

# Entropy, correlations, and ordering in two dimensions

F. Saija

*Istituto Nazionale per la Fisica della Materia (INFN), Unità di Ricerca di Messina, Italy*

S. Prestipino

*Istituto Nazionale per la Fisica della Materia (INFN), Unità di Ricerca di Messina, Italy and International School for Advanced Studies (SISSA-ISAS), I-34013 Trieste, Italy*

P. V. Giaquinta<sup>a)</sup>

*Istituto Nazionale per la Fisica della Materia (INFN), Unità di Ricerca di Messina, Italy and Dipartimento di Fisica, Università degli Studi di Messina, Contrada Papardo, 98166 Messina, Italy*

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The ordering of simple fluids in two dimensions was investigated using the residual multiparticle entropy (RMPE) as a measure of the relevance of correlations involving more than two particles in the configurational entropy of the system. To this end, we performed Monte Carlo simulations of two prototype systems, i.e., Lennard-Jones particles and hard discs. Consistent with previous studies, we found that, on approaching the freezing transition, the RMPE of the fluid undergoes a change from negative to positive values. However, in two dimensions the vanishing of the RMPE appears to be more directly related to the formation of six-fold orientationally ordered patches, a process which foreshadows the freezing transition. The specificity of the structural condition attained by the fluid in a state corresponding to a vanishing RMPE was further corroborated by an analysis of the shape of the radial distribution function (RDF): in fact, it turns out that the spatial profiles of the RDF of the Lennard-Jones fluid along a zero-RMPE locus can be superimposed at medium and large distances notwithstanding the difference of density and/or temperature of the corresponding thermodynamic states. The same long-range profile of the RDF is shared also by hard discs in the cited condition. Such a “scaling” property also holds in three dimensions where it provides a suggestive nexus between the ordering criterion based on the vanishing of the RMPE and the Hansen–Verlet freezing rule. © 2000 American Institute of Physics. [S0021-9606(00)51331-2]

## I. INTRODUCTION

The entropy of an even partially disordered material unfolds information on the state of the system which lies beyond the strictly thermodynamic level. In principle, this information can be extracted by resorting, in a classical statistical–mechanical framework, to a “representation” of the entropy in terms of the complete hierarchy of  $n$ -point distribution functions.<sup>1</sup> In general, this is rather obviously a prohibitive task. A few years ago, Giaquinta and Giunta focussed instead on a cumulative “measure” of the statistical weight associated with correlations involving at least three particles, the so-called residual multiparticle entropy (RMPE).<sup>2</sup> This quantity is obtained by subtraction of the “pair entropy,” i.e., the integrated contribution associated with the pair distribution function only, from the excess entropy of the fluid. Indeed, the pair entropy, while being quantitatively preponderant with respect to other terms, is a negative–definite quantity (whatever the system or the thermodynamic state) which does not convey any relevant “qualitative” information on the equilibrium structure of the system. On the contrary, the RMPE does not have a definite sign. The crossover undergone by the RMPE from negative to positive values was originally put in relation with the

freezing transition of hard spheres.<sup>2</sup> Since then, a similar analysis has been extended to a variety of model potentials,<sup>3–8</sup> including mixtures,<sup>9–12</sup> systems composed of nonspherical particles,<sup>13,14</sup> and lattice gases.<sup>15,16</sup> In all cases examined so far, the vanishing of the RMPE proves to be an intrinsic signature of the incipient ordering of the fluid, a condition which faithfully heralds the occurrence, at nearby densities and/or temperatures, of a phase transition into a more structured phase. In this respect, the zero-RMPE condition can be used as a one-phase ordering criterion which has been successfully tested against such diverse thermodynamic phenomena as freezing, fluid–fluid phase separation, nematic ordering, and the Kosterlitz and Thouless metal–insulator transition in a two-dimensional (2D) Coulomb lattice gas.

Many semiempirical rules have been proposed with the aim of locating, say, the transition from the liquid to the solid phase, without resorting to the knowledge of the free energy of the two phases. Perhaps, the very first of such proposals is the melting criterion proposed by Lindemann,<sup>17</sup> which states that in a solid the ratio of the root-mean-square displacement of a particle to the average nearest-neighbor distance is about 0.15 at the melting point. On the other hand, the most famous freezing criterion is that due to Hansen and Verlet, who observed that the height of the first peak of the structure factor,  $S(k)$ , is about 2.85 along the freezing line. This “uni-

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: Paolo.Giaquinta@unime.it

versal” feature has been verified by both numerical simulation and experiment for a wide class of three-dimensional (3D) systems.<sup>18</sup> Just to give a few more examples, we recall still another empirical rule, proposed by Wendt and Abraham, in terms of the ratio between the heights of the first minimum and of the first maximum, respectively, of the radial distribution function (RDF).<sup>19</sup> In many 3D liquids, this ratio is about 0.14 at freezing. On the dynamical side, Löwen noted that in a liquid with a Langevin dynamics the ratio of the long- to the short-time diffusion coefficient is about 0.1 at the freezing point.<sup>20</sup> More recently, Malessio and co-workers introduced a criterion based on the numerical instability of the iterative solution of the Ornstein–Zernike equation.<sup>21</sup>

