Thermodynamic properties of a polydisperse system

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We use the virial theorem to derive a closed analytic form of the Helmholtz free energy for a polydisperse system of sticky hard spheres (SHS) within the mean spherical model (MSM). To this end we calculate the free energy of the MSM for an N-component mixture of SHS via the virial route and apply to it—after imposing a Lorentz-Berthelot type rule on the interactions—the stochastic (i.e., polydisperse) limit. The resulting excess free energy of this polydisperse system is of the truncatable moment free energy format. We also discuss the compressibility and the energy routes.

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I. INTRODUCTION

In 1968 Baxter presented [1] sticky hard spheres (SHS) as an exactly solvable system of the Percus-Yevick (PY) equation beyond pure hard spheres (HS), introducing an attractive interaction on the surface of the particles. Meanwhile, HS have become a well-appreciated analytic model for colloidal systems (for an overview see, for instance, the introduction of [2]): typically, interactions of colloidal particles have a harsh repulsion in the core region and a short ranged and strong attraction at the surface of the particles [3]. The particularity of the composition of colloidal systems is their polydispersity: in contrast to atomic fluids, the particles of a polydisperse system are no longer equally sized, their size distribution does have a distinct influence both on the structure and the thermodynamic properties can be derived for the structural and thermodynamic properties of the polydisperse (stochastic) case.

So far, this was accomplished for the mean spherical model (MSM) for the following polydisperse systems in closed analytical form: HS structure [6] and thermodynamic properties [7], charged HS structure [8], and SHS structure [9,10].

In this contribution we consider a polydisperse system of SHS within the MSM. Starting from the explicit expressions for the structure functions presented in a recent contribution [9], we derive—via the virial route—a closed expression for the (specific) Helmholtz free energy, i.e., a thermodynamic quantity that is sufficient to determine phase coexistence.

The analysis starts from an N-component system; results for the polydisperse case are derived by imposing a Lorentz-Berthelot type of relation for the potential parameters and by applying then the stochastic limit: we replace the discrete concentrations via $c_i \rightarrow f_g(R)dR$, a prescription that is based on the law of large numbers [11]. The expressions obtained are rather complex. We also discuss the energy route and the compressibility route (pointing out in the latter case an inconsistency of the MSM).

In the next section we present the model and its analytic solution. In Sec. III we calculate the thermodynamic properties via the virial and the energy routes: we start with the discrete case and treat subsequently the polydisperse case. The paper closes with a discussion and a conclusion.

II. MEAN SPHERICAL MODEL FOR A MIXTURE OF STICKY HARD SPHERES

To define the model, we interpret an N-component system of SHS as limiting case of an N-component system with square-well interactions: a mixture of SHS being thus characterized by the set of interactions $\Phi_{ij}$

\begin{equation}
\beta \Phi_{ij}(r) = \lim_{\varepsilon \to 0} \left\{ \begin{array}{ll}
\infty & r \in [0,R_{ij}) \\
-\Theta(r-R_{ij}) \ln \frac{\gamma_{ij} R_{ij}}{\varepsilon} \Theta(R_{ij} + \varepsilon - r) & r \in [R_{ij}, \infty),
\end{array} \right.
\end{equation}

where $\Theta(r)$ is the usual Heaviside step function and the parameters $\gamma_{ij} \in R_{+}^{N \times N}$ represent the stickiness of the spheres. The $R_i$ are the core diameters of species $i \, (i = 1, \ldots, N)$, $R_{ij}=\frac{1}{2}(R_i+R_j)$, $S_{ij}=\frac{1}{2}(R_i-R_j)$, and we assume $S_{ij} > 0$. $\beta=\frac{1}{k_B T}$, $k_B$ being the usual Boltzmann constant and $T$ the temperature, $\rho$ stands for the total number density, $c_i$ are the concentrations of species $i$, and $\rho_i = c_i \rho$ are the partial number densities. The Boltzmann factor for the interaction (1) is given by [where $\delta(r)$ is the usual Dirac delta function]

