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ABSTRACT

We provide rigorous evidence that the ordered ground state configurations of a system of parallel oriented, ellipsoidal particles, interacting via a Gaussian potential (termed in the literature as Gaussian core nematics), *must* be infinitely degenerate; we have demonstrated that these configurations originate from the related ground state configuration of the corresponding symmetric Gaussian core system via a suitable stretching operation of this lattice in combination with an arbitrary rotation. These findings explain related observations in former investigations, which then remained unexplained. Our conclusions have far reaching consequences for the search of ground state configurations of other nematic particles.

I. INTRODUCTION

Reliable identification of ground state configurations of soft matter systems—i.e., to find the energetically most favorable (ordered) arrangement of particles at vanishing temperature—is of paramount relevance to understand the self-assembly strategies of these systems. In the overwhelming majority of the related investigation, it has been (and often still is) assumed that the particles are spherically symmetric. This assumption is mostly due to the fact that the numerical task of identifying ground state configurations is rather challenging and, from the computational point of view, rather expensive, as it amounts to finding, with the help of suitable numerical techniques in an efficient and reliable manner, the optimal particle arrangement in the space spanned by "all lattices" (see, e.g., Refs. 1–3).

Meanwhile, soft matter particles can be synthesized in essentially arbitrary shapes, thus moving beyond simple sphericity (for an overview, see, e.g., Ref. 4). This remarkable progress in particle synthesis urges theoreticians to extend the quest for ordered ground state configurations also to particles that are aspherical in their shape and/or in their interactions. The computational power of present-day computers provides the necessary numerical basis for this challenge.

Among the pioneering contributions, dedicated during the past years to systematically investigate the ordered ground state configurations for a simple aspherical system, we focus in this manuscript on a paper published by Prestipino and Saija (PS),[5] who investigated the ground state configurations of ellipsoidal particles, which interact via a suitably modified Gaussian potential; the aspect ratio of these particles will, henceforward, be denoted by λ. In an effort to reduce the complexity of the problem, the authors made a simplifying assumption that the directors of all the particles are oriented in the same direction, hence the name "Gaussian core nematics" (GCNs). Despite its simplicity, this model combines characteristic features of realistic soft particles, which have a pronounced impact on their self-assembly strategies: (i) asphericity, as witnessed prominently in liquid crystals,[6] and (ii) mutual penetrability, reflecting the often rather open internal architectures of typical soft matter

macromolecules, as they are observed, for instance, in dendrimers or polymers (see, e.g., Refs. 7–9 and citing articles), and leading in the most extreme case to so-called cluster-forming systems (see, e.g., Refs. 10 and 11 and citing articles).

The study by PS[5] and a subsequent contribution by Nikoubashman and Likos (NL)[12] on the very same system have revealed important features that apparently have not been sufficiently noticed within the community, so far: PS reported about the emergence of "topologically different degenerate structures," whereas NL observed that, for each value of λ, the system undergoes a phase transition at a density that is related to that of the fcc–bcc transition expected in the spherical system with $\lambda = 1$ by a simple scaling law.

Motivated by our own recent investigations of the ordered structures formed by yet another ultra-soft system[16] (based on classical density functional theory[13–15]), where we have encountered, similar to PS,[5] unexpected degeneracy issues, we have re-considered the problem from scratch. Eventually, we provide in this contribution formally exact evidence for the two following facts: (i) the energy of the aspherical system can be mapped exactly on the energy of the related spherically symmetric system; (ii) furthermore, we rigorously show that an infinite number of ordered ground state structures *must* exist for the aspherical system. These arguments allow us to fully understand the phenomena observed by PS and NL, and are closely related to those formerly developed by Schiller *et al.*[17,18] in the context of the crystal phases of hard-core ellipsoidal particles. Somewhat surprisingly, the relevance of their results to those reported by PS and NL seems not to have been noticed so far.

The impact of our findings can be appreciated in two respects: on one side, they provide rigorous justifications of the so far inexplicable observations and embed them in a broader context; on the other side, one has to conclude from our findings that the search of ground state configurations for the GCNs (and undoubtedly also for related systems) does not provide very conclusive results, as one has to end up with an infinitely degenerate ground state.

