

*Atti dell'Accademia Peloritana dei Pericolanti
Classe di Scienze Fisiche, Matematiche e Naturali
Vol. LXXXVI, C1A0802002 (2008)
Adunanza del 29 novembre 2007*

STATISTICAL ENTROPY AND CLUSTERING IN ABSENCE OF ATTRACTIVE TERMS IN THE INTERPARTICLE POTENTIAL

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ABSTRACT. Recently a new intriguing class of systems has been introduced, the so-called generalized exponential models, which exhibit clustering phenomena even if the attractive term is missing in their interaction potential. This model is characterized by a index n which tunes the repulsive penetrability of the potential. This family of potentials can represent the effective interactions for a large number of soft matter systems. In this paper we study the structural and thermodynamic properties in the fluid regime of the generalized exponential model with a value of index n suggested by Mladek *et al.* [B. M. Mladek, G. Kahl, and C. N. Likos, Phys. Rev. Lett. (2008)] to fit the effective potential of a typical amphiphilic dendrimers. We use the conventional approach of the liquid state theory based on the hypernetted chain closure of the Ornstein-Zernike equation together with some Monte Carlo numerical simulations. Moreover, we try to detect qualitatively the freezing line exploiting the predictive properties of a one-phase rule based on the expansion of the statistical entropy.

1. Introduction

The soft condensed matter concerns the study of that class of systems called complex liquids encompassing many materials used in our daily life [1]. From academic point of view, the most intriguing aspect of these systems leads to the possibility to model the architecture of the atomic entities which constitute them. The statistical mechanics approach to the soft matter allows to average out the huge number of freedom internal degrees of the constituent particles these macromolecules [2]. Hence it is possible to deal with the problem using the techniques typical of the liquid state theory. The macromolecules are identified as “effective” spherical particles (even if their shape is far from being spherical), while their mutual interaction is modelled by an “effective” pair potential. Through suitable methods the chemical-physical properties of the solvent, in which they are immersed, can be modified allowing a full freedom in tuning the interparticle potential [3]. In typical polymeric systems with low inner monomer concentration, such as polymer chains, dendrimers, microgels, or block copolymers, it is plausible that, as a consequence of their complex inner structure, the centers of mass of the macromolecules can overlap and upon compression even cross each other. Hence the resulting “effective” pair potential must remain finite and bounded at zero separation and at the same time must be soft enough to assure the interpenetrability between the “effective” particles [4].

In the last two years Mladek *al.* have considered a typology of interaction potentials which presents the above required functional features [5]. The thermodynamical and structural properties of the so-called generalized exponential model (GEM- n) have been described through accurate theoretical approaches and advanced numerical techniques [6–8]. Moreover, Likos *al.* have rationalized the behavior of GEM- n phase diagrams analyzing the Fourier Transform (FT) of the potential [9]. In particular if the FT is non-negative the system displays a reentrant melting with an upper freezing temperature. The simplest statistical model which after freezing re-melts upon further compression is the gaussian core model (GCM). The model was introduced in 1976 by Stillinger [10] and ultimately its phase diagram has been fully traced out through accurate theoretical and numerical methods [11, 12]. This curious phenomenon has been verified for several soft matter systems such as star polymers [13, 14], microgels [15–17], dendrimers [18, 19] or coarse-grained block copolymers [20, 21]. If the FT of the interparticle potential oscillates around zero then the system will freeze at all temperatures forming stable clusters. Compared to the reentrant melting scenario the clustering effect has obtained little attention. The fluid regime of the penetrable sphere model (PSM) was recently investigated using sophisticated integral-equation approaches [22] while the phase diagram was studied through density-functional techniques [23]. This model may be a prototype for the interaction between micelles in a solvent [24]. The functional suitability of the (GEM- n) consists in interpolating smoothly, through the parameter n , between two model systems above mentioned, *i.e.* the GCM and the PSM.