As a matter of fact, most of the above criteria are specific of a given transition. Furthermore, they may not be easily transferred, without modifications, to 2D systems where the crystalline phase is unstable at all temperatures  $T$ , save for  $T=0$ .<sup>22</sup> As a result, the Lindemann rule is useless in its original formulation.<sup>23</sup> All of the other criteria, while suitable in principle for 2D systems, are not valid in general and must be modified. For instance, in 2D the height of the first peak of the structure factor at freezing is much higher than 2.85; moreover, its precise value is more sensitive to the shape of the interaction potential than in 3D, suggesting that the Hansen–Verlet rule cannot be extended to arbitrary dimensionality in a simple way.<sup>24</sup> Löwen verified the validity of his dynamical criterion also for 2D soft-sphere fluids, by still using a Langevin equation for the dynamics. Again, the critical ratio of the two diffusion coefficients is close to 0.1 (actually, a bit smaller than that).<sup>25</sup> However, the real problem with this criterion is that it ceases to be valid when a different dynamics is considered, e.g., the Newtonian one, since in this case only one single diffusion coefficient can be defined.<sup>26</sup>

The 2D case is also particularly challenging in view of the many different scenarios that have been proposed for the freezing transition,<sup>27</sup> including a two-stage continuous transition from the fluid to the solid phase which would take place through the formation of a hexatic, bond-orientationally-ordered phase. Such a possibility was conjectured in the celebrated KTHNY theory.<sup>28</sup>

However, we do not aim here at investigating in detail the nature of the phase diagram of specific 2D models. We know that this is a difficult task to handle numerically even in simple cases.<sup>29,30</sup> Instead, we intend to ascertain the nature and sensitivity of the indications given by the RMPE in relation to latent tendencies to ordering, even of an unconventional type as that exhibited in the hexatic phase. Actually, this phase may ultimately prove to be metastable. However, even in such a case, signatures of angular ordering should show up in the dense fluid close to freezing and become manifest in the RMPE as well. In order to elucidate this aspect, we have chosen, as established prototype models, Lennard-Jones (LJ) particles and hard discs (HD).

This article is organized as follows: In Sec. II we introduce and discuss the RMPE. Section III is devoted to a description of the models and of the method. In Sec. IV, we present the results of this study with attention given to the

characterization of angular order in terms of the orientational correlation function (OCF). A rationalization of the zero-RMPE condition as an indication of the incipient ordering of a fluid is further discussed in Sec. V in terms of the scaling behavior of the RDF. Section VI is finally devoted to concluding remarks.

## II. THE RMPE: A BRIDGE BETWEEN ENTROPY AND CORRELATIONS

The statistical entropy of an open (i.e., grand-canonical) system can be expanded as an infinite series:<sup>1</sup>

$$s_{(\text{ex})} = \sum_{n=2}^{\infty} s_n, \quad (1)$$

where  $s_{(\text{ex})}$  is the excess entropy per particle in units of the Boltzmann constant,  $k_B$ , and  $s_n$  is the  $n$ -body entropy that is obtained from a suitable resummation of spatial correlations between up to  $n$  particles. An analogous expansion holds in the canonical ensemble,<sup>15</sup> with an identical expression for the partial quantities  $s_n$  in terms of reduced distribution functions. In particular, the pair entropy per particle reads

$$s_2 = -\frac{1}{2}\rho \int d\mathbf{r} [g(r)\ln g(r) - g(r) + 1], \quad (2)$$

where  $\rho$  and  $g(r)$  are the number density and RDF, respectively. The RMPE is defined as

$$\Delta s = s_{(\text{ex})} - s_2. \quad (3)$$

At variance with the pair entropy,  $\Delta s$  exhibits a nonmonotonic behavior as a function of either  $\rho$  or  $T$ . In particular, it is negative at low density or high temperature, and becomes positive as a more ordered phase is approached. A positive RMPE implies a *slowing down* in the reduction of the configurational space accessible to the system, caused by a decreasing volume and/or temperature. This effect, that is specifically associated with the inversion of trend of the RMPE, is the outcome of the *increase* of the number of states that, in the overall entropic balance, can be associated to correlations of order higher than two. This increase is obviously relative to the systematically negative background level set by the pair entropy. Such a feature is the underlying fingerprint of a new structural condition that is being built up by the system, “forced” to exploit a different form of aggregation by compelling thermodynamic constraints. Not at all surprising, the RMPE indicates that such a structural, cooperative rearrangement is ascribable to many-particle correlations.

The RMPE phenomenology that has been explored so far regards mostly first-order phase transitions in 3D. Recently, the connection between the vanishing of the RMPE and the ordering of the fluid has also been verified in 2D, even for long-ranged particle interactions.<sup>16</sup> In fact, it has been shown that the RMPE vanishes in a Coulomb lattice gas along the infinite-order Kosterlitz–Thouless transition line, which separates the insulating from the conducting fluid phase. This somewhat surprising circumstance proves the extreme sensitivity of the RMPE to all structural and thermodynamic changes which occur in a disordered system. With such premises, it is natural to ask what is the behavior of the

RMPE in a 2D continuous fluid system, where the reduced dimensionality may actually decouple the onset of orientational order from the long-ranged positional one, thus causing unconventional cooperative phenomena to occur as, for instance, the emergence of a hexatic phase.