The manuscript is organized as follows: In Sec. II, we present the model, and in Sec. III, we discuss our formalism, which provides rigorous evidence of the above statements; we also dedicate a short subsection to the related work published by Schiller *et al.*[17,18] Section IV is dedicated to a thorough revision and discussion of the data provided by PS and NL, in view of our formalism. The manuscript is closed with a concluding section which also addresses the possible future developments of our findings.

II. MODEL

We consider the *aspherical* Gaussian core model (as used in Refs. 5 and 12), whose functional form is given by

$$\Phi(\mathbf{r}) = \varepsilon\varphi\left[\frac{r}{\sigma(\hat{\mathbf{r}},\lambda)}\right] = \varepsilon\exp\left[-\left(\frac{r}{\sigma(\hat{\mathbf{r}},\lambda)}\right)^2\right]; \tag{1}$$

in this relation, $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$, where $\mathbf{r}$ is the center-to-center vector of two interacting particles, ε sets the length scale, and λ characterizes the asphericity of the particle. Since $\Phi(r)$ assumes a finite value at $r = 0$, this interaction belongs to the family of ultra-soft, aspherical potentials.

In particular, we choose $\sigma(\hat{\mathbf{r}},\lambda)$ to be given by

$$\sigma(\hat{\mathbf{r}},\lambda) = \frac{\sigma_0}{\sqrt{1+(\lambda^{-2}-1)\cos^2\vartheta}}, \tag{2}$$

where $\sigma_0 = \sigma(\hat{\mathbf{r}},\lambda = 1)$ sets the unit length and ϑ is the angle enclosed by $\hat{\mathbf{r}}$ and an arbitrary, but fixed, directional unit vector $\mathbf{u}$, which determines the orientation of the particles. We stress once more that this is assumed from the outset to be the same for all particles. If, without loss of generality, we identify the z-axis with the direction of $\mathbf{u}$, then $\cos\vartheta = z/r$, and Eq. (1) can be rewritten as

$$\Phi(\mathbf{r}) = \varepsilon\varphi\left(\frac{1}{\sigma_0}\sqrt{x^2+y^2+\left(\frac{z}{\lambda}\right)^2}\right) \tag{3}$$

so that the iso-surfaces of the potential are ellipsoids of revolution (spheroids) around the z-axis with aspect ratio λ.

Furthermore, we denote the related spherically symmetric potential by $\Phi_0(r)$, which is obtained from Eq. (3) for $\lambda = 1$, i.e.,

$$\Phi_0(r) = \varepsilon\varphi\left(\frac{r}{\sigma_0}\right) = \varepsilon\exp\left[-\left(\frac{r}{\sigma_0}\right)^2\right]. \tag{4}$$

Equation (3) can, thus, be rewritten as

$$\Phi(\mathbf{r}) = \Phi_0(\mathbf{r}_\lambda) = \Phi_0(r_\lambda), \tag{5}$$

with

$$\mathbf{r}_\lambda = \left(x, y, \frac{z}{\lambda}\right) \quad \text{and} \quad r_\lambda = \sqrt{x^2+y^2+\left(\frac{z}{\lambda}\right)^2}. \tag{6}$$

Similarly, the Fourier transform of $\Phi(\mathbf{r})$ (denoted by a tilde) has the form

$$\widetilde{\Phi}(\mathbf{k}) = \lambda\sigma_0^3\varepsilon\widetilde{\varphi}\left(\sigma_0\sqrt{k_x^2+k_y^2+(k_z\lambda)^2}\right) = \lambda\widetilde{\Phi}_0(\mathbf{k}_\lambda) = \lambda\widetilde{\Phi}_0(k_\lambda), \tag{7}$$

with

$$\mathbf{k}_\lambda = (k_x, k_y, k_z\lambda) \quad \text{and} \quad k_\lambda = \sqrt{k_x^2+k_y^2+(k_z\lambda)^2}. \tag{8}$$

Clearly, the iso-surfaces of $\widetilde{\Phi}(\mathbf{k})$ are also ellipsoids of revolution around the z-axis with aspect ratio $1/\lambda$.

The system is characterized by its number density, ρ. Throughout the paper the temperature has been set to zero.

