

Article

Entropy and Ordering of Hard Rods in One Dimension

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Abstract: We revisit the equilibrium properties of a classical one-dimensional system of hard-core particles in the framework provided by the multiparticle correlation expansion of the configurational entropy. The vanishing of the cumulative contribution of more-than-two-particle correlations to the excess entropy is put in relation with the onset of a solidlike behavior at high densities.

Keywords: Entropy; residual multiparticle entropy; hard rods; one dimension; Tonks gas.

1. Introduction

The entropy of a classical system can be expressed as an infinite sum of contributions associated with spatially integrated n -point density correlations:

$$S = \sum_{n=0}^{\infty} S_n, \quad (1)$$

where S_0 is the entropy of the corresponding non-interacting gas. The above expansion was separately derived for closed [1] and open systems [2], but the two apparently different expressions were later shown to be in fact equivalent [3]. In the absence of external fields, the leading and quantitatively dominant term of the series is the so called “pair entropy” S_2 , typically a function of the particle number density ρ and of the temperature T , whose ensemble-invariant *local* expression reads:

$$S_2/N = -\frac{1}{2}k_B\rho \int [g(r) \ln g(r) - g(r) + 1]d\mathbf{r}, \quad (2)$$

where N is the (average) number of particles, k_B is the Boltzmann constant, and $g(r)$ is the pair distribution function (PDF) of the fluid. The pair entropy is a (semi)negative-definite quantity, which just

vanishes at infinite dilutions [4]. This property holds for any underlying microscopic interaction between the constituent particles. As one can intuitively argue, the emergence of spatial correlations between pairs of particles ($g(r) \neq 1$) reduces the extension of the phase space effectively available to the fluid whose total entropy correspondingly drops below the value attained, at the same temperature, by an equally dense gas of non-interacting particles [5]. However, this is not generally the case of higher-order ($n \geq 3$) partial entropies. Their computation is far from trivial beyond the three-body term [6, 7] but, nonetheless, their cumulative contribution (ΔS) can be obtained upon subtracting the pair entropy from the excess (with respect to the ideal-gas value) entropy:

$$\Delta S(\rho, T) = S_{\text{ex}}(\rho, T) - S_2(\rho, T). \quad (3)$$

The resulting quantity, which has been referred to as the “residual multiparticle entropy” (RMPE) [8], is ordinarily negative at low densities and/or high temperatures just like the pair entropy but, somewhat counterintuitively, may also attain positive values: whenever this happens, density correlations involving more than two particles globally act in such a way as to *reduce* the entropy gap between the fluid and the corresponding ideal gas. In this respect, a positive RMPE is the sign of a structural condition of the fluid that is manifestly different from one where increasingly stronger multiparticle correlations cooperatively concur in lowering the entropy of the system. On this basis, it turns natural to conjecture that the *loci* along which $\Delta S(\rho, T) = 0$ may be in some, more or less direct, relation with the thermodynamic phase boundaries across which the structural condition of a substance is found to change in either a continuous or discontinuous way. This is the basic theoretical setting of the “zero-RMPE criterion” as originally formulated by Giaquinta and Giunta [8] in a review of the structural and dynamical behavior of a fluid of hard spheres subject to increasing pressures. The earlier mentioned authors observed that the RMPE of hard spheres changes its sign at freezing. Actually, they also showed that the overall density behavior of the RMPE can be put in close relation with the distinct dynamical regimes that are observed in such a prototype fluid. Thereafter, the RMPE has been found to vanish in proximity of the freezing thresholds of a number of other pure model fluids [9–20] as well as mixtures [21, 22], also in two dimensions [23]. In all such cases the claimed congruence between the zero-RMPE *loci* and the phase transition boundaries was observed along extended thermodynamic paths traced as a function of temperature, pressure, density or concentration.

Indeed, the zero-RMPE criterion turns out to be even more than a phenomenological one-phase freezing rule. In fact, the RMPE can also exhibit multiple crossovers from negative to positive values, also “detecting” transitions between two *fluid* phases. This is the case, for instance, of a gas condensing into a liquid which, upon further compression, eventually freezes into a solid [14]. In this respect, even more complex is the way in which the RMPE was found to change, as a function of the thermodynamic parameters, in a lattice gas [24, 25] of interacting positive and negative charges hosted on a two dimensional square lattice [26]. This model displays a variety of both insulating and conducting phases; particularly noteworthy is, in this case, the close correspondence between the zero-RMPE line and the (infinite-order) Kosterlitz and Thouless phase transition boundary separating the insulating-gas phase from the conducting-liquid phase. The analogue of surface preroughening in a two-dimensional lattice Coulomb gas was also studied in [27]. The RMPE has been found to be a sensitive indicator of other (even partial) *ordering* processes that may take place in a fluid. Such are the fluid-fluid phase separation undergone by a mixture [28, 29] also in two dimensions [30], the emergence of mesophases (nematic,

smectic) in model liquid crystals [31–35] or the formation of a hydrogen-bonded network in water [36].