In this paper we study the behavior of the so-called residual multiparticle entropy (RMPE) as a measure of the relevance of correlations involving more than two particles in the configurational entropy of the generalized exponential model with $n = 3$. The GEM-3.1 approximates with high accuracy the pair potential between the centers of mass of two amphiphilic dendrimers [25]. In a series of papers it has been shown that the condition of vanishing of RMPE is a reliable precursor of the ordering processes occurring in the fluid phase (for a review see Ref [26]). Very recently the reliability of this statistical entropic approach has been tested against the “exact” phase diagram of the GEM-4 [27]. Starting from this assumption we try to trace out qualitatively the freezing line of the GEM-3.

The rest of the paper is organized as follows: In Section 2, we introduce the generalized exponential model and the structural indicators able to detect an order-disorder phase transition. The Section 3 is devoted to the integral-equation theory and to the Monte Carlo simulation. Results are exposed in Section 4 and conclusions are deferred to Section 5.

2. The model and statistical entropy approach

For spherical particles the generalized exponential model (GEM- n) presents the following functional expression [3, 6]:

$$(1) \quad v(r) = \epsilon \exp(-r/\sigma)^n,$$

where ϵ and σ fix the energy and length scales, respectively. This law represents a purely repulsive bounded pair-potential as reported in figure 1 and n is an arbitrary positive number. We also introduce the reduced number density $\rho^* \equiv \rho\sigma^3$ and the reduced temperature $T^* \equiv k_B T/\epsilon$ being k_B the Boltzmann constant. It is direct to verify that for $n > 2$ the

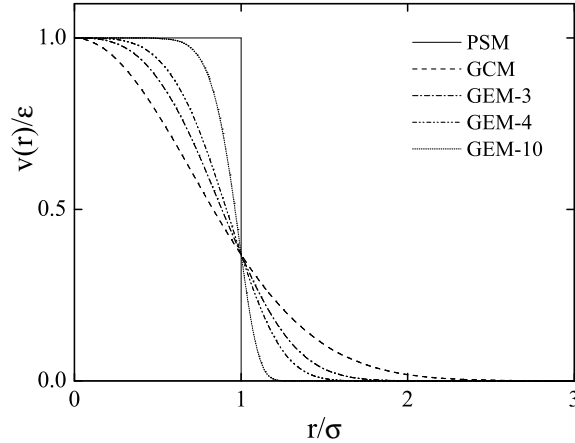


FIGURE 1. The potential GEM- n for $n = 2, 3, 4, 10$ and ∞ . The GEM-2 and GEM- ∞ are the Gaussian core model and the penetrable sphere model, respectively.

FT of this potential oscillates around zero and hence the system will freeze at all temperatures [23]. It has been shown that within a certain temperature range the GEM- n with $n > 2$ solidifies into crystals where lattice sites are multiply occupied [5]. This fascinating phenomenon has not been experimentally observed. However, it has been suggested that some amphiphilic dendrimers could form such crystals, but experiments are still lacking [25].

The exact phase diagram of GEM- n with index $n = 4$ has been, recently, traced through a new approach to evaluate the free energy of a reference multiply occupancy crystal, i.e., a solid with multiply occupied sites [7]. However, calculating the free energy of either a dense fluid or a hot solid still remains a demanding computational task that requires intensive simulations to be carried out at several state points as well as some preliminary selection of the most likely candidate solid structures.

For such reasons, a number of empirical rules have been proposed since the early years of statistical mechanics in an attempt to correlate phase-transition thresholds with the thermodynamic or structural properties of the solid and fluid phases, respectively. All such criteria are typically based on the properties of one phase only and, in general, can be easily implemented with a modest computational effort [28].