III. THE GROUND STATE ENERGY

A. Mapping of the energy between the aspherical and the spherical potentials

Consider an ordered configuration of N aspherical Gaussian particles at $T = 0$ (ground state configuration); its structure is given by a Bravais lattice with lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ and cell volume $v = 1/\rho$; these vectors can be collected in a matrix $\mathbf{A}$,

$$\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3). \tag{9}$$

We can then define the related reciprocal lattice with lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$; these vectors are collected in a matrix $\mathbf{B}$,

$$\mathbf{B} = (\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3). \tag{10}$$

At $T = 0$, the free energy reduces to the internal energy E of the system, given by

$$\frac{E}{N} = \frac{1}{2}\sum_{\mathbf{m}\neq\mathbf{0}}\Phi(\mathbf{r}_\mathbf{m}) = \frac{1}{2v}\sum_{\mathbf{n}}\widetilde{\Phi}(\mathbf{k}_\mathbf{n}) - \frac{1}{2}\Phi(0). \tag{11}$$

The first sum is taken over all lattice positions of the Bravais lattice, $\mathbf{r_m} = \sum_i m_i \mathbf{a}_i$ (with $|\mathbf{r_m}| \neq 0$) with $\mathbf{m} = (m_1, m_2, m_3)$ and the m_i being integers, while the second sum is taken over all lattice positions of the reciprocal lattice, $\mathbf{k_n} = \sum_i n_i \mathbf{b}_i$ with $\mathbf{n} = (n_1, n_2, n_3)$; again the n_i are integers.

By virtue of Eqs. (5) and (7), the above expression can be reformulated as

$$\frac{E}{N} = \frac{1}{2} \sum_{\mathbf{m}\neq\mathbf{0}} \Phi_0(r_{\lambda,\mathbf{m}}) = \frac{\lambda}{2v} \sum_{\mathbf{n}} \widetilde{\Phi}_0(k_{\lambda,\mathbf{n}}) - \frac{1}{2}\Phi_0(0), \tag{12}$$

using $\Phi(0) = \Phi_0(0)$; see Eq. (5). The $\mathbf{r}_{\lambda,\mathbf{m}}$ and $\mathbf{k}_{\lambda,\mathbf{n}}$ are specified in Eqs. (6) and (8), where x, y, and z and k_x, k_y, and k_z are identified with the components of the Bravais lattice vectors $\mathbf{r_m}$ and $\mathbf{k_n}$, respectively.

We now observe that $\mathbf{r}_{\lambda,\mathbf{m}}$ and $\mathbf{k}_{\lambda,\mathbf{n}}$ can also be regarded as vectors of a Bravais lattice with primitive vectors $\mathbf{a}_i^0$ and $\mathbf{b}_i^0$, $i = 1, 2, 3$,

$$\mathbf{r}_{\lambda,\mathbf{m}} = \sum_i m_i \mathbf{a}_i^0 \equiv \mathbf{r}_\mathbf{m}^0 \quad \text{and} \quad \mathbf{k}_{\lambda,\mathbf{n}} = \sum_i n_i \mathbf{b}_i^0 \equiv \mathbf{k}_\mathbf{m}^0. \tag{13}$$

The matrices $\mathbf{A}_0 = (\mathbf{a}_1^0, \mathbf{a}_2^0, \mathbf{a}_3^0)$ and $\mathbf{B}_0 = (\mathbf{b}_1^0, \mathbf{b}_2^0, \mathbf{b}_3^0)$ obtained by collecting these vectors are related to the matrices $\mathbf{A}$ and $\mathbf{B}$ by

$$\mathbf{A}_0 = \begin{pmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ \lambda^{-1}a_{1z} & \lambda^{-1}a_{2z} & \lambda^{-1}a_{3z} \end{pmatrix} = \mathbf{D}_\lambda^{-1}\mathbf{A}, \tag{14}$$

$$\mathbf{B}_0 = \begin{pmatrix} b_{1x} & b_{2x} & b_{3x} \\ b_{1y} & b_{2y} & b_{3y} \\ \lambda\, b_{1z} & \lambda\, b_{2z} & \lambda\, b_{3z} \end{pmatrix} = \mathbf{D}_\lambda\mathbf{B}, \tag{15}$$

where we have introduced the matrix $\mathbf{D}_\lambda$, defined as

$$\mathbf{D}_\lambda = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \lambda \end{pmatrix}. \tag{16}$$

Obviously, since $\mathbf{B}$ is the matrix of the reciprocal lattice vectors of $\mathbf{A}$, the same relation holds between $\mathbf{B}^0$ and $\mathbf{A}^0$.