As emphasized above, the variegated evidence that has been reported so far on the zero-RMPE criterion is intrinsically phenomenological, being currently founded on the inspection of the behavior of the RMPE in the thermodynamic regions where one typically observes the ordering of the system into a more structured state, be it crystalline or not. As such, the body of results outlined above cannot be considered a conclusive proof of the existence of an underlying systematic relation between phase transitions and the crossovers of the RMPE from negative to positive values. Neither can one exclude that in some cases such a relation be quantitatively poor or, even, entirely missing. In this respect, it can be instructive to analyze the behavior of the RMPE in a case where the comparison with the thermodynamic properties of the system may be critical in that no conventional phase transition is actually observed as, for instance, in a one-dimensional system of hard-core particles with no mutual attraction (hard rods). This is the simplest, yet nontrivial, continuum model accounting for excluded-volume effects in dense fluids [37]. The model is frequently referred to as the “Tonks gas” after the name of one of the authors who originally derived the equation of state which was found to display no discontinuity over the entire density range aside from the expected divergence at close packing [38, 39].

2. Phenomenology of the Tonks gas

2.1. Residual multiparticle entropy

Let us consider a system of N hard rods of length σ moving on a line of length $L\sigma$, with a “reduced” number density (packing fraction) $\rho^* \equiv \rho\sigma = N/L$. A vast literature has grown up over the years on this model [40, 41]. In fact, thanks to its topological simplicity, many structural and dynamical properties of the Tonks gas are amenable to be expressed in analytical form. For our current purposes, aside from the equation of state $\beta P\sigma = \rho^*(1 - \rho^*)^{-1}$, where P is the pressure and $\beta = 1/k_B T$, we just need the excess entropy $S_{ex}/N = k_B \ln(1 - \rho^*)$ and the PDF of the infinite system in the thermodynamic limit [42, 43]:

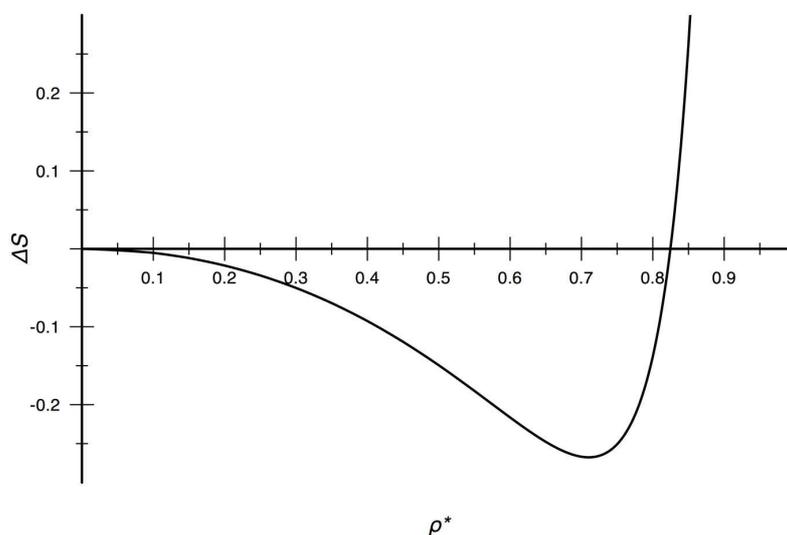
$$g(x) = \frac{\beta P}{\rho} \sum_{n=1}^{[x]} \frac{(\beta P\sigma)^{n-1}}{(n-1)!} (x-n)^{n-1} e^{-\beta P\sigma(x-n)} \Theta(x-n), \quad (4)$$

where x is the distance measured in units of σ , $\Theta(x)$ is the Heaviside step function, and the square brackets in the upper summation limit indicate the greatest integer function. The singular nature of the infinitely repulsive potential naturally implies that the PDF vanishes for relative separations shorter than σ .

To our knowledge, data for the pair entropy of the Tonks gas appeared for the first time in [44].

We plot the resulting RMPE in Fig. 1. The behavior of this quantity is analogous to that observed in two and three dimensions: the RMPE slowly decreases with ρ at low and intermediate densities until inverting its trend at $\rho_{\min}^* \simeq 0.71$ with a comparatively sharp increase which eventually leads to a crossover from negative to positive values for $\rho_0^* \simeq 0.825$. At first sight these features may seem devoid of physical significance since in one dimension, at variance with hard disks or spheres, hard rods do not notoriously exhibit any thermodynamic phase transition to which the vanishing of the RMPE can be possibly imputed [45]. However, we intend to show in this paper that, despite the absence of a freezing transition, the indications provided by the RMPE can be put in relation with a discernible change in the structural behavior of the compressed Tonks gas from a fluidlike to a solidlike regime.

Figure 1. Residual multiparticle entropy of hard rods plotted as a function of the reduced number density.



2.2. Structural properties at high densities

The Tonks gas is a highly anharmonic system. Moreover, when the thermodynamic limit is carried out, hard rods become totally delocalized in one dimension [46]. In fact, particle positions fluctuate with increasing amplitude as the size of the system is increased. In the long time limit the root-mean-square displacement of each rod is found to diverge, at any fixed density, as \sqrt{N} . Actually, this sort of Brownian motion reflects a global diffusive motion of the whole system whose effect on the high-density properties of the system can be discriminated by letting the specific volume approach the close-packing value as the inverse square root of the number of particles so as to compensate exactly the delocalization induced by the diffusive motion. This approach was proposed by Piasecki and Peliti [47] who could then demonstrate that, in such a properly defined high-density limit, hard rods do actually behave like a harmonic crystal. In fact, the one-particle density distribution function of dense hard rods acquires a Gaussian shape as is the case of a linear chain of strongly-coupled harmonically bound point particles: rods become asymptotically localized and oscillate about well defined mean positions (“lattice sites”). The analogies between the Tonks gas and a system of harmonic oscillators have been further discussed by Barnes and Kofke [48, 49]. We remark here that, as emphasized by Piasecki and Peliti, pure excluded-volume effects somewhat unexpectedly lead to harmonic-like behavior *over a whole range of densities*. One may then legitimately wonder whether such a range can be coarsely identified through a careful inspection of the structural properties of the system.

