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Exact bulk correlation functions in one-dimensional nonadditive hard-core mixtures

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In a recent paper [Phys. Rev. E **76**, 031202 (2007)], Schmidt proposed a fundamental measure density functional theory for one-dimensional nonadditive hard-rod fluid mixtures and compared its predictions for the bulk structural properties with Monte Carlo simulations. The aim of this Brief Report is to recall that the problem admits an exact solution in the bulk, which is briefly summarized in a self-contained way.

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Perhaps the most successful class of density functional theories are based on Rosenfeld's fundamental measure theory (FMT) [1]. In a recent paper [2], Schmidt has proposed a FMT for the excess free energy of inhomogeneous one-dimensional nonadditive hard-rod fluid mixtures. As a test of the theory, the FMT predictions for the pair correlation functions in the bulk region are compared with Monte Carlo simulations, a general good agreement being found. On the other hand, notwithstanding the merits of the FMT constructed in Ref. [2], it presents some limitations that become more important as the density and/or the nonadditivity increase. For instance, it yields nonzero values of the pair correlation functions inside the core and predicts a spurious demixing transition.

The fact that the one-dimensional nonadditive hard-rod problem admits an exact solution in the bulk seems to have been overlooked in Ref. [2]. Actually, any one-dimensional homogeneous system is exactly solvable, provided that every particle interacts only with its nearest neighbors [3–5]. The aim of this Brief Report is to fill the gap in Ref. [2] by presenting a brief and self-contained summary of the exact solution, particularizing to binary nonadditive mixtures, and comparing with the bulk FMT predictions for one of the cases considered in Ref. [2].

Let us consider an m-component one-dimensional fluid mixture with constant (bulk) number densities $\{\rho_i; i=1,\ldots,m\}$ and interaction potentials $\phi_{ij}(x)=\phi_{ij}(-x)$ acting only on nearest neighbors. Given a particle of species i at the origin, the probability that its lth neighbor belongs to species j and is located at a point between x and $x+dx$ is given by $p_{ij}^{(l)}(x)dx$, which defines the (conditional) probability density distribution $p_{ij}^{(l)}(x)$. In particular, $p_{ij}^{(1)}(x)$ is the nearest-neighbor distribution. The distributions $p_{ij}^{(l)}(x)$ verify the normalization condition

$$\sum_{j=1}^{m}\int_0^\infty dx\, p_{ij}^{(l)}(x)=1 \tag{1}$$

and obey the recurrence relation

$$p_{ij}^{(l)}(x)=\sum_{k=1}^{m}\int_0^x dx'\, p_{ik}^{(l-1)}(x')p_{kj}^{(1)}(x-x'). \tag{2}$$

Its solution in Laplace space is

$$\mathbf{P}^{(l)}(s)=[\mathbf{P}^{(1)}(s)]^l, \tag{3}$$

where $\mathbf{P}^{(l)}(s)$ is the $m\times m$ matrix whose elements $P_{ij}^{(l)}(s)$ are the Laplace transforms of $p_{ij}^{(l)}(x)$.

The total probability density of finding a particle of species j, given that a particle of species i is at the origin, is obtained as

$$\rho_j g_{ij}(x)=p_{ij}(x)=\sum_{l=1}^{\infty}p_{ij}^{(l)}(x), \tag{4}$$

where $g_{ij}(x)$ is the pair correlation function. In Laplace space,

$$G_{ij}(s)=\frac{1}{\rho_j}P_{ij}(s),\qquad \mathbf{P}(s)=\mathbf{P}^{(1)}(s)[\mathbf{I}-\mathbf{P}^{(1)}(s)]^{-1}, \tag{5}$$

where use has been made of Eq. (3). Therefore, the knowledge of the nearest-neighbor distributions $\{p_{ij}^{(1)}(x)\}$ suffices to obtain the pair correlation functions $\{g_{ij}(x)\}$. Note that the Fourier transform $\widetilde{h}_{ij}(k)$ of the total correlation function $h_{ij}(x)\equiv g_{ij}(x)-1$ is simply related to the Laplace transform $G_{ij}(s)$ of $g_{ij}(x)$ by $\widetilde{h}_{ij}(k)=G_{ij}(\imath k)+G_{ij}(-\imath k)$, where $\imath$ is the imaginary unit.

It can be proven that the nearest-neighbor distribution possesses the following explicit form [4,5]:

$$p_{ij}^{(1)}(x)=\rho_j K_{ij}e^{-\beta\phi_{ij}(x)}e^{-\xi x}, \tag{6}$$

where $\beta=1/k_BT$ and $\xi=\beta p$, k_B, T, and p being the Boltzmann constant, the temperature, and the pressure, respectively. The Laplace transform of Eq. (6) is

$$P_{ij}^{(1)}(s)=\rho_j K_{ij}\Omega_{ij}(s+\xi), \tag{7}$$

where $\Omega_{ij}(s)$ denotes the Laplace transform of $e^{-\beta\phi_{ij}(x)}$.