Equations (12) and (13) provide evidence that the internal energy E of the *aspherical* potential with the direct lattice generated by $\mathbf{A}$ is mapped exactly onto that of the *spherical* potential with the direct lattice generated by $\mathbf{A}_0$. Under the inverse transformation, the (spherical) neighbor shells of the lattice of the spherical potential are mapped onto ellipsoids,

$$x^2 + y^2 + \left(\frac{z}{\lambda}\right)^2 = \text{const.} \quad \text{and} \quad k_x^2 + k_y^2 + (k_z\lambda)^2 = \text{const.}, \tag{17}$$

for the direct and reciprocal lattices, respectively. Of course, these ellipsoids are not neighbor shells. However, the number of lattice points on each of the ellipsoids is the same as that on the neighbor shells of the spherical case.

We remark that, according to Eq. (14), the volume v_0 of the primitive cell of the spherical potential is related to v by $v_0 = v/\lambda$. Therefore, the density ρ_0 of the spherical potential is related to ρ via

$$\rho_0 = \frac{1}{v_0} = \frac{\lambda}{v} = \lambda\rho. \tag{18}$$

In the light of the above considerations, the ground state of the aspherical potential can be obtained straightforwardly, provided that of the spherical potential is known: the matrices $\mathbf{A}$ and $\mathbf{A}^0$ of the lattice vectors are related by Eq. (14), and the lattice constant is determined by Eq. (18). For instance, if the ground state of the spherical potential at ρ_0 is known to be a bcc crystal, then the edge of its conventional cubic cell must have a length ℓ_{bcc} such that

$$\ell_{\text{bcc}} = \left(\frac{2}{\rho_0}\right)^{1/3} = \left(\frac{2}{\lambda\rho}\right)^{1/3}, \tag{19}$$

and the energy of such a crystal is equal to that of the ground state of the aspherical potential at ρ. Similarly, if the ground state of the spherical potential is an fcc or sc crystal, one has

$$\ell_{\text{fcc}} = \left(\frac{4}{\rho_0}\right)^{1/3} = \left(\frac{4}{\lambda\rho}\right)^{1/3} \tag{20}$$

or

$$\ell_{\text{sc}} = \left(\frac{1}{\rho_0}\right)^{1/3} = \left(\frac{1}{\lambda\rho}\right)^{1/3}. \tag{21}$$

B. Occurrence of degeneracy

A straightforward implication of the above results is that for any ground state configuration of the aspherical potential at density ρ, there are actually *infinitely many* different Bravais lattices that have the same energy E. Let us say that one such lattice is determined by the primitive vector matrix $\mathbf{A}$. Then, as shown in Sec. III A, $\mathbf{A}_0 = \mathbf{D}_\lambda^{-1}\mathbf{A}$ [with $\mathbf{D}_\lambda$ given by Eq. (16)] is a primitive vector matrix of the lattice of the spherical potential at $\rho_0 = \lambda\rho$. Now, we rotate this lattice by multiplying $\mathbf{A}_0$ by an arbitrary rotation matrix $\mathbf{R}$ to obtain $\mathbf{A}_0' = \mathbf{R}\mathbf{A}_0 = \mathbf{R}\mathbf{D}_\lambda^{-1}\mathbf{A}$, where $\mathbf{R}$ is given, for instance, by the conventional parameterization in terms of Euler angles. Clearly, $\mathbf{A}_0$ and $\mathbf{A}_0'$ correspond to the same kind of Bravais lattice. Finally, we go back to the aspherical potential at ρ by multiplying $\mathbf{A}_0'$ by $\mathbf{D}_\lambda$ to obtain $\mathbf{A}' = \mathbf{D}_\lambda\mathbf{A}_0'$, i.e.,

$$\mathbf{A}' = \mathbf{D}_\lambda\mathbf{R}\mathbf{D}_\lambda^{-1}\mathbf{A} = \begin{pmatrix} r_{11} & r_{12} & \lambda^{-1}r_{13} \\ r_{21} & r_{22} & \lambda^{-1}r_{23} \\ \lambda\, r_{31} & \lambda\, r_{32} & r_{33} \end{pmatrix}\mathbf{A}, \tag{22}$$

where r_{ij}, $i, j = 1, 2, 3$, are the elements of $\mathbf{R}$.