To our knowledge, the first explicit indication of an extended “solidlike” density range was given by Haus and Raveché [50] who noted that for $\rho^* \geq 0.85$ the local structure of hard rods resembles that of a “crystal” in that the distance between maxima in the PDF is represented to within a few percent by the average interparticle separation $1/\rho^*$. We illustrate their point by focusing on the first two intermaxima

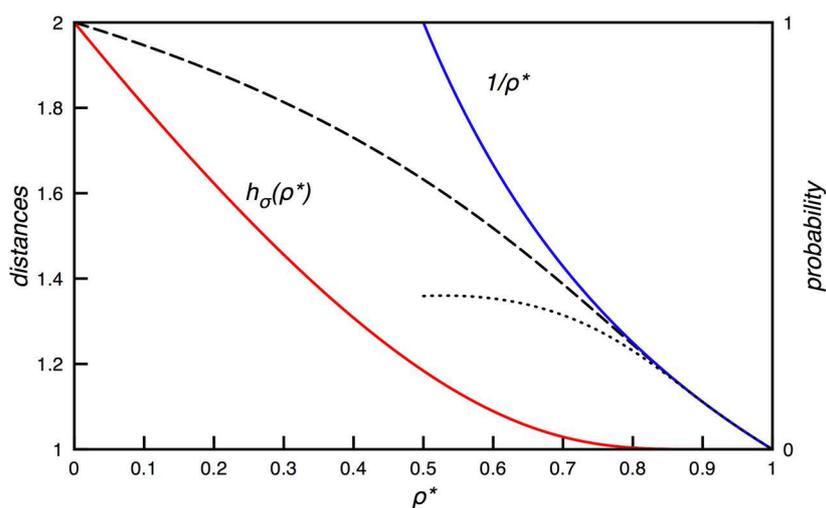
distances:

$$x_{\max}^{(2)} - x_{\max}^{(1)} = 1 + \frac{1}{\beta P \sigma} (1 - e^{-\beta P \sigma}) \tag{5}$$

$$x_{\max}^{(3)} - x_{\max}^{(2)} = 1 + \frac{1}{\beta P \sigma} [1 - 2(\beta P \sigma) e^{-\beta P \sigma} - e^{-2(\beta P \sigma)}]^{1/2} \tag{6}$$

where $x_{\max}^{(i)}$ is the position of the i th maximum, $x_{\max}^{(1)} = 1$, and the second expression is valid for $\rho^* \geq 1/2$ only. As shown in Fig. 2, both relative separations coalesce onto the average distance $1/\rho^*$ for $\rho^* \gtrsim 0.8$.

Figure 2. Distances between adjacent maxima in the PDF of hard rods plotted in units of the rod length as a function of the reduced number density: dashed line, $(x_{\max}^{(2)} - x_{\max}^{(1)})$; dotted line, $(x_{\max}^{(3)} - x_{\max}^{(2)})$. The solid blue line represents the average interparticle distance $1/\rho^*$. The probability of finding “holes” large σ is also plotted as a continuous red line; the values of $h_{\sigma}(\rho^*)$ are referred to the right axis.



In an analysis of the stability of a fluid toward solid formation, that was based on the Fourier transform of the direct correlation function, Lovett [51] had also observed that a spatial periodicity $\lambda \sim 1.2\sigma$ is a reasonable candidate for an *incipient* solid solution in a one-dimensional system of hard rods, even if no point of mechanical instability is ever actually reached. In this regard, we note that the mean nearest-neighbor distance between hard rods $l/\sigma = \frac{1}{2}(1 + 1/\rho^*)$ attains the value indicated by Lovett for $\rho^* \simeq 0.71$ [52]. On the other hand, as seen from Fig. 2, the spatial modulation of the local density profile matches this same value for $\rho^* \simeq 0.83$, at least as far as the first two coordination shells are concerned. Hence, on a prudent basis we argue that, according to Lovett’s “criterion”, one would locate the emergence of an incipient solid phase in the range of densities $0.71 \lesssim \rho^* \lesssim 0.83$.

More recently, Truskett and coworkers have further noted that, upon compressing the Tonks gas, a natural packing symmetry gradually develops about a generic reference particle [53]. Such a symmetry can be uncovered by investigating the probability that, given a particle at some position in the system, a

“sphere” of radius r encompassing this central particle contains exactly n additional particle centers [53]. The resulting set of quantities $E_P(r; n)$ can be computed analytically for one-dimensional hard rods. The odd-number curves ($n = 1, 3, 5, \dots$), plotted as a function of r , display maxima whose heights level off, with increasing densities, at 0.5. Instead, the maxima in the even-number curves ($n = 2, 4, 6, \dots$) grow with the density to values which may increase up to 1. In other words, the coordination shells which enfold a given particle predominantly consist, over a range of distances which expands with the density, of pairs of particles, one to the left and one to the right of the central particle, the probability of finding “unpaired” particles being significantly lower.