To close the problem, one needs to determine the amplitudes $K_{ij}=K_{ji}$ and the damping coefficient ξ. A convenient way of doing so is by enforcing basic consistency conditions. Note first that the normalization condition (1) for $l=1$ is equivalent to

$$\sum_{j=1}^{m}P_{ij}^{(1)}(0)=1. \tag{8}$$

Next, since $\lim_{x\to\infty} g_{ij}(x)=1$, one must have

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$$\lim_{s\to 0} sG_{ij}(s) = 1. \tag{9}$$

A subtler consistency condition [4] dictates that $\lim_{x\to\infty} p_{ij}^{(1)}(x)/p_{ik}^{(1)}(x)$ must be independent of the choice of species i. From Eq. (6) this implies that

$$\frac{K_{ij}}{K_{ik}} = \text{independent of } i. \tag{10}$$

Equations (8)–(10) are sufficient to obtain K_{ij} and ξ. To be more specific, let us consider the case of a binary mixture ($m=2$). Thus, Eq. (5) yields

$$G_{11}(s) = \frac{Q_{11}(s)[1-Q_{22}(s)]+Q_{12}^2(s)}{\rho_1 D(s)}, \tag{11}$$

$$G_{22}(s) = \frac{Q_{22}(s)[1-Q_{11}(s)]+Q_{12}^2(s)}{\rho_2 D(s)}, \tag{12}$$

$$G_{12}(s) = \frac{Q_{12}(s)}{\sqrt{\rho_1\rho_2}D(s)}, \tag{13}$$

where

$$Q_{ij}(s) \equiv \sqrt{\rho_i/\rho_j}P_{ij}^{(1)}(s) = \sqrt{\rho_i\rho_j}K_{ij}\Omega_{ij}(s+\xi), \tag{14}$$

$$D(s) \equiv [1-Q_{11}(s)][1-Q_{22}(s)]-Q_{12}^2(s). \tag{15}$$

The behavior of $Q_{ij}(s)$ for small s is

$$Q_{ij}(s) = \sqrt{\rho_i\rho_j}K_{ij}[\Omega_{ij}(\xi)+\Omega_{ij}'(\xi)s+O(s^2)], \tag{16}$$

where $\Omega_{ij}'(s)$ is the first derivative of $\Omega_{ij}(s)$. Application of Eq. (8) yields

$$K_{11} = \frac{1-\rho_2 K_{12}\Omega_{12}(\xi)}{\rho_1\Omega_{11}(\xi)}, \tag{17}$$

$$K_{22} = \frac{1-\rho_1 K_{12}\Omega_{12}(\xi)}{\rho_2\Omega_{22}(\xi)}. \tag{18}$$

Next, Eq. (9) implies

$$\rho_1^2 K_{11}\Omega_{11}'(\xi)+\rho_2^2 K_{22}\Omega_{22}'(\xi)+2\rho_1\rho_2 K_{12}\Omega_{12}'(\xi) = -1. \tag{19}$$

Finally, Eq. (10) becomes

$$K_{11}K_{22} = K_{12}^2. \tag{20}$$

Equations (17)–(20) constitute a set of four independent equations whose solution gives K_{11}, K_{12}, K_{22}, and ξ. Inserting Eqs. (17) and (18) into Eqs. (19) and (20) one gets

$$K_{12} = \frac{1}{\rho_1\rho_2\Omega_{12}(\xi)}\frac{1+\rho_1 L_{11}(\xi)+\rho_2 L_{22}(\xi)}{L_{11}(\xi)+L_{22}(\xi)-2L_{12}(\xi)}, \tag{21}$$

$$1-\rho K_{12}\Omega_{12}(\xi)+\rho_1\rho_2[\Omega_{12}^2(\xi)-\Omega_{11}(\xi)\Omega_{22}(\xi)]K_{12}^2 = 0, \tag{22}$$

where we have called $L_{ij}(s)\equiv\Omega_{ij}'(s)/\Omega_{ij}(s)$ and $\rho=\rho_1+\rho_2$ is the total density. Substitution of Eq. (21) into Eq. (22) yields a single equation for ξ, which in general is transcendental. Once solved, the coefficients K_{ij} are obtained from Eqs. (17), (18), and (21). The exact pair correlation functions are then entirely determined in Laplace space through Eqs. (11)–(15).