### III. MODELS AND METHOD

We performed Monte Carlo (MC) simulations, in the canonical ensemble, of a system of 450 particles interacting in 2D through a LJ potential:

$$u_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (4)$$

where  $r$  is the interparticle distance. The potential was truncated at  $r = 2.5\sigma$ , and the usual correction was made to take into account the effect of the neglected tail on the thermodynamical quantities.<sup>18</sup> The same technique was also used to simulate a system of 450 hard discs. Particles were enclosed in a square box with periodic boundary conditions. The initial configuration was always that of a perfectly ordered hexagonal crystal. The equilibration of the samples typically took  $(2 \times 10^5) - (1 \times 10^6)$  MC cycles, depending on the density. A cycle consisted of one attempt to sequentially change the position of all the particles. The maximum displacement of a particle was tuned, during the run, so as to keep the acceptance ratio of the MC moves as close to 0.5 as possible. The relevant thermodynamic averages were computed over  $(4 \times 10^5) - (7 \times 10^5)$  MC cycles. The RDF histogram was constructed with a spatial resolution  $\Delta r = \sigma/20$ , and updated every 100–500 MC cycles. The RDF was evaluated up to  $R_{\text{max}} = L/2$ , where  $L = (N/\rho)^{1/2}$  is the simulation-box length. At a distance of order  $R_{\text{max}}$ , the RDF was never found to differ significantly from unity. The fulfillment of this condition is important since, otherwise, a bad estimate of the pair entropy would be obtained, owed to the fact that, in the high-density regime, several peaks of the RDF beyond the first give a sizeable contribution to the integral in Eq. (2).

In the case of the LJ system, we spanned a wide density range at two supercritical temperatures,  $T^* = 0.7$  and 1, where  $T^* = k_B T / \epsilon$  is the reduced temperature (we shall use, in the following, also  $\rho^* = \rho \sigma^2$ ), so as to calculate the equation of state of the fluid. The present estimates for the thermodynamical properties of the LJ fluid are in excellent agreement with previous simulation data<sup>31</sup> (see Tables I and II), as well as with the values obtained using a semiempirical equation of state.<sup>32</sup> The excess entropy was computed through the equation

$$s_{(\text{ex})} = \beta(u_{(\text{ex})} - f_{(\text{ex})}), \quad (5)$$

where  $u_{(\text{ex})}$  and  $f_{(\text{ex})}$  are the excess energy and Helmholtz free energy, respectively. A thermodynamic integration was performed in order to compute  $f_{(\text{ex})}$ , using a spline approximant for the data reported in Tables I and II:

$$\beta f_{(\text{ex})}(\rho) = \int_0^{\rho} \frac{\rho d\rho'}{\rho'} \left[ \frac{\beta P(\rho')}{\rho'} - 1 \right]. \quad (6)$$

TABLE I. Compressibility factor of a 2D LJ fluid for  $T^* = 0.7$ .

$\rho^*$	$\beta P / \rho$	
	Present work	Ref. 31
0.10	0.77	
0.20	0.64	
0.30	0.57	
0.40	0.56	
0.50	0.60	
0.60	0.83	
0.70	1.50	1.45
0.75	2.32	2.29
0.78	3.01	
0.80	3.55	
0.83	4.37	4.22

The amount of orientational order that develops in the fluid for increasing densities was assessed through the six-fold OCF:

$$h_6(r) = \langle \cos\{6[\theta(\mathbf{r}') - \theta(\mathbf{r}'')]\} \rangle, \quad (7)$$

where  $r$  is the distance between two particles located at positions  $\mathbf{r}'$  and  $\mathbf{r}''$ . The quantity  $\theta(\mathbf{r}')$  is the angle formed by a randomly chosen nearest-neighbor bond at  $\mathbf{r}'$  with a fixed reference axis. First neighbors of a particle in a given configuration were defined through the Voronoi construction. As for the RDF, the histogram of the OCF was updated every 100–500 MC cycles. A similar analysis was performed for hard discs.

In order to complement our study of the RDF in 2D with some information in 3D, we performed canonical NVT simulations of a 3D LJ system with 864 particles in two subcritical states, namely ( $\rho^* = 0.856$ ;  $T^* = 0.75$ ) and ( $\rho^* = 0.96$ ;  $T^* = 1.15$ ), and at the supercritical temperature  $T^* = 2.74$ . We simulated a hard-sphere system as well at the reduced density  $\rho^* = 0.936$ .

### IV. RESULTS

The RDFs of the LJ and HD fluids in 2D are shown in Fig. 1. The corresponding RMPE is plotted in Fig. 2 as a function of the density. For later comparison with the HD system, we also show a few points obtained through a MC

TABLE II. Compressibility factor of a 2D LJ fluid for  $T^* = 1$ .