\begin{equation}
e^{-\beta \Phi_{ij}(r)} = \Theta(r-R_{ij}) + \gamma_{ij} R_{ij} \delta(r-R_{ij}).
\end{equation}
An analytic solution of the Ornstein-Zernike (OZ) equations along with the MSM closure relation for the system under consideration can be given in terms of the total correlation functions \( h_{ij}(r) \): If we use the Wiener-Hopf (WH) technique [12], then the \( h_{ij}(r) \) of the MSM for an \( N \)-component system of SHS are found to be (in the following the summation indices are running—unless otherwise stated—from 1 to \( N \))

\[
\Delta(k) = \text{det} \left[ \delta_{ij} - 2 \pi \rho_i \rho_j \int e^{ikr} Q_{ij}(r) dr \right] > 0
\]

for all \( \text{Im}(k) > 0 \). (7)

A necessary condition for the above criterion is the requirement that \( \Delta(0) > 0 \) [12].

III. THERMODYNAMIC PROPERTIES

A. \( N \)-component system

1. Virial route

Introducing the cavity functions \( y_{ij}(r) \),

\[ 1 + h_{ij}(r) = e^{-\beta q_{ij}(r)} y_{ij}(r), \]

we obtain the virial pressure

\[
\beta p = \rho + \frac{2\pi}{3} \sum_{ij} \rho_i \rho_j Q_{ij}^{(2)} y_{ij}(R_{ij}) + \left[ y_{ij}(r) \right]_{r=R_{ij}}.
\]

By combining Eqs. (2) and (8) with Eqs. (3) and (4) we derive the contact values

\[
\left[ y_{ij}(r) \right]_{r=R_{ij}} = 2 \pi \sum_k \rho_k S_{ik}(S_k) R_{ij} + a_i R_{ij} + b_i
\]

and the (right-hand side) derivatives of the regular part of the \( h_{ij}(r) \) at contact

\[
\left[ y_{ij}(r) \right]_{r=R_{ij}} = a_i + 2 \pi \sum_k \rho_k (a_i S_k + b_i) R_{ij} + 2 \pi \sum_k \rho_k S_{ik} \left[ y_{kj}(r) \right]_{r=R_{ij}}.
\]

The latter expression can be calculated explicitly using Eqs. (4) and (10). Inserting these expressions into Eq. (9) and introducing \( \eta_a = (\pi/6) \sum_i \rho_i \xi_i R_i^2 \), \( a = 0,1,2 \), one obtains finally

\[
\Delta(k) = \text{det} \left[ \delta_{ij} - 2 \pi \rho_i \rho_j \int e^{ikr} Q_{ij}(r) dr \right] > 0
\]

for all \( \text{Im}(k) > 0 \). (7)
\[
\frac{288\pi}{6} \sum_i \rho_i \xi_i R_i \frac{\pi}{6} \sum_j \rho_j \xi_j \Gamma_{ij} - \frac{72\xi_2 \pi}{6} \sum_i \rho_i \xi_i R_i^2 \frac{\pi}{6} \sum_j \rho_j \xi_j \Gamma_{ij} (1 - \xi_3)^2
\]

if \(\Delta(0)>0\), undefined otherwise. Note that the corresponding expression for the PY equation is given for the one-component case in [1] and for the \(N\)-component case in [15].