2.3. The unconstrained system versus the single occupancy cell model

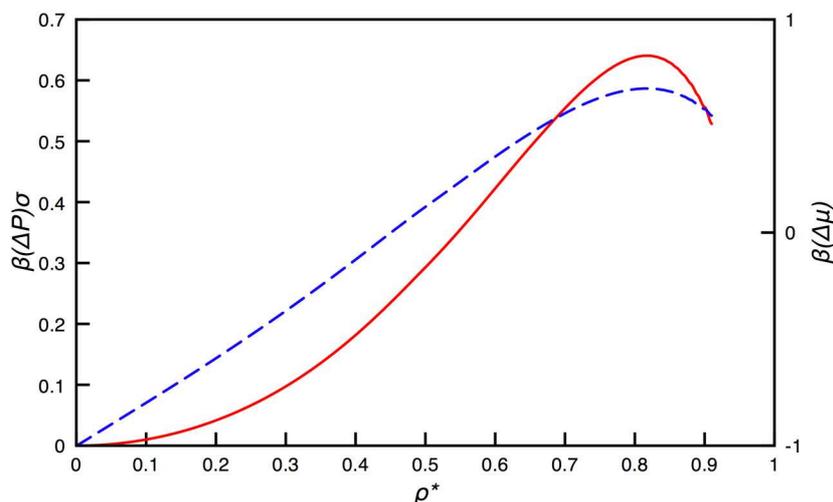
The observation made by Haus and Raveché on intermaxima distances naturally suggests an independent way to confirm the *nearly “solidlike” ordering* [54] that is spontaneously exploited by hard rods at high densities. In fact, the emergence of a spatial periodicity close to $1/\rho$ naturally evokes the characterizing feature of the so-called single occupancy cell (SOC) model, representing an *artificial* one-dimensional crystal in which each rod is confined to a “cell” of length $L\sigma/N = \rho^{-1}$ [55]. It is well known that the properties of the Tonks gas merge into those of the corresponding SOC model in the limit of close packing. However, one may wonder whether it is possible to identify a density threshold beyond which the SOC model becomes *de facto* a sort of underlying structural “watermark” for the local arrangement in a Tonks gas. In this regard, a lower bound can be plausibly fixed upon observing that, in the absence of attractive interactions, it would be altogether inappropriate to describe the Tonks gas as a pseudocrystal if a generic particle sweeps out, on average, a “free volume” $\frac{1}{N}L_{free} = (1/\rho^* - 1)$ larger than its own length. After noting that the space available to each particle is shared with its two nearest neighbors, one easily finds that the above condition corresponds to a reduced density $\rho^* = 2/3$. However, a more reliable indication can be obtained upon inspecting how the probability of finding somewhere in the system a “hole” large σ , *i.e.*, a region of radius σ empty of particle centers, changes with increasing densities [52, 56]:

$$\begin{aligned} h_\sigma(\rho^*) &= e^{-\beta\mu_{ex}(\rho^*)} \\ &= (1 - \rho^*)e^{-\frac{\rho^*}{(1-\rho^*)}}, \end{aligned} \quad (7)$$

where μ_{ex} is the excess chemical potential. The above quantity drops from one at infinite dilution to values that are at least three orders of magnitude lower for $\rho^* \gtrsim 0.8$ (see Fig. 2): hence, the dissolution of “holes” large enough to accommodate another particle appears as the statistical-geometrical counterpart of the emergence in the system of a sufficiently well defined spatial periodicity. We can now verify whether and to which extent the above considerations are consistent with the thermodynamics of the two models. Figure 3 shows the differences, plotted as a function of the reduced number density, between the two significant intensive properties (*i.e.*, pressure and chemical potential) of the Tonks gas and the corresponding quantities calculated in the SOC model.

The partition function of the SOC model is related, in the thermodynamic limit, to the smallest zero of a polynomial whose coefficients can be written in closed analytical form but whose order increases with the density as $2 + [\rho^*/(1 - \rho^*)]$, where the square brackets indicate the greatest integer function [55]. This latter feature causes numerical difficulties in the search of the smallest zero for $\rho^* \gtrsim 0.92$.

Figure 3. Differences between the intensive properties of the Tonks gas and of the corresponding single occupancy cell model plotted as a function of the reduced number density: pressure, red continuous line (left axis); chemical potential, blue dashed line (right axis).



As seen from Fig. 3, the pressure gap between the two model systems rises from zero (ideal-gas regime) to a maximum at $\rho_{\max}^* \simeq 0.82$, beyond which it drops back to zero. Correspondingly, the difference in chemical potential grows from the value (modulo the sign and in units of the Boltzmann constant) of the “communal entropy” [57] per particle of the ideal one-dimensional gas to a maximum located at ρ_{\max}^* as well. The position of this maximum marks, consistently with the inferences based on the probability of occurrence of particle-sized voids, the lower-density edge of the phase diagram region in which the Tonks gas and the corresponding SOC model qualitatively overlap in that their respective thermodynamic trends become more and more similar, all the way up to close packing.