$\rho^*$	$\beta P / \rho$	
	Present work	Ref. 31
0.10	0.92	
0.20	0.88	
0.30	0.90	0.89
0.40	0.97	0.96
0.50	1.15	
0.60	1.54	
0.70	2.43	2.39
0.75	3.24	3.19
0.80	4.42	4.39
0.83	5.33	
0.856	6.19	

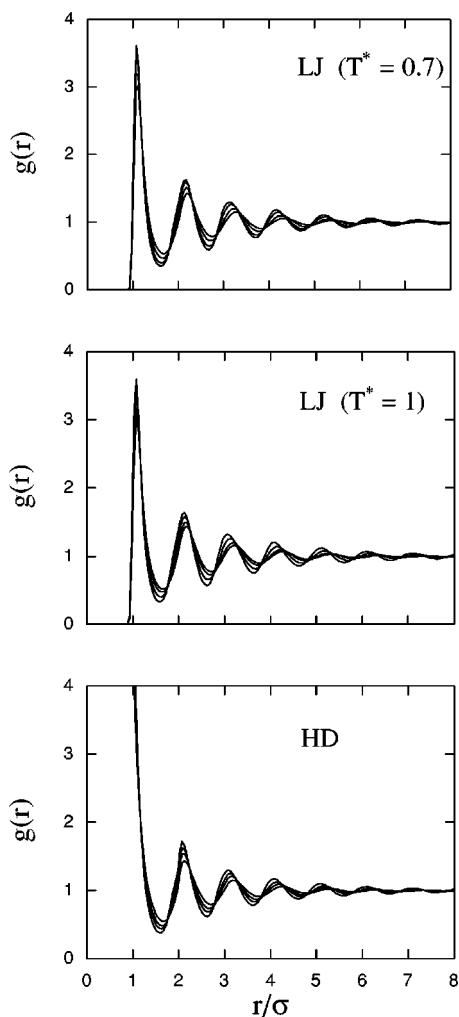


FIG. 1. Radial distribution functions of the 2D models investigated: top, Lennard-Jones fluid at  $T^*=0.7$  and reduced densities  $\rho^* = 0.70, 0.75, 0.79, 0.81$ ; center, Lennard-Jones fluid at  $T^*=1$  and reduced densities  $\rho^* = 0.75, 0.78, 0.82, 0.85$ ; bottom, hard discs at reduced densities  $\rho^* = 0.764, 0.802, 0.828, 0.853$ .

simulation of 2000 hard calottes embedded on the surface of a sphere.<sup>33,34</sup> All the curves displayed in Fig. 2 have a profile that is morphologically similar to that found in 3D: at low densities,  $\Delta s$  is a negative, decreasing function of  $\rho^*$  until it reaches a minimum. Thenceforward,  $\Delta s$  starts growing rapidly to, eventually, become positive. However, at significant variance with what has been already ascertained in relation to the freezing of the LJ and HD models in 3D,<sup>2,3</sup> the RMPE turns out to vanish at a density  $\rho_0^*$  that is slightly but definitely lower than the freezing-point density. In fact, at  $T^*=0.7$  we find  $\rho_0^* \approx 0.79$  for the LJ system, while the currently estimated freezing density is  $\rho_f^* = 0.83$ .<sup>31</sup> In the higher-temperature state ( $T^*=1$ ),  $\rho_0^* \approx 0.82$  and  $\rho_f^* = 0.85$ , respectively.<sup>31</sup> The RMPE of hard discs changes sign at  $\rho_0^* \approx 0.83$ , while the freezing is expected to occur at  $\rho_f^* \approx 0.88$ .<sup>26</sup> Actually, the exact location of the freezing point and the very nature of the transition in 2D are still controversial for both models. In fact, evidence of a narrow hexatic window, close to the hitherto accepted freezing point, has been reported. Large-scale simulations of the 2D LJ system suggest the existence of a (possibly, metastable) hexatic state for tempera-

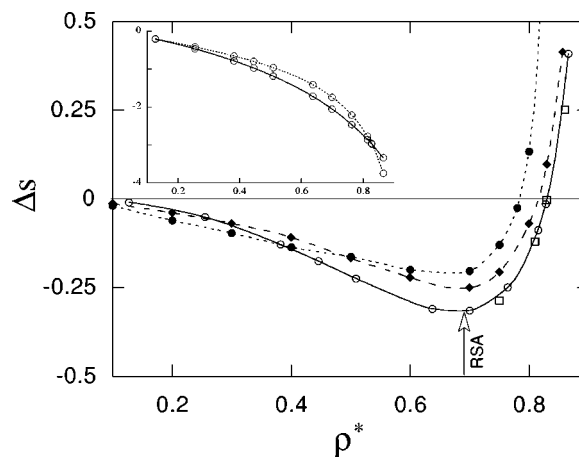


FIG. 2. Residual multiparticle entropy plotted as a function of the reduced density: full circles, 2D Lennard-Jones fluid at  $T^*=0.7$ ; full diamonds: 2D Lennard-Jones fluid at  $T^*=1$ ; open circles: hard discs; squares: hard calottes (Ref. 33). The lines are interpolating spline functions. An arrow identifies the random sequential addition (RSA) threshold of hard discs (Ref. 39). The inset shows the excess (solid line) and pair entropy (dotted line) of hard discs also plotted as a function of the reduced density. The crossover undergone by the two curves corresponds to the zero-RMPE condition. The density behavior of the above quantities in the LJ fluid is analogous to that shown in the inset for hard discs.