In contrast to the PY equation, the MSM solution allows to derive a closed expression for the specific Helmholtz free energy (free energy per unit volume), \(f\), associated with Eq. (12): if we use the thermodynamic relation

\[
\rho^{-2} p(\beta, \rho) = \frac{\partial}{\partial \rho} \left[ \rho^{-1} f(\beta, \rho) \right],
\]

we find for the excess (over the ideal gas) specific free energy \(\tilde{f}\) of Eq. (12)

\[
\frac{\pi}{6} \beta \tilde{f} = -\varepsilon_0 \ln[1 - \xi_3] + \frac{3 \xi_3}{\xi_3^2} \ln[1 - \xi_3] + \frac{3 \xi_3^2}{1 - \xi_3} + \frac{3 \xi_3^3}{\xi_3^2(1 - \xi_3)} + 12 \rho^{-2} \sum_i \rho_i \xi_i^2 - 12 \left[ \rho^{-2} \sum_i \rho_i \xi_i^2 \right] + 10 \frac{\pi}{6} \sum_i \rho_i \xi_i^2
\]

if \(\Delta(0)>0\), undefined otherwise.

2. Compressibility route

For an \(N\)-component system of SHS within the MSM a closed analytical expression is also available for the direct correlation functions \(c_{ij}(r)\) [16]. From this the compressibility pressure is obtained via

\[
\beta \frac{\partial p}{\partial \rho_i} = 1 - 4 \pi \sum_k \rho_k \int r^2 c_{ik}(r) dr = \varphi_i(\rho).
\]

The explicit, rather lengthy expression for the \(c_{ij}(r)\) [from which follow the \(\varphi_i(\rho)\)] is given in Eq. (25) of [16]. However, a closer inspection of this relation reveals that

\[
\frac{\partial \varphi_i(\rho)}{\partial \rho_j} \neq \frac{\partial \varphi_j(\rho)}{\partial \rho_i},
\]

i.e., the compressibility pressure does depend on the thermodynamic path, an inconsistency that is certainly due to the MSM.

3. Energy route

If we use the energy equation of state, then the excess (over a HS reference mixture) specific free energy via the energy route, \(\tilde{f}\), is determined by [17,15]

\[
\frac{\partial \tilde{f}}{\partial \beta} = -2 \pi \sum_{i,j} \rho_i \rho_j R_{ij}^3 \varphi_{ij} \frac{\partial \gamma_{ij}}{\partial \beta},
\]

\[
\frac{\partial \varphi_i(\rho)}{\partial \rho_j} = \frac{\partial \varphi_j(\rho)}{\partial \rho_i}.
\]
which can be directly integrated and yields

\[ \frac{\pi}{6} \beta \tilde{J} = - \frac{18 \eta_1 \xi_2}{(1 - \xi_2^2)} + 12 \eta_0 + \frac{72 \pi}{6} \sum_i \rho_i \xi_i^2 \]

\[-48 \pi \sum_i \rho_i \pi \tilde{J} + \sum_i \rho_i \tilde{J}_{i} \sum_j \rho_j \tilde{J}_{k} \quad (18)\]

where we have used the symmetry relation \( \gamma_{ij} = \frac{1}{2} (\gamma_{ii} + \gamma_{jj}) \); for the PY solution cf. [17] (one-component case) and [15] (multicomponent case). Again, expression (18) is valid for \( \Delta(0) > 0 \) and undefined else.

### B. Stochastic limit

The expressions derived in the preceding section allow to perform the stochastic limit (cf. Sec. IV in [9]), arriving thus at a polydisperse system. In such a system each particle is "uniquely associated with a value of some characteristic parameter \( X \), distributed according to a probability distribution function \( f_X(x) \); \( X \) is a continuous random variable" [11]. In our case the diameter \( R \) of the particles is the natural choice for the continuous random variable, \( X = R \), \( R \) being distributed according to a probability distribution \( f_R(R) \). The prescription for this stochastic limit is to replace the discrete concentrations \( c_i \) and partial densities \( \rho_i \) of an \( N \)-component system via

\[ c_i \rightarrow f_R(R)dR, \quad \rho_i \rightarrow \rho f_R(R)dR, \quad (19) \]