By construction, the points of the lattices generated by $\mathbf{A}$ and $\mathbf{A}'$ lie on the same ellipsoidal shells, and the number of points on each shell is the same for both lattices. Equation (12) then shows that the internal energy is *exactly* the same. However, the two lattices will in general be different: their points, even though lying on the same ellipsoids, will have different distances from the center of the ellipsoids. Thus, we have an infinite number of lattices having the same energy E.

In reciprocal space, one obtains

$$\mathbf{B}' = \mathbf{D}_\lambda^{-1}\mathbf{R}\mathbf{D}_\lambda\mathbf{B} = \begin{pmatrix} r_{11} & r_{12} & \lambda\, r_{13} \\ r_{21} & r_{22} & \lambda\, r_{23} \\ \lambda^{-1}r_{31} & \lambda^{-1}r_{32} & r_{33} \end{pmatrix}\mathbf{B}, \tag{23}$$

where $\mathbf{B}$ and $\mathbf{B}'$ are, respectively, the original and the transformed matrix of the primitive vectors of the reciprocal lattice of the aspherical potential.

Figure 1 illustrates what stated above for a two-dimensional analog: the triangular lattice shown in Fig. 1(a) is rotated by 90°

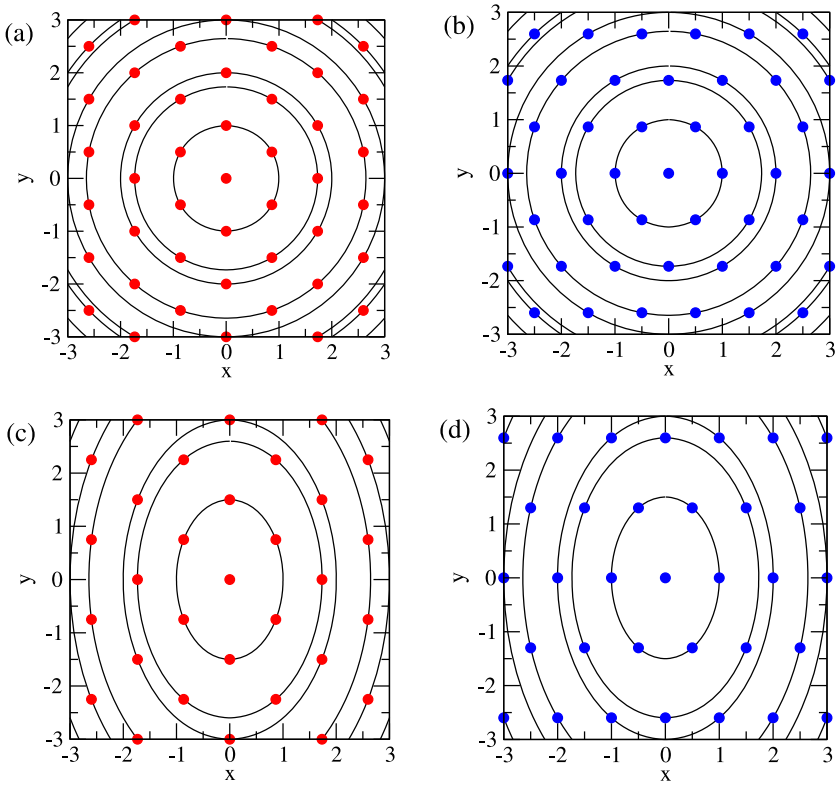

FIG. 1. The lattices of (c) and (d) are obtained by the same expansion along y of the triangular lattices shown in (a) and (b), respectively. While (a) and (b) display the same Bravais lattice, (c) and (d) do not.

to obtain the triangular lattice of Fig. 1(b). The two lattices actually correspond to the same crystal. Expanding these lattices along y by the same factor $\lambda = 1.5$ gives the two lattices shown in Figs 1(c) and 1(d), which have the same number of points on the same elliptic shells, but do *not* describe the same crystal: for instance, the lattice of Fig. 1(c) has four nearest neighbors and two next-nearest neighbors, whereas the lattice of Fig. 1(d) has two nearest neighbors and four next-nearest neighbors; still, the two lattices have the same energy.