In the particular case of nonadditive hard rods, one has $e^{-\beta\phi_{ij}(x)}=\Theta(x-\sigma_{ij})$, where $\Theta(x)$ is Heaviside's step function, so that

$$\Omega_{ij}(s) = \frac{e^{-\sigma_{ij}s}}{s}, \quad L_{ij}(s) = -\sigma_{ij}-s^{-1}, \tag{23}$$

$$Q_{ij}(s) = \sqrt{\rho_i\rho_j}K_{ij}\frac{e^{-\sigma_{ij}(s+\xi)}}{s+\xi}. \tag{24}$$

The constraint to nearest-neighbor interactions implies that $\sigma_{ij}\le\sigma_{ik}+\sigma_{jk}$ for all $\{i,j,k\}$. In the binary case this amounts

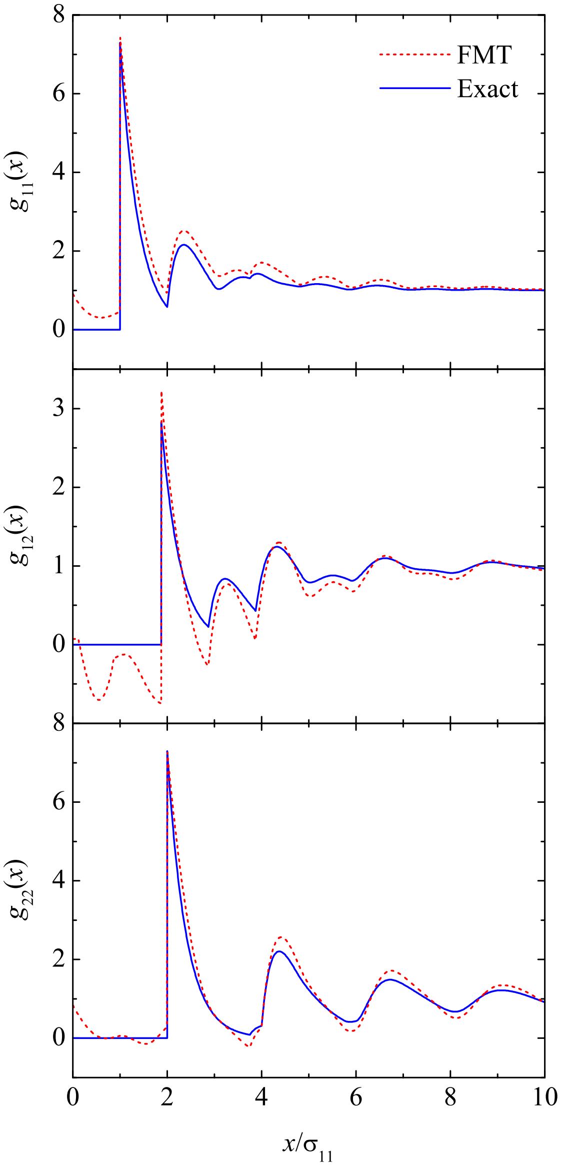

FIG. 1. (Color online) Bulk pair correlation functions $g_{ij}(x)$ for a one-dimensional binary hard-rod mixture with $\sigma_{22}/\sigma_{11}=2$, $\sigma_{12}/\sigma_{11}=15/8$, and $\rho_1=\rho_2=\sigma_{11}^{-1}/4$. The solid lines are the exact results and the dashed lines are the FMT predictions of Ref. [2].

to $2\sigma_{12} > \max(\sigma_{11}, \sigma_{22})$. The recipe described by Eqs. (17), (18), and (21)–(23) for the thermodynamic quantity $\xi = \beta p$ and the amplitudes K_{ij}, and by Eqs. (11)–(15) and (24) for the structural $G_{ij}(s)$quantities are easy to implement. In order to go back to real space and obtain the pair correlation functions $g_{ij}(x)$ one can use any of the efficient numerical schemes described in Ref. [6]. On the other hand, the simplicity of Eq. (24) allows one to get a fully analytical representation. Note first that

$$\frac{1}{D(s)} = \sum_{m=0}^{\infty} [Q_{11}(s) + Q_{22}(s) + Q_{12}^2(s) - Q_{11}(s)Q_{22}(s)]^m . \tag{25}$$