a replacement that is based on the law of large numbers [11]. As a consequence, summations over species \( i \) transform into integrals over \( R \). Similar to the diameters \( R_i \), we have to transform the stickiness \( \gamma_{ii} \) into a random variable \( G = G(R) \), which is—by definition of polydisperse systems—a function of the random variable \( R \). In an effort to make the stochastic limit possible and to preserve at the same time the analyticity of the expressions, we have to introduce—as already explained in [9]—a further restriction on the \( \gamma_{ij} \). This assumption is known in literature as the Berthelot rule and is frequently used in mixtures [18]. Its multicomponent form, \( \gamma_{ij}(R_{ij}) = \gamma_{ii}(R_{ii}) \gamma_{jj}(R_{jj}) \), transforms for the stochastic case into the functional relation

\[ G^2 \left( \frac{1}{2} (R + R') \right) = G(R) G(R') \quad (20) \]

with the unique continuous solution

\[ G(R) = \gamma_0 e^{G^2}, \quad (21) \]

\( \gamma_0 \) and \( z \) being two positive adjustable parameters.

### 1. Virial route

On substituting the multicomponent form of Eq. (21) in Eq. (14) and applying to the resulting expression the stochastic limit, we arrive at the excess (over the ideal gas) specific free energy via the virial route of the MSM for a polydisperse system of SHS

\[ \pi \beta \tilde{J} = - \xi_0 \ln[1 - \xi_3] + 3 \xi_1 \xi_2 \ln[1 - \xi_3] + \frac{3 \xi_1 \xi_2}{1 - \xi_3} + \frac{3 \xi_2}{1 - \xi_3} + 12 \xi_1(1 - \xi_3) + \frac{6 \xi_1}{1 - \xi_3} + 10 \xi_3(0) - 2 \xi_2(0) - 2 \xi_1 \xi_2 \]

\[-3 \xi_1 \xi_2 - \eta_0 \xi_3 + 12 \xi_2(0) - 12 \left[ \frac{\ln[1 - \xi_3]}{\xi_3} + \frac{1}{1 - \xi_3} \right] \eta_1 \xi_2 - \eta_2 \xi_1 - 36 \left[ \frac{\ln[1 - \xi_3]}{\xi_3} + \frac{2}{1 - \xi_3} \right] \eta_2 \xi_1 \]

\[-3 \sum_{i,j,k=0}^{2} \left( \frac{2}{i} \right) m_{4-i-j}(2z) \left( \frac{2}{j} \right) m_{i+k}(2z) \left( \frac{2}{k} \right) m_{2+j-k}(2z) \gamma_0^3 + 12 \left[ \frac{\ln[1 - \xi_3]}{\xi_3} \right] \eta_0 - 144 \left[ \frac{2 \ln[1 - \xi_3]}{\xi_3} + \xi_3(2 + \xi_3) \right] \eta_0 \]

\[ \times 2 \xi_1 \xi_2(1 + \xi_2) - 72 \left[ \frac{1}{1 - \xi_3} + \frac{2 \ln[1 - \xi_3]}{\xi_3} + \xi_3(2 + \xi_3) \right] \xi_2(1 + \xi_2) + 2 \eta_1 \eta_2 \]

\[-3 \sum_{i,j,k=0}^{2} \left( \frac{2}{i} \right) m_{4-i-j}(2z) m_{i+i+j}(2z) \left( \frac{2}{j} \right) m_{2+j-k}(2z) \left( \frac{2}{k} \right) m_{2+j-k}(2z) \left( \frac{2}{l} \right) \gamma_0^4 \quad (22)\]

with the generalized moments

\[ m_i(t) = \frac{\pi}{6} \rho \int f_R(R) e^{R^2 R^i} dR, \quad (23) \]

with

\[ m_i(0) = \xi_i, \quad i = 0, \ldots, 3, \]