As already anticipated in the Introduction we shall use an entropic criterion originally proposed by Giaquinta and Giunta for the freezing of hard spheres [29]. This approach is based on the possibility to expand the excess entropy of a fluid as an infinite series [30]:

$$(2) \quad s_{\text{ex}} = \sum_{n=2}^{\infty} s_n ,$$

where s_{ex} is the excess entropy per particle in units of the Boltzmann constant and the partial entropies s_n are obtained from the integrated contributions of the spatial correlations between n -tuples of particles. In particular, the two-body term can be written as [31]:

$$(3) \quad s_2 = -\frac{1}{2}\rho \int \{g(r)\ln g(r) - g(r) + 1\}dr ,$$

where the quantities $g(r)$ are the radial distribution functions (RDF). The residual multi-particle entropy (RMPE)

$$(4) \quad \Delta s \equiv s_{\text{ex}} - s_2$$

turns out to be a sensitive indicator of the structural changes which take place in the system. It has been shown that the zeros of this function systematically correlate with the thresholds of thermodynamic stability of the homogeneous fluid phase [26,32].

Recently, we have verified the reliability of this empirical rule for the localization of the fluid-solid transition thresholds of bounded and soft interaction potentials [33,34]

3. Integral equation theory and Monte Carlo simulation

The Ornstein-Zernike (OZ) integral equation reads:

$$(5) \quad h(r) = c(r) + \rho \int h(r')c(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}'$$

where $h(r)$ and $c(r)$ are the total and the direct correlation functions, respectively. A closure relationship is introduced when a functional form is given for $h(r)$. The hypernetted chain (HNC) corresponds to

$$(6) \quad h(r) = \exp[-\beta v(r) + h(r) - c(r)] - 1$$

where $v(r)$ is the interaction potential [35]. Within the HNC framework the excess chemical potential can be expressed through a closed form in terms of the distribution functions. Hence, it is direct to derive the expression of the excess free energy [36]. The integral equation was solved numerically for $T^* = 0.2, 0.5, 0.8, 1.0$, using the method originally proposed by Gillan with 1024 equally spaced grid points, setting the mesh size to 0.01 [37]. We have performed Monte Carlo (MC) simulations in the canonical ensemble (NVT) of the GEM-3 for the following isothermal ($T^* = 0.2, 0.5, 0.8, 1.0$) and isochoric ($\rho^* = 4.8$ and 8.0) quasistatic paths in order to verify the reliability of the HNC estimates. The phase space points of MC simulations are shown in figure 2. We have used the standard Metropolis algorithm for sampling the equilibrium distribution in configurational space. The typical system consisted of 500 particles enclosed in a square box with periodic boundary conditions which provides a sufficiently reliable results in the fluid regime. However, further runs with larger number of particles have been occasionally analyzed in order to detect

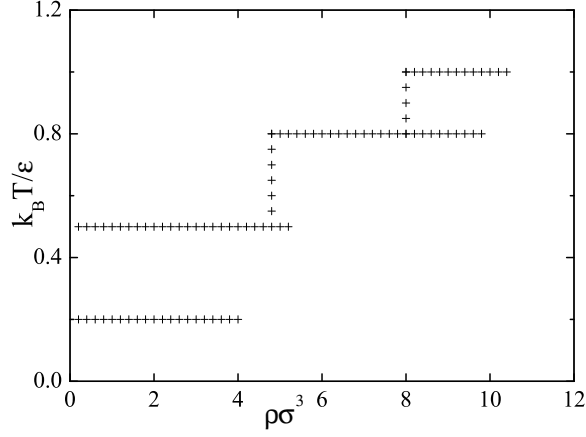


FIGURE 2. Monte Carlo simulation points in the phase space.

any dependence of our results on the size of the system. As a rule the last MC configuration at a given ρ has served, after suitable rescaling of particle coordinates, as the starting configuration for the run at a slightly higher density. For each ρ^* and T^* , equilibration of the sample typically takes 5×10^3 MC sweeps, a sweep consisting of one attempt to sequentially change the position of all particles. The maximum random displacement of a particle in a trial MC move has been adjusted once a sweep during the run so to keep the acceptance ratio of the moves as close as possible to 50%, with only small excursions around this value. For given NVT conditions, the relevant thermodynamic averages have been computed over a trajectory whose length ranges from 2×10^4 to 6×10^4 sweeps. In particular, the excess energy per particle u_{ex} and the pressure P are carefully monitored. Pressure comes from the virial formula,

$$(7) \quad P = \rho k_B T + \frac{\langle Vir \rangle}{V}, \quad Vir = -\frac{1}{3} \sum_{i < j} r_{ij} v'(r_{ij})$$