tures around  $T^*=2.16$ , at a fixed reduced pressure  $P^*=20$ .<sup>29</sup> The stability of such a phase has also been postulated for hard discs, in the density interval  $0.90-0.91$ .<sup>30</sup> The thermodynamic behavior of the RMPE is consistent with the hypothesis that the freezing of a fluid in 2D is anticipated by the growth of extended angular correlations. This statement can be made more precise by extracting the angular correlation length  $\xi_6(\rho)$  which characterizes the space behavior of the OCF (see Fig. 3) at large distances. We fitted the heights of a few peaks of  $h_6(r)$ , assuming an exponential decay of the maxima as a function of  $r$ . The fit included the first five peaks beyond the third shell, so as to avoid the interference of local-structure effects. The result of this analysis is presented in Fig. 4. As expected, the angular correlation function increases steadily as a function of the density. However, both fluids exhibit two distinct correlation regimes, as is clearly witnessed by the sharp change of slope undergone by  $\xi_6(\rho)$  in a very narrow range of densities. In the LJ fluid, the demarcation between the two regimes is particularly evident at low temperatures. As shown in Fig. 4, at  $T^*=0.7$  the quantity  $\xi_6(\rho)$  bends abruptly upward at a density  $\rho^* \approx 0.79$ , which is also the threshold (marked in Fig. 4 with an arrow) that was just *independently* identified through the contribution of multiparticle *positional* correlations to the configurational entropy of the system. It thus appears that the vanishing of the RMPE of the 2D LJ fluid records the onset of extended angular correlations which may eventually be responsible for the emergence of a hexatic phase. This consistent, two-fold indication also persists at higher temperatures, but for a more rounded “knee” of  $\xi_6(\rho)$  and its expected shift to larger densities.

Also in the HD case, the existence of two distinct regimes is ostensibly manifested in the density dependence of the angular correlation length whose slope shows a “discon-

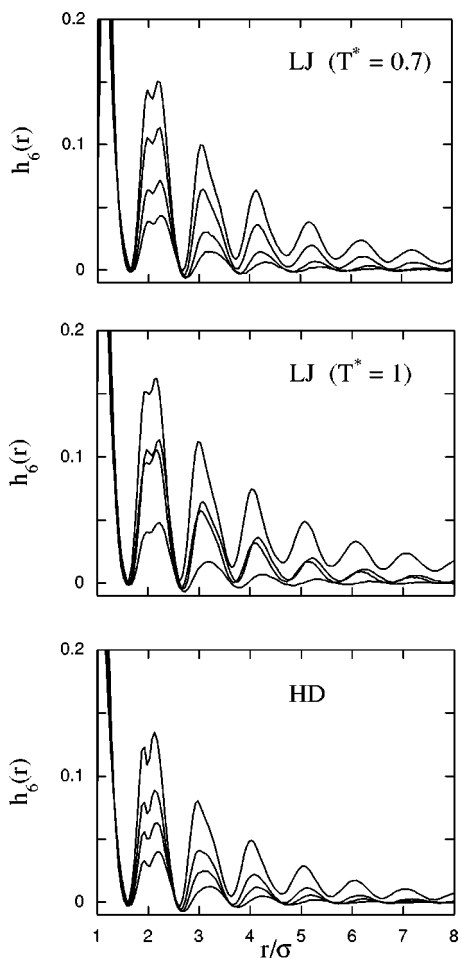


FIG. 3. Orientational correlation functions of the 2D models investigated at the same temperatures and densities as in Fig. 1.

tinuity'' at a density close to 0.86 (see also Ref. 34). However, at variance with the LJ fluid, the RMPE of hard discs vanishes at a density ( $\rho^* \approx 0.83$ ) which slightly anticipates the sharp rise of  $\xi_6(\rho)$ . Indeed, the buildup of extended angular correlations in the system is made possible by some precursory structural phenomena. More specifically, we refer to the pairing of disclinations to form dislocations and, contextually, to the binding of dislocation pairs to form "rings," a process that is invoked by the KTHNY theory to explain the formation of the solid phase. An analysis of point defects that are observed in a dense fluid of hard calottes shows that the fraction of rings increases sharply at  $\rho^* \approx 0.83$  at the expense of isolated disclinations.<sup>35</sup> This conclusion can also be safely extended to the HD fluid, since any "spurious" effect originated by the finite curvature of the host surface emerges only at larger densities.<sup>34,35</sup> This circumstance can also be visually appreciated through an inspection of Fig. 2, where it is apparent that the data referring to the RMPE of hard calottes distribute smoothly along the curve relative to the HD fluid. The emergence of ordered structures which "prepare the stage" for the formation of angularly correlated patterns is also reflected in the RDF of the HD fluid. In fact, just at  $\rho^* \approx 0.83$  we observe that the second maximum of the RDF starts deforming: its shape becomes asymmetrical until a shoulder appears for densities in the range corresponding to