In the following, it will be necessary to establish whether, given two lattices with primitive vectors identified by two matrices $\mathbf{A}$ and $\mathbf{A}'$, one can be obtained from the other by the transformation described above. While this is obviously so, if $\mathbf{A}$ and $\mathbf{A}'$ satisfy Eq. (22), the converse is not true, i.e., two matrices $\mathbf{A}$ and $\mathbf{A}'$ corresponding to degenerate lattices are not necessarily related by Eq. (22). The (trivial) reason is that the primitive vectors of a Bravais lattice are not uniquely determined. We then proceed to generalize Eq. (22). To this end, suppose that the matrices $\mathbf{C}$ and $\widetilde{\mathbf{C}}$ generate the same lattice. Then, for any vector $\mathbf{m}$, there must be some vector $\mathbf{n}$ such that

$$\mathbf{C}\cdot\mathbf{m} = \widetilde{\mathbf{C}}\cdot\mathbf{n} \tag{24}$$

and vice versa, where both $\mathbf{m}$ and $\mathbf{n}$ are vectors with integer components. This is equivalent to requiring that both $\mathbf{C}^{-1}\widetilde{\mathbf{C}}$ and its inverse must have integer elements, which in turn is equivalent to requiring that $\mathbf{C}^{-1}\widetilde{\mathbf{C}}$ must have integer elements, and its determinant satisfies the relation

$$\det(\mathbf{C}^{-1}\widetilde{\mathbf{C}}) = \frac{1}{\det(\mathbf{C}^{-1}\widetilde{\mathbf{C}})}, \tag{25}$$

i.e., $\det(\mathbf{C}^{-1}\widetilde{\mathbf{C}}) = \pm 1$. Hence, $\mathbf{C}$ and $\widetilde{\mathbf{C}}$ are related by

$$\widetilde{\mathbf{C}} = \mathbf{C}\mathbf{C}^{-1}\widetilde{\mathbf{C}} = \mathbf{C}\mathbf{L}, \tag{26}$$

where $\mathbf{L} = \mathbf{C}^{-1}\widetilde{\mathbf{C}}$ is a matrix with integer elements such that $\det\mathbf{L} = \pm 1$. Therefore, Eq. (22) can be generalized to

$$\mathbf{A}' = \mathbf{D}_\lambda\mathbf{R}\mathbf{D}_\lambda^{-1}\mathbf{A}\mathbf{L}, \tag{27}$$

that is,

$$\mathbf{L} = (\mathbf{D}_\lambda\mathbf{R}\mathbf{D}_\lambda^{-1}\mathbf{A})^{-1}\mathbf{A}' \tag{28}$$

for some rotation matrix $\mathbf{R}$. Equation (28) does not determine this rotation univocally because, for given $\mathbf{A}$, $\mathbf{A}'$, and λ, it contains two unknown matrices, namely, $\mathbf{R}$ itself and $\mathbf{L}$. However, whether it holds or not can be easily established numerically by spanning the whole group of rotation matrices and checking if for some of them the matrix $\mathbf{L}$ obtained by Eq. (28) satisfies the above-mentioned properties. Actually, in our case, one requires from the outset that the density of the lattices generated by $\mathbf{A}$ and $\mathbf{A}'$ be the same, so one has that $|\det\mathbf{A}| = |\det\mathbf{A}'|$. Equation (28) then shows that the condition $\det\mathbf{L} = \pm 1$ is already satisfied, and one has to check only that the elements of $\mathbf{L}$ are integers. Clearly, the matrices $\mathbf{A}'$ given by Eq. (27) for the same λ, $\mathbf{R}$, and $\mathbf{A}$ and different $\mathbf{L}$ generate the same lattice.

As a final remark, we observe that the considerations put forth in the present section can be straightforwardly generalized to aspherical potentials $\Psi(\mathbf{r})$ with ellipsoidal iso-surfaces of the form

$$\Psi(\mathbf{r}) = \varepsilon\psi\left(\frac{1}{\sigma_0}\sqrt{\left(\frac{x}{\nu}\right)^2 + \left(\frac{y}{\mu}\right)^2 + \left(\frac{z}{\lambda}\right)^2}\right) \tag{29}$$

so that the mapping onto a spherical potential and the ensuing degeneracy of the ground state holds also for generic ellipsoids.