3. Three-body correlations, Kirkwood’s coupling and periodic states at high density

In a classical system composed of hard particles, which discontinuously repel each other through elastic collisions while exerting no mutual attraction, a phase transition can only emerge as the macroscopic outcome of a competition – for assigned values of the pressure and of the chemical potential – between different packing strategies which can be potentially exploited by the system. Such a competition is ruled entirely by the entropy since the internal energy of nonattracting hard particles does not change with the macroscopic configuration of the system, depending just on the temperature as in a noninteracting gas. Hence, in a three-dimensional system of hard spheres the ordered crystalline state becomes thermodynamically stable at high densities since the entropy of the solid is larger than that of the equally dense (metastable) fluid. The phenomenology discussed in the preceding Section indicates that even hard rods in one dimension undergo a sort of *diffuse* transition, over the range of densities $0.71 \lesssim \rho^* \lesssim 0.83$, from a fully disordered fluid state onto a pseudo-crystalline state consisting of a regularly spaced sequence of

particles that become “self-confined”, on average, inside regions $1/\rho$ wide. However, such an ordering process, that is exclusively driven by the statistical-geometrical quest for optimal packing efficiency, does not emerge as a conventional thermodynamic transition between two macroscopically distinct phases for reasons that are obviously related with the somewhat “pathological” nature of the hard-sphere model in one dimension. In this regard, a distinguishing feature of the Tonks gas is that any particle effectively divides the system into two *independent* subsystems. As noted in [42], if we fix particle n of an arbitrary subset of $n + 1$ particles, then the position of particle $n + 1$ is independent of the positions of particles $1, 2, \dots, n - 1$ and depends on the position of particle n only. For one-dimensional systems in which the interactions are restricted to nearest neighbors, this statement can be formalized in terms of conditional multiparticle probabilities as follows:

$$\frac{g_{n+1}(1, 2, \dots, n, n + 1)}{g_n(1, 2, \dots, n)} = \frac{g_2(n, n + 1)}{g_1(n)}, \quad (8)$$

where $g_n(1, 2, \dots, n)$ is the n th order reduced distribution function whose arguments are the positions of particles 1 to n . In the absence of symmetry-breaking fields $g_2(1, 2) = g(|x_2 - x_1|)$ is the ordinary pair (radial) distribution function and $g_1(n) = 1$. It thus follows that all reduced distribution functions can be factorized as products of pair distribution functions. In particular, the triplet distribution function (TDF) reads:

$$g_3(1, 2, 3) = g(1, 2)g(2, 3), \quad (9)$$

particle 2 lying between particles 1 and 3. As is seen from Eq. 9, PDF couplings between nearest neighbors only are present in the TDF, the influence of particle 1 on particle 3 (and *vice versa*) being transferred at this level through intermediate particle 2. One might putatively wonder how the thermodynamics of the Tonks gas would change if a PDF coupling between next-nearest neighbors (*viz.*, particles 1 and 3) was present as well in the TDF:

$$\tilde{g}_3(1, 2, 3) = g(1, 2)g(2, 3)g(3, 1). \quad (10)$$

The reader is obviously aware that the above expression for the TDF does in fact coincide with the celebrated Kirkwood superposition approximation (KSA) [58, 59], which has been widely used in the past as an approximate “closure” of the Born-Green-Yvon (BGY) integro-differential equation for the calculation of the PDF in liquids, both in two and three dimensions [60]. However, here we intend to exploit the “augmented” form of the TDF – which, as an *approximation*, is obviously unneeded in one dimension aside from being manifestly wrong – in a different speculative context: we suggest to re-read Eq. 10 as an autonomous case study in which the added coupling between non-nearest neighbors is thought as being originated by some effective (possibly, state-dependent) field inducing an overall *enhancement* of structural correlations in the system. We are not so much interested in the justification of the mechanical origin of such a field [61] as in the effects it produces on the properties of the system through the extra coupling between next-nearest neighbors. We shall refer to the system with the modified TDF as the “perturbed” Tonks gas. On the mathematical side, the BGY equation implemented with the KSA closure (Eq. 10) is a nonlinear equation in the PDF [62, 63]. As such, its solution may not be unique, for assigned boundary conditions, over some ranges of the “parameter” (either the density or the pressure) for which numerical solutions of the equation are being sought. And, in fact, this is precisely

what happens for densely packed hard spheres, even in one dimension: two distinct structural regimes emerge whose features are manifestly evocative of an underlying thermodynamic transition from a fluid to a crystalline phase. The PDF of unperturbed hard rods (Eq. 4) and that obtained upon numerically solving the BGY/KSA equation are found to differ in a negligible way in the low to intermediate density regime ($\rho^* \lesssim 0.5$) [62]. However, the latter function starts showing for larger densities a damped periodic profile that is not evident in the analytic PDF, whereas the contact values of both functions (and, correspondingly, the equations of state of the two systems) remain essentially identical up to $\rho^* \simeq 0.7$. For this value of the density, corresponding to a pressure $\beta P\sigma \simeq 2.3$, the PDF of the perturbed Tonks gas changes abruptly from a damped to an undamped oscillatory behavior. Moreover, other (disconnected) branches of undamped periodic solutions appear for pressures larger than the reported threshold value. We note that the solidlike behavior distinctly monitored by the PDF emerges in the system on the lower density side of the ordering range that has been identified above on the basis of other independent indicators.