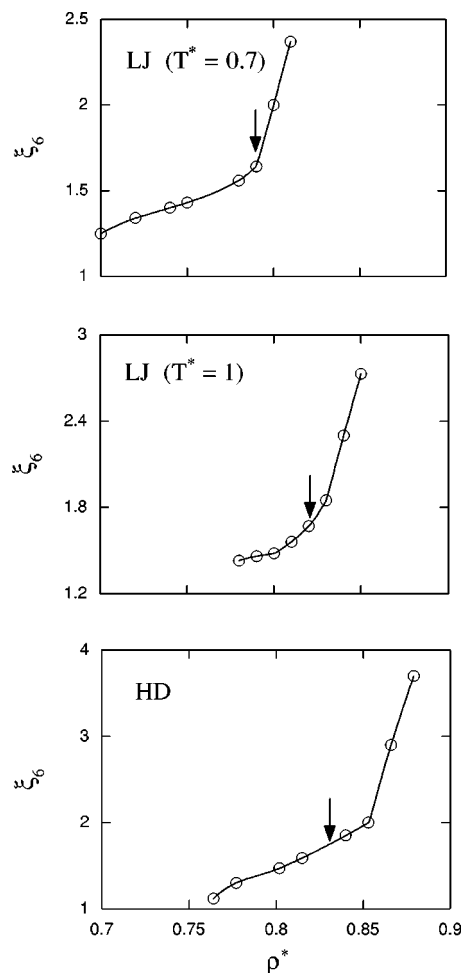


FIG. 4. Orientational correlation length plotted as a function of the reduced density: top, Lennard-Jones fluid at  $T^* = 0.7$ ; center, Lennard-Jones fluid at  $T^* = 1$ ; bottom: hard discs. An arrow marks the density where the residual multiparticle entropy is found to vanish.

the position of the knee in the angular correlation length. Such a shoulder eventually evolves into a distinct prepeak, located at a characteristic distance of the triangular lattice corresponding to the next-nearest-neighbor coordination shell, namely  $r/a = \sqrt{3}$ , where  $a = \sigma(\rho_{CP}/\rho)^{1/2}$  is the hexagonal lattice constant on a plane and  $\rho_{CP}$  is the HD density at close packing. This feature had been explicitly observed in 2D by Prestipino Giarritta and co-workers,<sup>34</sup> and has been discussed, more recently, in relation to the freezing of hard-core systems.<sup>26</sup> Of course, it is not surprising to verify that the sprouting of orientational order is accompanied by the appearance, on a local scale, of spatially ordered arrangements that also become progressively resolved in the RDF. As to the nature of the information conveyed on this specific matter by the RMPE, the evidence discussed above clearly shows that this structural indicator monitors the very first germination of order which, in a HD fluid, is heralded by closely related precursory phenomena such as the formation of rings and of "minimal" clusters of hexagonally ordered particles. We argue, retrospectively, that in a soft-core-potential model (like the LJ fluid), these phenomena show up concurrently with the sharp rise of the angular correlation

length at the same density threshold, sensitively recorded by the vanishing of the RMPE.

We close this section with a comment on the position,  $\rho_{\min}$ , of the dip exhibited by  $\Delta s(\rho)$ . Giaquinta and Giunta diffusely discepted, in their original article on this subject,<sup>2</sup> on the significance of the minimum of the RMPE of hard spheres, and also gave a critical overview of the related evidence on the thermodynamic, structural, and dynamical behavior of the model.<sup>36</sup> This evidence consistently leads to the conclusion that, for densities larger than  $\rho_{\min}$ , the condition of the hard-sphere fluid is strongly reminiscent of that of “liquids” as originally defined by Bernal, namely “*homogeneous, coherent, and essentially irregular* assemblages of molecules containing no crystalline regions or holes large enough to admit another molecule.”<sup>37</sup> In fact, beyond the minimum of the RMPE, such holes or cavities substantially disappear.<sup>2</sup> This condition, which at thermodynamic equilibrium applies only in a statistical sense, also has an intriguing counterpart in a different framework, such as that provided by the random sequential addition (RSA) of nonoverlapping spheres onto a given volume. An RSA experiment is, by definition, irreversible (particles are not allowed to move) and, thus, is not *a priori* significant for the properties of the system at thermodynamic equilibrium.<sup>38</sup> In spite of this, Giaquinta and Giunta noted that the saturation density,  $\rho_{\text{RSA}}$ , at which a system of hard spheres becomes jammed because no other particles can be added, coincides with the position of the minimum in  $\Delta s(\rho)$ .<sup>2</sup> In 2D, the RSA limit density is:  $\rho_{\text{RSA}} \approx 0.696$ .<sup>39</sup> As seen in Fig. 2, this value corresponds to the position of the dip in the RMPE of discs. Summing up, it turns out that the change of behavior undergone by the RMPE of hard spherical particles, from a decreasing to an increasing trend when plotted as a function of  $\rho$ , occurs at a density which corresponds to the RSA jamming limit both in 2D and in 3D. Such a characteristic threshold, that is manifested by the model at equilibrium as well as out of equilibrium, marks the limit beyond which cooperative, i.e., intrinsically many-body, effects come into play in determining the state of the fluid.

