of microstates is uniquely determined if we require it to satisfy the Markov property (2), i.e.,  $\chi(\mathbf{n}) = \chi_{\mathbf{p}}(\mathbf{n})$ . One could get the impression that this is more general than the uniqueness implied by the Mermin theorem, which states that the prescription of  $\mathbf{p}$  fixes the external potential

$u_k^\alpha = u_k^\alpha[\mathbf{p}]$  in the sense that the Boltzmann distribution yields  $\mathbf{p}$  in equilibrium in the presence of  $u_k^\alpha[\mathbf{p}]$ . However, since the Boltzmann distributions satisfy the Markov property (2), and  $\chi_{\mathbf{p}}(\mathbf{n})$  is unique, there is in fact no more generality; i.e., the microstate distribution for given  $\mathbf{p}$  satisfying the Markov property (2) and the Boltzmann distribution generating  $\mathbf{p}$  in equilibrium must be the same [27]. We can thus identify the ‘‘Mermin potential’’  $U_{\mathbf{p}}(\mathbf{n}) = \sum_{k,\alpha} u_k^\alpha[\mathbf{p}] n_k^\alpha$  by setting  $\beta U_{\mathbf{p}}(\mathbf{n}) \propto -\ln \chi_{\mathbf{p}}(\mathbf{n})$ , which, up to irrelevant constant contributions, yields (after some rearrangement of summations)

$$u_k^\alpha[\mathbf{p}] = \ln p_k^\alpha - \ln(1 - S_k^{(0)}) + \sum_{j=k}^{k+l_\alpha-1} \ln \left( \frac{1 - S_j^{(0)}}{1 - S_j^{(1)}} \right). \quad (9)$$

Based on the Gibbs-Bogoliubov inequality the density functional in an external potential  $U(\mathbf{n}) = \sum_{k,\alpha} u_k^\alpha n_k^\alpha$  is defined as

$$\begin{aligned} \Omega[\mathbf{p}] &= \sum_{\mathbf{n}} \chi_{\mathbf{p}}(\mathbf{n}) \left[ k_B T \ln \chi_{\mathbf{p}}(\mathbf{n}) + U(\mathbf{n}) - \sum_{\alpha=1}^q \mu_\alpha N_\alpha \right] \\ &= F[\mathbf{p}] + \sum_{k=1}^L \sum_{\alpha=1}^q (u_k^\alpha - \mu_\alpha) p_k^\alpha, \end{aligned} \quad (10)$$

where  $F[\mathbf{p}] = k_B T \sum_{\mathbf{n}} \chi_{\mathbf{p}}(\mathbf{n}) \ln \chi_{\mathbf{p}}(\mathbf{n})$  is the free energy functional. Inserting  $\chi_{\mathbf{p}}(\mathbf{n})$  one obtains

$$\begin{aligned} \beta F[\mathbf{p}] &= \sum_{k=1}^L \left\{ (1 - S_k^{(1)}) \ln(1 - S_k^{(1)}) \right. \\ &\quad \left. - (1 - S_k^{(0)}) \ln(1 - S_k^{(0)}) + \sum_{\alpha=1}^q p_k^\alpha \ln p_k^\alpha \right\}. \end{aligned} \quad (11)$$

Minimizing  $\Omega[\mathbf{p}]$  with respect to the  $p_j^\alpha$  yields the density profile in equilibrium.

Following Lafuente and Cuesta [17], one can define an ‘‘ideal part’’  $F_{\text{id}}[\mathbf{p}]$  by

$$\beta F_{\text{id}}[\mathbf{p}] = \sum_{k=1}^L \sum_{\alpha=1}^q p_k^\alpha (\ln p_k^\alpha - 1). \quad (12)$$

This differs from the expression  $\sum_k \{ p_k^\alpha \ln p_k^\alpha - (1 - \sum_\alpha p_k^\alpha) \ln(1 - \sum_\alpha p_k^\alpha) \}$  for a noninteracting multicomponent Fermionic lattice gas, but has the advantage to lead to a fundamental measure structure of the excess free energy part  $F_{\text{exc}}[\mathbf{p}] = F[\mathbf{p}] - F_{\text{id}}[\mathbf{p}]$ . When using Eqs. (11) and (12), and  $\sum_\alpha p_k^\alpha = S_k^{(1)} - S_k^{(0)}$ , this becomes

$$\begin{aligned} \beta F_{\text{exc}}[\mathbf{p}] &= \sum_{k=1}^L \left\{ [S_k^{(1)} + (1 - S_k^{(1)}) \ln(1 - S_k^{(1)})] \right. \\ &\quad \left. - [S_k^{(0)} + (1 - S_k^{(0)}) \ln(1 - S_k^{(0)})] \right\}. \end{aligned} \quad (13)$$

The terms in the square brackets have the same functional form as the excess free energy  $f_{\text{exc}}(\eta) = \eta + (1 - \eta) \ln(1 - \eta)$  of a zero-dimensional cavity with mean occupation  $\eta$  [28]. Approximate fundamental measure functionals in higher dimensions can be constructed by considering the two terms in the square brackets as resulting from a one-dimensional difference operator and by generalizing this operator together with the weighted densities to higher dimensions (for details, see Refs. [16,17]).

The excess free energy in Eq. (13) is equal to that found by Lafuente and Cuesta for an additive mixture. To recover their expressions, occupation numbers  $\tilde{n}_k^\alpha = 0, 1$  need to be assigned to the rod centers, which amounts to a simple translation of the site indices,  $n_k^\alpha \rightarrow \tilde{n}_k^\alpha = n_{k+(l_\alpha-\epsilon)/2}^\alpha$ , where  $\epsilon = 0$  if all  $l_\alpha$  are even and  $\epsilon = 1$  if all  $l_\alpha$  are odd.

Nonadditive mixtures appear when considering a setup where the rod centers fall onto lattice sites and both even and odd  $l_\alpha$  are present, since in this case neighboring rods with even and odd  $l_\alpha$  have a minimum separation of half a lattice unit between their ends. For such nonadditive mixtures one can construct the corresponding functional from that for additive mixtures [17]. When the rod ends fall onto lattice sites, the mixtures are always additive irrespective of having mixed parities of rod lengths.

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