C. Relation with previous investigations: Schiller *et al.*

The findings of Secs. III A and III B are closely related to the results described in Refs. 17 and 18 by Schiller, Krüger, Wahab, and Mögel (SKWM). While the present work is focused on soft spheroids, those papers were concerned with the crystal phases of hard-core spheroids with additional attractive or repulsive interactions, e.g., of dispersion, depletion, or electrostatic origin, which were evaluated in the Derjaguin approximation. When the size of the ellipsoids is much larger than the range of the forces, the interaction can be represented as a purely contact potential which depends on the Gaussian curvature of the ellipsoids at the point of contact[17] so that each particle interacts only with its first neighbors. SKWM studied the case in which the crystal consists of parallel ellipsoids, similar to the situation considered here, and found that "there exist families of lattices with geometrically different arrangements of the spheroids but the same lattice energy,"[18] including, but not limited to, close-packed configurations.

The source of this degeneracy was clearly identified in Ref. 18 and is the same as the rescaling–rotation–rescaling procedure described in Sec. III B: by a suitable rescaling of the axes, a crystal of parallel ellipsoids is mapped onto a crystal of spherical particles. In doing so, the number density is changed according to Eq. (18), but the packing fraction is conserved, since the volume of the particles and the volume of the primitive cell are rescaled by the same factor. Subsequently, the crystal is rotated and the rescaling is unfolded so as to end up with another crystal of ellipsoids; see Fig. 2 of Ref. 18 and Fig. 1 of the present paper. The structures generated in such a way can be classified according to the associated lattice of spherical particles onto which the original lattice is mapped.

However, the Gaussian model of this paper differs in two important respects from the system studied in Refs. 17 and 18: on the one hand, in the present case, the hard-core interaction between ellipsoids is replaced by a soft repulsion, whereby each particle does not interact only with its neighbors, but with all the other particles of the lattice. On the other hand, the potential considered by SKWM does not depend only on the center-to-center vector $\mathbf{r}$ because of the additional contact forces, which are absent in our case (indeed, they would make little physical sense for mutually penetrable particles).

As a consequence, the internal energy per particle that they obtain by mapping the spheroids onto spheres by means of the rescaling (14) is not necessarily invariant under rotation, inasmuch as it depends on the contact points of a sphere with its neighbors via the sum of the squares of their abscissae with respect to a system with its origin at the center of the sphere; see Eq. (9) of Ref. 18. Whether such a quantity is conserved by a rotation depends on the lattice in which the spheres are arranged: SKWM find that rotational invariance is fulfilled by lattices that have at least a threefold, a fourfold, or a sixfold rotation axis, whereas it is not fulfilled by lattices with a lower degree of symmetry, such as the orthorhombic, monoclinic, or triclinic lattices. Lattices of spheroids whose associated lattice of spherical particles belongs to the higher-symmetry class have by construction the same energy, even though their geometrical properties are generally different: in this case, the rescaling–rotation–rescaling procedure does lead to infinitely many degenerate structures. Instead, for associated lattices of the low-symmetry class, a rotation leads to a change in the internal energy so that the lattices of spheroids obtained by applying different rotations to the same associated lattice are not degenerate. Moreover, the degeneracy is removed also in the special case of associated lattices that have only one threefold, fourfold, or sixfold rotation axis, if the axis $\mathbf{u}$ of the spheroids is aligned along it. In this situation, the rotations around $\mathbf{u}$ are immaterial as they leave the lattice unchanged, whereas all the other rotations lead to a change in the internal energy.

In summary, for the crystals of hard, parallel spheroids studied by SKWM establishing whether the ground state is degenerate requires some knowledge of its structure, specifically concerning the associated lattice of spherical particles onto which it is mapped via the rescaling procedure. If the ground state corresponds to a configuration with a cubic associated lattice, the degeneracy is certainly present, but other instances are possible, in which the degeneracy would not occur.