## V. THE SCALING OF THE RDF AND THE HANSEN-VERLET CRITERION

As discussed above, the RMPE of a simple 2D fluid, such as HD or LJ particles, records—in a sensitive and reliable way—the onset of extended orientational order in the system. As far as we can say, this indication is present anyway, viz., independently of the existence—in the phase diagram of the system—of a thermodynamically stable hexatic phase which may anticipate the freezing of the fluid. The nature of this indication is consistent with the evidence gathered so far on other model systems in different thermodynamic scenarios: in fact, as discussed in the introduction, in all cases investigated the vanishing of the RMPE pinpoints the incipient ordering of the fluid into a more structured state, not necessarily a crystalline solid. In this respect, the zero-RMPE condition proves to be a rather general though indirect “measure” of the degree of spatial order developed in the system. In order to scrutinize this aspect further, we compared the RDFs of both models for states where

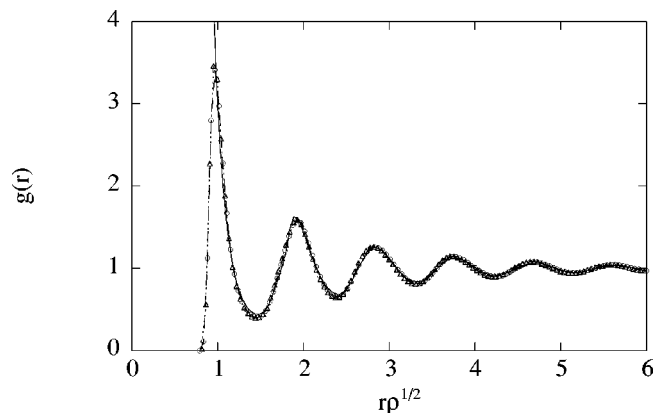


FIG. 5. Radial distribution functions of the 2D Lennard-Jones and hard-disc fluids in a state where the residual multiparticle entropy is found to vanish: triangles, Lennard-Jones fluid at  $T^*=0.7$  and  $\rho^*=0.79$ ; circles, Lennard-Jones fluid at  $T^*=1$  and  $\rho^*=0.82$ ; solid line: hard-disc fluid at  $\rho^*=0.83$ . The contact value of the hard-disc RDF is 5.69.

$\Delta s(\rho, T) = 0$ . However, for the comparison not to be biased by the “trivial” effect associated with the density, whose value changes slightly from one system to the other, we rescaled the distances by referring them to the *average* separation between neighboring particles which is roughly proportional to  $\rho^{-1/2}$ . As is seen from Fig. 5, where we plotted the RDF of hard discs and of the LJ fluid at two supercritical temperatures, the three profiles do substantially coincide aside from the first coordination shell whose detailed shape obviously depends on the very nature of the interaction potential at short distances. Indeed, even for the LJ fluid, the height of the first maximum is slightly different in the two states that were singled out. The comparison unambiguously shows that, after scaling and as long as  $\Delta s(\rho, T) = 0$ , the RDFs of the HD and LJ systems can be superimposed from the first peak onwards. Such a scaling relation is not equally effective for the OCFs (see Fig. 6), inasmuch as the amplitude of the oscillations is not the same for two corresponding states or systems, within the accuracy registered for the RDFs ( $\sim 1\%$ ). On the basis of the evidence discussed above,

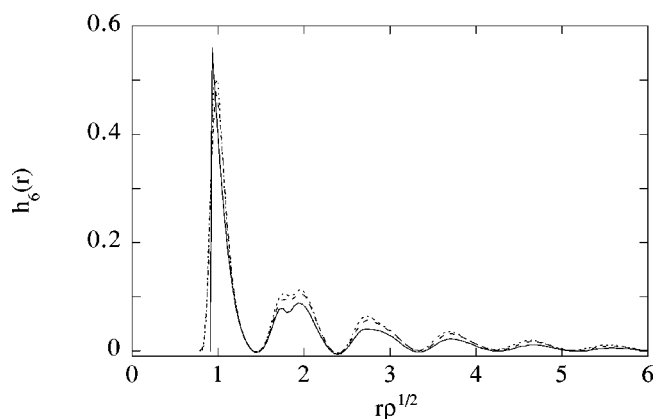


FIG. 6. Orientational correlation functions of the 2D Lennard-Jones and hard-disc fluids in a state where the residual multiparticle entropy is found to vanish: dotted line, Lennard-Jones fluid at  $T^*=0.7$  and  $\rho^*=0.79$ ; dashed line (intermediate curve), Lennard-Jones fluid at  $T^*=1$  and  $\rho^*=0.82$ ; solid line: hard-disc fluid at  $\rho^*=0.83$ .