and with

\[ \xi_{uv}^{(w)} = \left( \frac{\gamma_0}{4} \right)^2 \sum_{i,j=0}^{2} m_{4-i-j+w}(2z) \left( \frac{2}{i} \right) m_{i+w}(2z) \left( \frac{2}{j} \right) m_{i+w}(2z). \]
\[ \eta = \frac{\gamma_0}{4} \sum_{i=0}^{2} m_{2-i+z}(z) \left( \begin{array}{c} 2 \\ i \end{array} \right) m_{j+1}(z), \]  
\[ \xi^{(w)}_u = \left( \frac{\gamma_0}{4} \right)^3 \sum_{i,j,k=0}^{2} \left( \begin{array}{c} 2 \\ j \end{array} \right) m_{4-j-k+u}(2z) m_{i+j}(z) \]  
\[ \times \left( \begin{array}{c} 2 \\ k \end{array} \right). \]  
\[ \text{Note that the ideal gas part has to be treated separately [11].} \]

A closer inspection of the expression (22) reveals that the knowledge of only 15 (generalized) moments \( \{m_i(0), i = 0, \ldots, 3, m_i(z), i = 0, \ldots, 4, m_i(2z), i = 0, \ldots, 5\} \) is sufficient to calculate the complete thermodynamic properties of the system. Hence, Eq. (22) is of what Sollich et al. [19] call the “truncatable moment free energy format.”

As shown in [9], condition (7) becomes in the stochastic limit \( \lim_{N \to \infty} \Delta(k) = \det (D(-ik)) \)
\[ \det D(s) > 0 \quad \forall \text{Re}(s) > 0, \]  
with \( E_5 \) being the five-dimensional unit matrix

\[ D(s) = E_5 - 3 \begin{pmatrix} 4 \xi^{(0)}_{220} + 2 \xi^{(0)}_{110} & 4 \xi^{(0)}_{100} & 4 \xi^{(0)}_{001} & 4 \xi^{(0)}_{010} & 4 \xi^{(0)}_{011} \\ 2 \xi^{(2)}_{210} + \xi^{(2)}_{120} & 2 \xi^{(2)}_{110} & 2 \xi^{(2)}_{011} & 2 \xi^{(2)}_{010} & 2 \xi^{(2)}_{001} \\ \xi^{(1)}_{211} + \frac{1}{2} \xi^{(1)}_{131} & \xi^{(1)}_{121} & \xi^{(1)}_{022} & \xi^{(1)}_{032} \xi^{(1)}_{042} \\ 2 \xi^{(2)}_{211} + \xi^{(2)}_{121} & 2 \xi^{(2)}_{111} & 2 \xi^{(2)}_{012} & 2 \xi^{(2)}_{022} & 2 \xi^{(2)}_{032} \\ \xi^{(1)}_{201} + \frac{1}{2} \xi^{(1)}_{111} & \xi^{(1)}_{101} & \xi^{(1)}_{002} & \xi^{(1)}_{001} & \xi^{(1)}_{000} \end{pmatrix} \]  

and

\[ \xi_{ijk}(s) = \frac{1}{s} \left[ m_j(kz) - m_j(kz - 2s) \right] \gamma_0^{k/2}, \]  
\[ \tilde{\xi}_{ijk}(s) = \frac{1}{s} \left[ \xi_{(i-1)jk}(s) - \left( -\frac{1}{2} \right)^{i-1} \gamma^{k/2} m_{j+1}(kz) \right], \quad i = 1, 2, \ldots, \]  
\[ \xi_{ijk}(s) = \frac{\tilde{\xi}_{ijk}(s)}{1 - \xi_3}, \]  
\[ \xi^{(a)}_{ijk}(s) = \tilde{\xi}_{ijk}(s) + \frac{3 \xi_2 \xi_{i(j+1)k}(s)}{(1 - \xi_3)^2} \]  
\[ - \frac{3}{1 - \xi_3} \sum_{u=0}^{2} \xi_{i(2+j-u)(k+1)}(s) \left( \begin{array}{c} 2 \\ u \end{array} \right) m_{u+1}(z) \gamma_0^{u/2}. \]  