(r_{ij} is the distance between particles i and j). The RDF histogram has been constructed with a spatial resolution of $\Delta r = r_m/100$ and updated every 10 MC sweeps. We found that the RDF was never significantly different from unity for low and moderate density. The fulfillment of this condition is important since it may obviously affect the numerical precision of the estimate obtained for the pair entropy using Eq. (3). In fact, some discrepancies between the HNC and MC pair-entropy estimates were noted at high density in proximity of the zero-RMPE. The stability of the RDF contact values was considered (within the numerical accuracy of the calculation) a good indicator of the equilibration achieved in proximity of the phase-separation threshold. In order to evaluate the numerical errors affecting the main statistical averages, we have divided the MC trajectory into

ten blocks and estimated the length of the error bars as being twice the empirical standard deviation of the block averages from the mean (under the implicit assumption that the decorrelation time of any relevant variable is less than the size of a block). Typically, the relative errors of energy and pressure is smaller than few tenths of a percent also at high density.

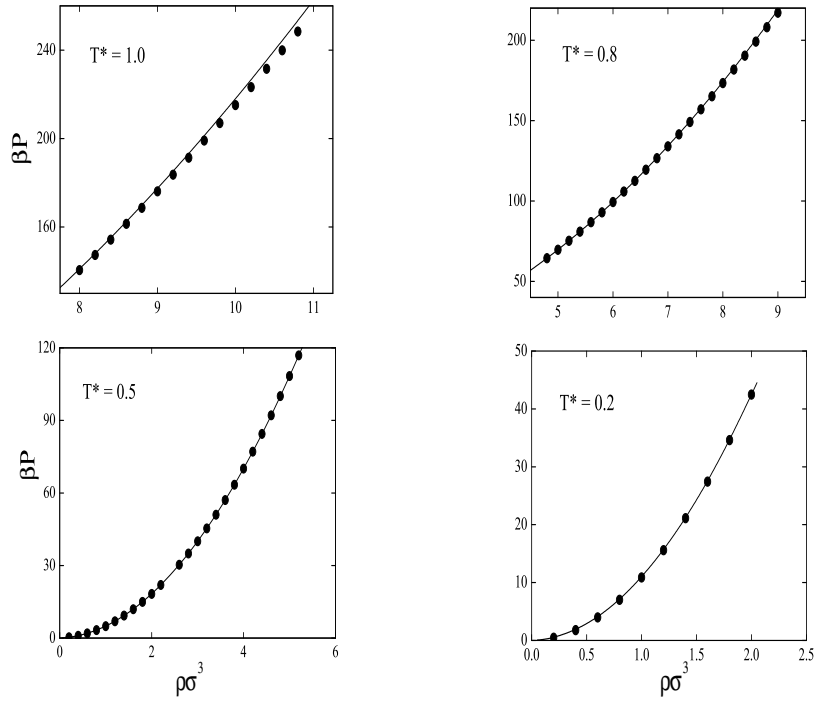


FIGURE 3. Pressure of the GEM-3 for $T^* = 0.2, 0.5, 0.8$ and 1.0 plotted as a function of the reduced density. MC results: filled circles; HNC-closure: solid line.