When Eq. (25) is inserted into Eqs. (11)–(13), one can express $G_{ij}(s)$ as linear combinations of terms of the form

$$Q_{11}^{n_{11}}(s)Q_{22}^{n_{22}}(s)Q_{12}^{n_{12}}(s) = \frac{e^{-a(s+\xi)}}{(s+\xi)^n}(\rho_1 K_{11})^{n_{11}+n_{12}/2} \times (\rho_2 K_{22})^{n_{22}+n_{12}/2}, \tag{26}$$

where $a \equiv n_{11}\sigma_{11} + n_{22}\sigma_{22} + n_{12}\sigma_{22}$ and $n \equiv n_{11} + n_{22} + n_{12}$. The inverse Laplace transforms $g_{ij}(x) = \mathcal{L}^{-1}[G_{ij}(s)]$ are readily evaluated by using the property

$$\mathcal{L}^{-1}\left[\frac{e^{-a(s+\xi)}}{(s+\xi)^n}\right] = e^{-\xi x}\frac{(x-a)^{n-1}}{(n-1)!}\Theta(x-a). \tag{27}$$

It is important to realize that if one is interested in distances x smaller than a certain value R, only a finite numbers of terms contribute to $g_{ij}(x)$, namely, those with $\{n_{11}, n_{22}, n_{12}\}$ such that $n_{11}\sigma_{11} + n_{22}\sigma_{22} + n_{12}\sigma_{22} < R$. In particular, for the most nonadditive case considered in Ref. [2], i.e., $\sigma_{22}/\sigma_{11} = 2$ and $\sigma_{12}/\sigma_{11} = 15/8$, only those terms satisfying $8n_{11} + 16n_{22} + 15n_{12} < 80$ are needed for $x < 10\sigma_{11}$. Moreover, $g_{ij}(x) = \rho_j^{-1} p_{ij}^{(1)}(x) = K_{ij} e^{-\xi x}$ in the first shell, i.e., for $\sigma_{ij} < x < \sigma_{ij} + \Delta_{ij}$, where $\Delta_{11} = \min(\sigma_{11}, 2\sigma_{12} - \sigma_{11})$, $\Delta_{22} = \min(\sigma_{22}, 2\sigma_{12} - \sigma_{22})$, and $\Delta_{12} = \min(\sigma_{11}, \sigma_{22})$.

Let us consider a specific system with $\sigma_{22}/\sigma_{11} = 2$, $\sigma_{12}/\sigma_{11} = 15/8$, and $\rho_1 = \rho_2 = \sigma_{11}^{-1}/4$. The corresponding solution of the transcendental equation for ξ is $\xi \simeq 2.52964\sigma_{11}^{-1}$, so that $\beta p/\rho \simeq 5.05927$. The numerical values of the amplitudes K_{ij} and the contact values $g_{ij}(\sigma_{ij}^+)$ are $K_{11} \simeq 91.5298$, $K_{22} \simeq 1148.60$, $K_{22} \simeq 324.24$, $g_{11}(\sigma_{11}^+) = g_{22}(\sigma_{22}^+) \simeq 7.29382$, and $g_{12}(\sigma_{12}^+) \simeq 2.82473$. The property $g_{11}(\sigma_{11}^+) = g_{22}(\sigma_{22}^+)$ is common to all the equimolar cases $(\rho_1 = \rho_2)$, since then Eqs. (17) and (18) imply that $K_{11}\Omega_{11}(\xi) = K_{22}\Omega_{22}(\xi)$. Figure 1 compares the three exact bulk correlation functions $g_{ij}(x)$ with those predicted by the FMT proposed in Ref. [2]. The discrepancies are similar to those found in Ref. [2] between Monte Carlo simulations and FMT.

It must be emphasized that the scheme (5)–(10) provides the exact bulk correlation functions for a one-dimensional mixture in the absence of external fields. The more general problem addressed in Ref. [2], namely the excess free energy as a functional of the inhomogeneous densities, is much more complicated and, to the best of my knowledge, its exact solution is not known. On the other hand, the exact density profiles $\rho_j(x)$ induced by external potentials $V_j(x)$ can be obtained under certain conditions. The trick consists of assuming that one of the species (here labeled as $i = 0$) has a vanishing concentration $(\rho_0 = 0)$ and interacts with the other species via the potentials $\phi_{0j}(x) = V_j(x)$. The knowledge of the bulk correlation functions $g_{ij}(x)$ (with $\rho_j \to \rho_j^{\text{bulk}}$) can then be exploited to get $\rho_j(x) = \rho_j^{\text{bulk}} g_{0j}(x)$. The important limitation, however, is that $V_j(x)$ must represent the potential exerted by a wall that acts only on its nearest particles.

To conclude, it is expected that the exact solutions for one-dimensional homogeneous systems derived elsewhere [3–5] and summarized in this paper can be useful as benchmarks to construct, test, and refine approximate theories such as the FMT of Ref. [2]. This would allow one to gain some illuminating insight into the subtleties and difficulties of the problem of interest, which can be helpful in its extension to the more realistic case of three-dimensional systems.

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