The BGY/KSA equation can also be linearized. In fact, Siders and Kozak [63] demonstrated that the linear problem is equivalent to a BGY equation for the same system but with a different closure that is obtained from Eq. 10 upon replacing one of the three PDFs, say $g(1, 2)$, with its low-density limit which, for a hard-core system with no attraction, reduces to the Heaviside step function. The linearizing closure is found to reproduce the exact superposition law (Eq. 9) for a certain class of configurations attained by the particle triad (*viz.*, when particle 3 lies between particles 1 and 2). In this respect, we may argue that the modified closure gives rise – in our field-based interpretative scheme – to a *weaker* structural “perturbation” of the Tonks gas than that implied by the original KSA closure. However, one may also suspect that resorting to the low-density expression for one of the PDF couplings, with the consequent loss of the original symmetry property with respect to particle interchange and of the correct asymptotic behavior as particle 3 moves away from particles 1 and 2, may also *weaken* the overall correlation texture of the gas at moderate to high densities. In fact, the resulting equation of state shows a less steep rise with the density as compared with the analogous property of the unperturbed Tonks gas. However, the interesting feature is again the bifurcation of the solution for tight packings: two branches of undamped oscillatory solutions were found to depart from the damped (fluidlike) solution for pressures $\beta P\sigma > 2.3$, the same threshold value that discriminates the damped/undamped behavior of the solutions to the nonlinear BGY/KSA equation [63]. However, at variance with the nonlinear case, the system may now undergo an abrupt transition from the lower pressure branch (damped) to the higher pressure one (undamped) for reduced number densities not less than 0.83 [63]. *A posteriori*, a larger threshold value of the density appears justified as the result of an overall weaker structural perturbation. Intriguingly, this larger value falls on the upper side of the ordering range discussed in the preceding section.

4. Conclusions

In this paper we have revisited the equilibrium properties of the Tonks gas, a classical system of hard particles confined to one dimension, with a twofold objective: i) understanding whether it is possible to distinguish a high-density regime, with features reminiscent of the properties of a crystalline solid, from a low-density fluidlike regime, notwithstanding the absence of a conventional freezing transition;

ii) verifying whether the density evolution of the so-called residual multiparticle entropy (RMPE) can be put in direct quantitative correspondence with the thermodynamic and structural behavior of the model.

As far as the first point is concerned, comparative evidence from a number of different properties indicates that the highly packed fluid orders into a pseudo-crystalline state consisting of a quasi regularly spaced sequence of particles “self-confined” inside equipartitioned regions of length equal to the average length per particle $1/\rho$. Such an ordering process takes place over an extended range of densities whose lower and upper boundaries can be consistently fixed with reasonable accuracy, *viz.*, $0.7 \lesssim \rho^* \lesssim 0.83$.

It is in such a range of densities that one also observes an inversion in the trend of the RMPE from a decreasing to an increasing behavior as a function of the density, the minimum at $\rho_{\min}^* \simeq 0.71$ being followed by a crossover from negative to positive values at the reduced density $\rho_0^* \simeq 0.825$. In this perspective, the Tonks gas sheds a new and, in some respects, unexpected light on the zero-RMPE criterion. In fact, it appears that the RMPE of hard rods, far from yielding meaningless predictions not at all pertinent to the physics of the model, does actually signal the spontaneous ordering of the dense fluid into a state that closely resembles that of a crystal. It is worth emphasizing that the corresponding indication is present in the RMPE notwithstanding the fact that such a process does (or can) not emerge at the macroscopic level as a proper thermodynamic transition to a fully ordered state for reasons that are obviously related to the markedly different topology of the hard-sphere model in one dimension as compared to that of the same model in higher dimensions.

Within such a framework, the (for certain aspects) puzzling results emerging from the use of Kirkwood’s closure in the one-dimensional Born-Green-Yvon equation have been re-read and re-interpreted as revealing indications of a pseudo structural transition from a fluid to a solidlike regime that would take place in the system if some extra field would force a direct “binding” between next-nearest neighbors at the level of three-body correlations.

References

1. Green, H. S. *The molecular theory of fluids*. North-Holland, Amsterdam, **1952**.
2. Nettleton, R. E.; Green, M. S. Expression in terms of molecular distribution functions for the entropy density in an infinite system. *The Journal of Chemical Physics* **1958**, *29*(6), 1365–1370.
3. Baranyai, A.; Evans, D. J. Direct entropy calculation from computer simulation of liquids. *Physical Review A* **1989**, *40*(7), 3817–3822.
4. Yvon, J. *Correlations and entropy in classical statistical mechanics*. Pergamon Press, Oxford, **1969**.
5. Leff, H. S. Entropy differences between ideal and nonideal systems. *American Journal of Physics* **1969**, *37*(5), 548–553.
6. Baranyai, A.; Evans, D. J. Three-particle contribution to the configurational entropy of simple fluids. *Physical Review A* **1990**, *42*(2), 849–857.
7. Baranyai, A.; Evans, D. J. On the entropy of the hard sphere fluid. *Zeitschrift für Naturforschung A* **1991**, *46*, 27–31.
8. Giaquinta, P. V.; Giunta, G. About entropy and correlations in a fluid of hard spheres. *Physica A* **1992**, *187*, 145–158.
9. Giaquinta, P. V.; Giunta, G.; Prestipino Giarritta, S. Entropy and the freezing of simple liquids.

Phys. Rev. A **1992**, 45(10), R6966–R6968.