The difference in excess free energy between two equilibrium states of the system, say 1 and 2, lying *within the same phase* is computed through the combined use of the formulae

$$(8) \quad \frac{f_{\text{ex}}(T_2, \rho)}{T_2} = \frac{f_{\text{ex}}(T_1, \rho)}{T_1} - \int_{T_1}^{T_2} dT \frac{u_{\text{ex}}(T, \rho)}{T^2}$$

and

$$(9) \quad \beta f_{\text{ex}}(T, \rho_2) = \beta f_{\text{ex}}(T, \rho_1) + \int_{\rho_1}^{\rho_2} d\rho \frac{1}{\rho} \left[\frac{\beta P(T, \rho)}{\rho} - 1 \right],$$

where f_{ex} is the excess Helmholtz free energy per particle and $\beta = (k_B T)^{-1}$. The above

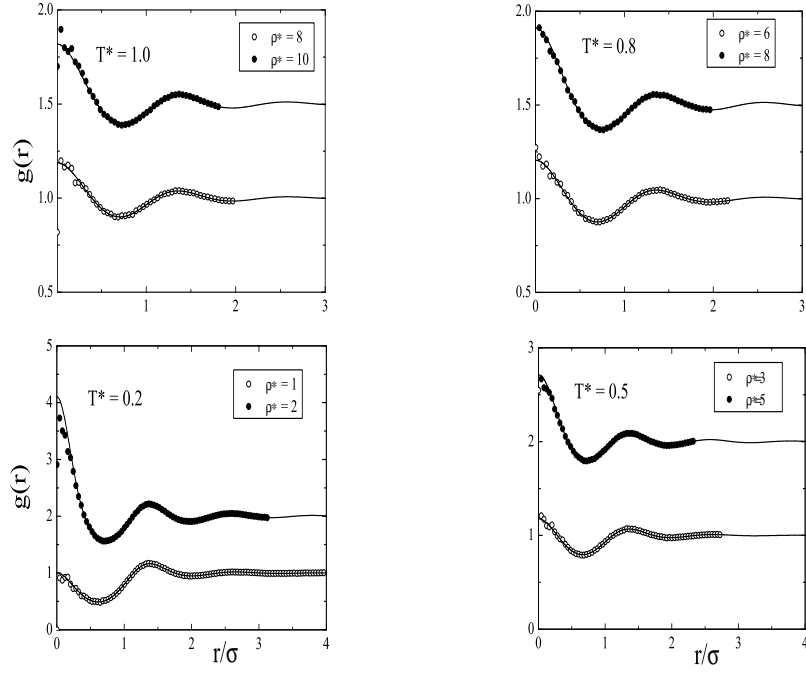


FIGURE 4. Radial distribution functions of the GEM-3 model as obtained by Monte Carlo simulations (filled and open circles) and from the HNC-closure (solid lines) for $T^* = 0.2, 0.5, 0.8$ and 1.0 . For clarity, on each panel the RDF corresponding to the larger density have been shifted upwards by a certain amount.

formulas are, however, useless if one does not have an independent estimate of the system free energy in a reference state. Only in this case do Eqs. (8) and (9) help in finding the free energy of any other state in the same phase. As a reference state for the fluid, we can choose any equilibrium state that is characterized by a very small ρ value and arbitrary T (say, a nearly ideal gas), since then the excess chemical potential of the system can be

accurately estimated by the Widom or particle-insertion method [38].

$$(10) \quad \mu_{\text{ex}} = -k_B T \ln \langle \exp(-\beta E_{\text{ins}}) \rangle ,$$

where E_{ins} comprises all interaction terms between a randomly-inserted ghost particle and all the system particles. The average in Eq. (10) is evaluated numerically during a run of