Thus, the necessary condition \( \det D(0) > 0 \) is also calculated by a limited number of moment densities only: we obtain from Eqs. (30), (31), and (23),
\[ \lim_{s \to 0} \xi_{ijk}(s) = \frac{(-1)^i}{(i+1)!} m_{i+j+1}(kz) \gamma_0^{k/2}, \quad i = 0, 1, 2; \]  
\[ \text{hence, } D(0) \text{ depends on } m_i(0), i = 2, 3, 4, m_i(z), i = 1, \ldots, 5, \text{ and } m_i(2z), i = 1, \ldots, 5, \text{ i.e., on 13 moments.} \]

2. Energy route

On substituting the multicomponent form of Eq. (21) in Eq (18) and applying to the resulting expression the stochastic limit, we arrive at the excess (over a polydisperse HS system) specific free energy via the energy route of the MSM for a polydisperse system of SHS

\[ \pi = \frac{1}{6} \beta f = -\frac{18 \eta_1 \xi_2}{(1 - \xi_3)^2} \frac{12 \eta_0}{1 - \xi_3} + \frac{72 \xi^{(0)}_{11}}{1 - \xi_3}, \]  
\[ -\frac{3}{4} \sum_{i,j,k=0} \left( \begin{array}{c} 2 \\ i \end{array} \right) m_{4-i-j}(2z) \left( \begin{array}{c} 2 \\ j \end{array} \right) m_{i+j}(2z) \]  
\[ \times \frac{2}{k} m_{2+j-k}(2z) \gamma_0^{3}. \]  

if \( \det D(0) > 0, \) undefined else. Here, 11 (generalized) moments are sufficient to calculate \( f \) \( m_i(0), i = 2, 3, m_i(z), i = 0, \ldots, 3, m_i(2z), i = 0, \ldots, 4. \) Hence again, \( f \) is a so-called "truncatable moment free energy" [19].

IV. DISCUSSION AND CONCLUSION

In this contribution we have shown that the thermodynamic properties of a polydisperse SHS system within the MSM can be derived from the expressions for an \( N \)-component system by fully maintaining the analyticity of the expressions. The model presented here is the most simple extension beyond a polydisperse system of HS, including attractive interactions; hence a spinodal decomposition is to be expected. We summarize in the following the criteria for
phase stability and spinodal decomposition: (i) the system is stable, if $\det D(s) > 0$ for all $\Re(s) \geq 0$; (ii) a necessary condition for this criterion is $\det D(0) > 0$; (iii) the spinodal is determined via the equation $\det D(0) = 0$ [12,20,21].

We have presented closed expressions for the specific free energy $f$ obtained via the virial and the energy route; the compressibility route has to be discarded due to an inconsistency of the MSM. These expressions are sufficient to derive all thermodynamic quantities that are required to determine phase coexistence. The chemical potentials $\mu_i$ become—as a consequence of the stochastic limit—$\mu(R)$, i.e., functions of the particle size $R$. They are obtained from the specific free energy $f$ via functional derivative with respect to $\rho_f(R)$,

$$\frac{\delta f(\beta, \rho; [f_R])}{\delta \rho_f(R)} = \mu(\beta, \rho, R; [f_R]).$$

Explicit application of this rule to the excess part of $f$ requires only conventional partial derivatives with respect to the moments, the inner functional derivatives are then given by the weights of these moments (see also [19]). Both, the expressions for the pressure and the chemical potentials turn out to be rather lengthy (for applications we recommend the use of symbolic computer languages), and hence are not presented here.

The special attractive feature of the model presented here is that both, for the virial and the energy route, the full information on the excess thermodynamic properties can be obtained from a limited number of (generalized) moments of the given distribution function $f_R(R)$. Other examples of this class, called “truncatable systems” [19], are the (well-known) polydisperse HS [7], and, more recently considered in [22], the polydisperse Zwanzig model of hard rods.

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