10. Caccamo, C.; Giaquinta, P. V.; Giunta, G. Phase diagram of simple fluids: a comprehensive theoretical approach. *Journal of Physics: Condensed Matter* **1993**, 5(34B), B75–B82.
11. Cheng, A.; Klein, M. L.; Caccamo, C. Prediction of the phase diagram of rigid C₆₀ molecules. *Phys. Rev. Lett.* **1993**, 71(8), 1200–1203.
12. Lomba, E.; Almarza, N. G. Role of the interaction range in the shaping of phase diagrams in simple fluids. The hard sphere Yukawa fluid as a case study. *The Journal of Chemical Physics* **1994**, 100(11), 8367–8372.
13. Lomba, E.; López-Martín, J. L.; Cataldo, H. M.; Tejero, C. F. Phase transitions in simple fluids: An application of a one-phase entropic criterion to Lennard-Jones and point Yukawa fluids. *Phys. Rev. E* **1994**, 49(6), 5164–5168.
14. Giaquinta, P. V.; Giunta, G.; Malescio, G. Entropy versus correlations in simple fluids: The gas-liquid and freezing transitions. *Physica A* **1998**, 250, 91–102.
15. Saija, F.; Prestipino, S.; Giaquinta, P. V. Scaling of local density correlations in a fluid close to freezing. *The Journal of Chemical Physics* **2001**, 115(16), 7586–7591.
16. Giaquinta, P. V.; Saija, F. Re-entrant melting in the Gaussian-core model: The entropy imprint. *ChemPhysChem* **2005**, 6(9), 1768–1771.
17. Prestipino, S.; Saija, F.; Giaquinta, P. V. Phase diagram of the Gaussian-core model. *Physical Review E (Statistical, Nonlinear, and Soft Matter Physics)* **2005**, 71(5), 050102.
18. Saija, F.; Prestipino, S.; Giaquinta, P. V. Evaluation of phenomenological one-phase criteria for the melting and freezing of softly repulsive particles. *The Journal of Chemical Physics* **2006**, 124(24), 244504.
19. Saija, F. An entropy-based approach to the freezing of the generalized exponential model. *The Journal of Chemical Physics* **2008**, 128(13), 136101.
20. Saija, F. Statistical entropy and clustering in absence of attractive terms in the interparticle potential. *Atti della Accademia Peloritana dei Pericolanti - Classe di Scienze Fisiche, Matematiche e Naturali* **2008**, 86(2), C1A0802002.
21. Saija, F.; Giaquinta, P. V.; Giunta, G.; Prestipino Giarritta, S. On entropy and ordering in binary hard-sphere mixtures. *Journal of Physics: Condensed Matter* **1994**, 6(46), 9853–9865.
22. Saija, F.; Giaquinta, P. V. Statistical entropy of a binary hard-sphere mixture: the low-density limit. *Journal of Physics: Condensed Matter* **1996**, 8(43), 8137–8144.
23. Saija, F.; Prestipino, S.; Giaquinta, P. V. Entropy, correlations, and ordering in two dimensions. *The Journal of Chemical Physics* **2000**, 113(7), 2806–2813.
24. Prestipino, S.; Giaquinta, P. V. Statistical entropy of a lattice-gas model: Multiparticle correlation expansion. *Journal of Statistical Physics* **1999**, 96(1), 135–167.
25. Prestipino, S.; Giaquinta, P. V. Errata: Statistical entropy of a lattice-gas model: Multiparticle correlation expansion. *Journal of Statistical Physics* **2000**, 98(1), 507–509.
26. Donato, M. G.; Prestipino, S.; Giaquinta, P. V. Entropy and multi-particle correlations in two-dimensional lattice gases. *The European Physical Journal B* **1999**, 11(4), 621–627.
27. Prestipino, S. Analog of surface preroughening in a two-dimensional lattice Coulomb gas. *Physical Review E* **2002**, 66(2), 021602.
28. Saija, F.; Pastore, G.; Giaquinta, P. Entropy and fluid-fluid separation in nonadditive hard-sphere