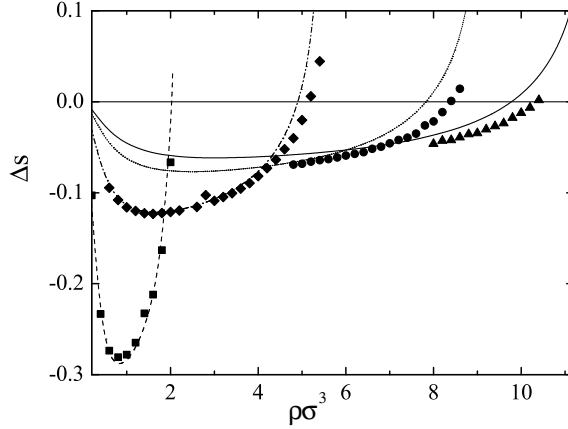


FIGURE 5. Residual multiparticle entropy of the GEM-3 for different temperatures plotted as a function of the reduced density. Symbols and lines represent the MC and HNC results, respectively. Squares (MC) and dashed line (HNC) for $T^* = 0.2$; Diamonds (MC) and dash-dotted line (HNC) for $T^* = 0.5$; Circles (MC) and dotted line (HNC) for $T^* = 0.8$; Triangles (MC) and solid line (HC) for $T^* = 1.0$.

typically 5×10^4 equilibrium sweeps, with an insertion attempted at the completion of every sweep. Once μ_{ex} is given, the excess values of free energy and entropy will follow from

$$(11) \quad \beta f_{\text{ex}} = \beta \mu_{\text{ex}} - \frac{\beta P}{\rho} + 1 \quad \text{and} \quad \frac{s_{\text{ex}}}{k_B} = \beta(u_{\text{ex}} - f_{\text{ex}}).$$

It is useful to note that, from a strictly numerical point of view, choosing a very dilute gas as a reference state for the fluid is far better than starting the thermodynamic integration in Eq. (9) from the ideal gas of equal temperature. In fact, unless one has a lot of thermodynamic points in the very-dilute region of the phase diagram, a spline interpolant of $\beta P/\rho$ that is sufficiently accurate in this region is hard to construct.

4. Results and discussion

In figure 3 we report the comparison between the MC and HNC pressure estimates for $T^* = 0.2, 0.5, 0.8$ and 1.0 . The agreement is excellent until the iterative procedure to

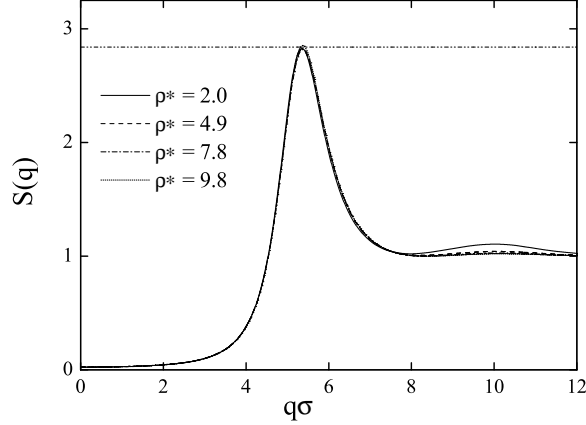


FIGURE 6. Structure factors $S(q)$ as a function of $q\sigma$ obtained by the HNC-closure for a fluid GEM-3 for $T^* = 0.2, 0.5, 0.8, 1.0$ and at the corresponding densities where the RMPE vanishes. The dashed horizontal line indicates the freezing threshold (2.85) of the Hansen-Verlet rule.

solve the HNC equation converges. Slightly discrepancies are visible only for $T = 1.0$ and at very high density. In figure 4 the RDF evaluated by the numerical simulation and integral equation are compared. As for the pressure case the agreement is good. Some tiny discrepancies between the HNC and MC results appear only at the highest density and for distances near to zero separation as already reported in [9] for $n = 4$. Now we present the RMPE profile for different values of the reduced temperature. Figure 5 shows the density dependence of this quantity. The differences between the HNC and MC zero-RMPE values is ascribable to the fact that at very high density the RDF's computed by the simulations with $N = 500$ differ from unity giving rise a not-negligible error in the pair-entropy estimate (see Eq. (3)). The error grows increasing the temperature and, as consequence, the density. As already noted elsewhere, the zero of the RMPE identifies a structural threshold beyond which the system enters a liquidlike regime where cooperative, i.e., intrinsically manybody, effects come into play in determining the state of the fluid. The zero-RMPE density was found to increase for increasing the temperature. However, we recall that the one-phase character of this criterion does not allow for an exact characterization of the phase transition occurring in the vicinity where the RMPE vanishes. Indeed, within such a framework we cannot easily detect what kind of phase transition the mixture undergoes. Notwithstanding, this entropic approach, likewise more famous freezing one-phase rules [39,40], can be used as a sort of "litmus paper" to indicate qualitatively the threshold of ordering processes occurring in the system. In figure 6 we show the HNC structure