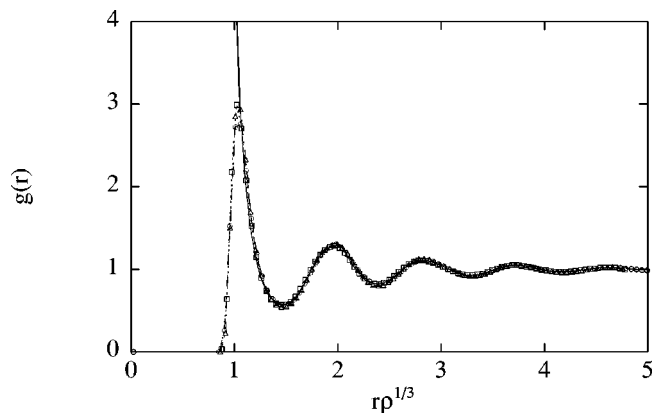


FIG. 7. Radial distribution functions of the 3D Lennard-Jones and hard-sphere fluids in a state where the residual multiparticle entropy is found to vanish: squares, Lennard-Jones system at  $T^*=0.75$  and  $\rho^*=0.86$ ; triangles, Lennard-Jones system at  $T^*=1.15$  and  $\rho^*=0.96$ ; circles, Lennard-Jones system at  $T^*=2.74$  and  $\rho^*=1.11$ ; solid line: hard-sphere fluid at  $\rho^*=0.94$ . The contact value of the hard-sphere RDF is 5.65.

we argue that the vanishing of the RMPE identifies a (structural) condition of the fluid that is alike—at least, as far as radial correlations are concerned—for both systems, independently of the specific thermodynamic state as well as of the detailed shape of the interaction potential.

Even in 3D, the RDFs scale, under the zero-RMPE condition, in a very accurate way. Figure 7 shows the corresponding data for hard spheres as well as for the LJ fluid in three different thermodynamic states (one being supercritical). In this case, the interparticle distances were obviously referred to the quantity  $\rho^{-1/3}$ . We recall that in 3D the vanishing of the RMPE is more directly related to the freezing of the fluid.<sup>2,3</sup> This circumstance gives us the possibility of reconsidering the celebrated Hansen–Verlet (HV) freezing criterion<sup>18</sup> from a different perspective. The HV rule is a one-phase criterion as is the currently investigated one. Actually, the affinity between the two criteria becomes clear after observing that the first maximum of the structure factor results, to a major extent, from the mapping in Fourier space of the long-range oscillations exhibited by the RDF in real space. More specifically, the frequency, damping, and amplitude of these oscillations determine the position, width, and area (and, consequently, height) of the first maximum of  $S(k)$ .<sup>40</sup> Hence, the HV criterion, upon fixing a “universal” reference value for the height of the first maximum of the structure factor in order for freezing to occur, is actually “tagging” a related amplitude of the oscillations observed in the RDF profile. But, the existence of a characteristic spatial profile associated with the incipient ordering of the fluid is precisely what follows from the RMPE criterion through the scaling of the RDFs in those thermodynamic states where the condition  $\Delta s(\rho, T) = 0$  is satisfied. We conclude that the two criteria manifestly rest on a common rationale, namely the identification of a specific condition of the fluid which, *a posteriori*, unravels as the underlying stage for the occurrence, at a macroscopic level, of a thermodynamic transition into a more ordered state. Note, however, that, at variance with the *ad hoc* formulation of the HV rule, which rests on an external input (i.e., the height of the principal maximum

of the structure factor at the transition point), the vanishing of the RMPE is an internal, self-contained statement whose physical content is rather straightforward, in view of the fact that it more directly hits at the very core of the phenomenology that is being investigated. Last, as already recalled in the introduction, the zero-RMPE ordering criterion is more general than the HV freezing rule inasmuch as it applies *without modifications* to a larger variety of physical situations both in 2D and 3D, not just freezing.

## VI. SUMMARY AND CONCLUDING REMARKS

In this article we have revisited the structural properties of simple dense fluids in two dimensions (2D), in the framework provided by the multiparticle correlation expansion of the configurational entropy.<sup>1</sup> In particular, we computed—using Monte Carlo simulation techniques—a quantity which weighs up the contribution of many-body (where “many” stands for triplets, at least) correlations in the overall balance of states that are available to the system at given density and temperature. Such a quantity, called residual multiparticle entropy (RMPE), is a sensitive indicator of the ordering phenomena which take place in a fluid in rather disparate thermodynamic conditions. In the case of hard discs and Lennard-Jones particles, the vanishing of the RMPE witnesses an accelerated growth of bond-angle correlations which preludes to the freezing of the fluid into a solid phase. The search for structural precursors to the freezing of simple fluids has brought many authors to introduce one-phase criteria, which aim at locating the transition without resorting to the comparison of the free energies of the coexisting phases. However, aside from other conceptual aspects, most of such empirical rules fail, in their original 3D formulation, in a lower dimensionality. In this respect, the zero-RMPE condition, used as a preliminary ordering criterion in relation to a variety of thermodynamic phenomena, keeps valid in 3D as well as in 2D.

Finally, the comparison of the long-range profiles of the radial distribution function in those states where the RMPE is zero for each of the two systems, suggests an illuminating correspondence with the freezing criterion formerly introduced by Hansen and Verlet.

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