- mixtures. *Journal of Physical Chemistry B* **1998**, *102*(50), 10368–10371.
29. Saija, F.; Giaquinta, P. Entropy and fluid-fluid separation in nonadditive hard-sphere mixtures: The asymmetric case. *Journal of Physical Chemistry B* **2002**, *106*(8), 2035–2040.
 30. Saija, F.; Giaquinta, P. V. Monte Carlo simulation and phase behavior of nonadditive hard-core mixtures in two dimensions. *The Journal of Chemical Physics* **2002**, *117*(12), 5780–5784.
 31. Costa, D.; Saija, F.; Giaquinta, P. Angular correlations and statistical entropy of hard spherocylinders: the isotropic-nematic transition. *Chemical Physics Letters* **1998**, *283*(1-2), 86–90.
 32. Costa, D.; Saija, F.; Giaquinta, P. Erratum to: “Angular correlations and statistical entropy of hard spherocylinders: the isotropic-nematic transition”. *Chemical Physics Letters* **1999**, *290*(2), 252–252.
 33. Costa, D.; Micali, F.; Saija, F.; Giaquinta, P. Entropy and correlations in a fluid of hard spherocylinders: The onset of nematic and smectic order. *Journal of Physical Chemistry B* **2002**, *106*(47), 12297–12306.
 34. Costa, D.; Saija, F.; Giaquinta, P. Smectic ordering of parallel hard spherocylinders: An entropy-based Monte Carlo study. *Journal of Physical Chemistry B* **2003**, *107*(35), 9514–9519.
 35. Prestipino, S.; Giaquinta, P. V. The entropy multiparticle-correlation expansion for a mixture of spherical and elongated particles. *Journal of Statistical Mechanics: Theory and Experiment* **2004**, *2004*(09), P09008.
 36. Saija, F.; Saitta, A. M.; Giaquinta, P. V. Statistical entropy and density maximum anomaly in liquid water. *The Journal of Chemical Physics* **2003**, *119*(7), 3587–3589.
 37. Lord Rayleigh. On the virial of a system of hard colliding bodies. *Nature* **1891**, *45*(1152), 80–82.
 38. Herzfeld, K. F.; Goepfert-Mayer, M. On the states of aggregation. *The Journal of Chemical Physics* **1934**, *2*(1), 38–45.
 39. Tonks, L. The complete equation of state of one, two and three-dimensional gases of hard elastic spheres. *Phys. Rev.* **1936**, *50*(10), 955–963.
 40. Lieb, E. H.; Mattis, D. C., editors. *Mathematical Physics in One Dimension*. Perspectives in Physics. Academic Press, New York, **1966**.
 41. Percus, J. K. Exactly solvable models of classical many-body systems. In Lebowitz, J. L., editor, *Simple models of equilibrium and nonequilibrium phenomena*, volume 13 of *Studies in Statistical Mechanics*, chapter 1, pages 1–158. North-Holland Physics Publishing, Amsterdam, **1987**.
 42. Salsburg, Z. W.; Zwanzig, R. W.; Kirkwood, J. G. Molecular distribution functions in a one-dimensional fluid. *The Journal of Chemical Physics* **1953**, *21*(6), 1098–1107.
 43. Sells, R. L.; Harris, C. W.; Guth, E. The pair distribution function for a one-dimensional gas. *The Journal of Chemical Physics* **1953**, *21*(8), 1422–1423.
 44. Borzsák, I.; Baranyai, A. On the convergence of Green’s entropy expansion. *Chemical Physics* **1992**, *165*(2-3), 227–230.
 45. Krekelberg, W. P.; Shen, V. K.; Errington, J. R.; Truskett, T. M. Residual multiparticle entropy does not generally change sign near freezing. *The Journal of Chemical Physics* **2008**, *128*(16), 161101.
 46. Hoover, W. G. *Computational Statistical Mechanics*. Elsevier, Amsterdam, **1991**.
 47. Piasecki, J.; Peliti, L. Harmonic properties of hard-sphere crystals: a one-dimensional study. *Journal of Physics A: Mathematical and General* **1993**, *26*(19), 4819–4825.
 48. Barnes, C. D.; Kofke, D. A. Exact solution for the singlet density distributions and second-order

- correlations of normal-mode coordinates for hard rods in one dimension. *The Journal of Chemical Physics* **1999**, *110*, 11390–11398.
49. Barnes, C. D.; Kofke, D. A. A comparison of some variational formulas for the free energy as applied to hard-sphere crystals. *The Journal of Chemical Physics* **2002**, *117*, 9111–9115.
 50. Haus, J. W.; Raveché, H. J. Computer studies of dynamics in one dimension: Hard rods. *The Journal of Chemical Physics* **1978**, *68*(11), 4969–4976.
 51. Lovett, R. On the stability of a fluid toward solid formation. *The Journal of Chemical Physics* **1977**, *66*(3), 1225–1230.
 52. Torquato, S.; Lu, B.; Rubinstein, J. Nearest-neighbor distribution functions in many-body systems. *Physical Review A* **1990**, *41*(4), 2059–2075.
 53. Truskett, T. M.; Torquato, S.; Debenedetti, P. G. Density fluctuations in many-body systems. *Physical Review E* **1998**, *58*(6), 7369–7380.
 54. Bishop, M.; Whitlock, P. A.; Klein, D. The structure of hyperspherical fluids in various dimensions. *The Journal of Chemical Physics* **2005**, *122*(7), 074508.
 55. Hoover, W. G.; Alder, B. J. Cell theories for hard particles. *The Journal of Chemical Physics* **1966**, *45*(7), 2361–2367.
 56. Elkoshi, Z.; Reiss, H.; Hammerich, A. D. One-dimensional rigorous hole theory of fluids: Internally constrained ensembles. *Journal of Statistical Physics* **1985**, *41*(3-4), 685–709.
 57. Hirschfelder, J.; Stevenson, D.; Eyring, H. A theory of liquid structure. *The Journal of Chemical Physics* **1937**, *5*(11), 896–912.
 58. Kirkwood, J. G. Statistical mechanics of fluid mixtures. *The Journal of Chemical Physics* **1935**, *3*(5), 300–313.
 59. Kirkwood, J. G.; Monroe Boggs, E. The radial distribution function in liquids. *The Journal of Chemical Physics* **1942**, *10*(6), 394–402.
 60. Cole, G. H. A. Classical fluids and the superposition approximation. *Reports on Progress in Physics* **1968**, *31*(2), 419–470.
 61. Kunin, W.; Frisch, H. L. Comment on Kirkwood instability. *The Journal of Chemical Physics* **1969**, *50*(4), 1817–1818.
 62. Green, K. A.; Luks, K. D.; MacCarthy, J. E.; Kozak, J. J. The influence of closure on the behaviour of the Yvon-Born-Green equation for a system of hard rods. *Molecular Physics* **1982**, *45*(4), 897–913.
 63. Siders, P.; Kozak, J. J. The Kirkwood superposition approximation for hard rods at high pressure. *The Journal of Chemical Physics* **1984**, *81*(10), 4594–4602.