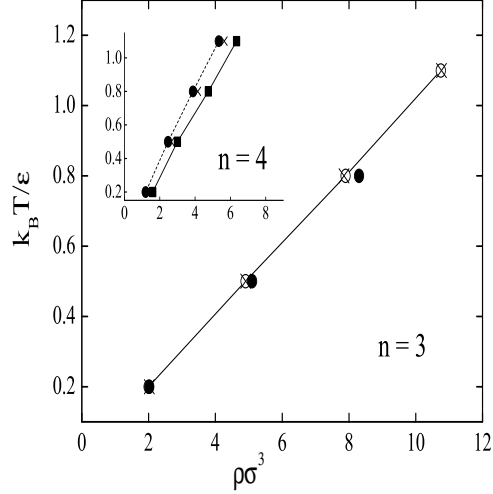


FIGURE 7. Zero-RMPE freezing temperature plotted in reduced units as a function of the reduced density as obtained from MC simulations (filled circles) and from HNC-closure (open circles). The crosses indicates the freezing estimates obtained from the Hansen-Verlet rule. The inset shows the phase diagram of the GEM-4. The squares are the freezing estimates obtained from “exact” free-energy calculations [7], while the filled circles are the Zero-RMPE freezing temperature. The crosses indicates the freezing estimates obtained from the Hansen-Verlet rule. The lines are a guide for the eye.

factors for some reduced temperatures corresponding to the density where the RMPE vanishes. We note that the first peak is about 2.85 which is the value according to which the Hansen-Verlet criterion indicates the freezing phase transition in harshly repulsive liquids. However, it has been correctly emphasized for the GEM-4 that the first peak of the structure factor close to freezing considerably exceeds the value of 2.85 demonstrating that the ultrasoft systems can support a higher degree of spatial correlations than hard matter systems before they freeze [6].

In figure 7 we trace the locus of points associated with the vanishing of the RMPE. The resulting line qualitatively could represent the freezing line of the GEM-3. In the same graph we report the Hansen-Verlet freezing estimates which basically coincide with the RMPE results. In the inset we plot the comparison between the entropic criterion freezing estimates [27] and the fluid-solid line evaluated through “exact” free-energy calculations

for $n = 4$ [7]. Hence we can expect that the both RMPE and Hansen-Verlet freezing estimates behave similarly for $n = 3$, anticipating and underestimating systematically the “correct” fluid-solid coexistence line of an amount which, however, does never overcome the 10%.

5. Concluding remarks

In this paper we have qualitatively traced out the freezing line of the GEM-3 by means of an one-phase empirical criterion based on the expansion of the statistical entropy. It has been suggested that a GEM with $n = 3.1$ may approximate with high accuracy the effective potential of typical amphiphilic dendrimers [25]. We have used the HNC closure and MC numerical simulations to obtain the thermodynamic and structural ingredients for the evaluation of the RMPE. We have also noted a good agreement between the freezing predictions obtained from RMPE and Hansen-Verlet rule. Indeed, as already evidenced [32] both criteria identify an intrinsic structural condition of the fluid which, in the enlightening perspective offered by the multiparticle correlation expansion of the statistical entropy, reveals itself as the microscopic backstage of the incoming transition of the fluid into a more ordered state.

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Presented: November 29, 2007
Published on line: May 8, 2008