In this respect, the system considered here is simpler, since the rescaling (14) maps the potential $\Phi(\mathbf{r})$ onto the spherically symmetric potential $\Phi_0(r)$ so that the internal energy per particle given by Eq. (12) is obviously invariant under rotation for any lattice. Therefore, the degeneracy is always present, whatever the lattice. The ground state of the aspherical Gaussian potential to be discussed in Sec. IV is obtained by deforming highly symmetric cubic structures, but the degeneracy would have been there irrespective of that, unlike in the case considered by SKWM.

IV. THE ASPHERICAL GAUSSIAN POTENTIAL

A. General remarks

On the basis of the considerations put forth above, the phase behavior of the aspherical Gaussian potential at $T = 0$ can be straightforwardly determined. As $\widetilde{\Phi}_0(k)$ is a Gaussian and, thus, positive for all k-vectors, this also holds for $\widetilde{\Phi}(\mathbf{k})$ by virtue of Eq. (7). Consequently, the potential at hand belongs, according to the classification of Ref. 19, to the class of Q^+ potentials: these systems crystallize in single-occupancy crystals, i.e., their occupancy number n is unity.

The phase diagram of the *spherical* Gaussian model has been studied in detail in Refs. 20–25. In the following, we will adopt standard reduced quantities by measuring lengths in units of σ_0 and energies in units of ϵ. These will be denoted by an asterisk, such as $T^* = k_B T/\epsilon$, $\rho^* = \rho\sigma_0^3$, etc. The system shows a (re-entrant) transition at low temperatures T: below a threshold temperature, the system freezes with increasing density ρ_0 either into an fcc lattice and then via a first-order transition into a bcc lattice or directly into a bcc; upon further increasing the density, the system melts again. Both types of lattices show single occupancy ($n = 1$), i.e., no cluster formation can be observed. Above the threshold temperature (i.e., above $T^* \simeq 0.01$), the system never freezes. At $T = 0$, the system forms a crystal at all densities, and the boundary between the fcc and bcc phases has been determined analytically,[21] the fcc being favored for $\rho_0^* < 1/\pi^{3/2}$ and the bcc for $\rho_0^* > 1/\pi^{3/2}$.

The ground state of the aspherical potential is then obtained by identifying the matrix $\mathbf{A}_0$ of the primitive vectors of the spherical potential with that of the bcc or fcc lattices $\mathbf{A}_{0,\mathrm{bcc}}$ or $\mathbf{A}_{0,\mathrm{fcc}}$ and deforming $\mathbf{A}_0$ according to Eq. (14). If one adopts the standard forms for $\mathbf{A}_{0,\mathrm{bcc}}$ and $\mathbf{A}_{0,\mathrm{fcc}}$, the expressions of the related matrices $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ are

$$\mathbf{A}_{\mathrm{bcc},\lambda} = \frac{\ell_{\mathrm{bcc}}}{2}\begin{pmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -\lambda & \lambda & \lambda \end{pmatrix} \tag{30}$$

and

$$\mathbf{A}_{\mathrm{fcc},\lambda} = \frac{\ell_{\mathrm{fcc}}}{2}\begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & \lambda & \lambda \end{pmatrix}, \tag{31}$$

where ℓ_{bcc} and ℓ_{fcc} are given by Eqs. (19) and (20), respectively. If the above condition for the occurrence of the bcc or fcc lattices is expressed in terms of density ρ of the aspherical model via Eq. (18), one obtains that the lattices generated by $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ are favored for $\rho^* > \rho_c^*(\lambda)$ and $\rho^* < \rho_c^*(\lambda)$, respectively, where the reduced transition density $\rho_c^*(\lambda)$ is given by

$$\rho_c^*(\lambda) = \frac{1}{\pi^{3/2}\lambda}. \tag{32}$$

Besides those deformed bcc and fcc lattices, on both sides of $\rho_c^*(\lambda)$ there are infinitely many degenerate lattices, which are obtained by applying to $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ the transformation (22) involving an arbitrary rotation matrix $\mathbf{R}$.

In order to ascertain the validity of this picture, we also minimized the internal energy per particle given by Eq. (11) with respect to the lattice vectors by an independent procedure, i.e., without relying on the mapping on the spherical potential described in Sec. III. The minimization was carried out numerically by a conjugate-gradient algorithm similar to that used in Ref. 26 for several values of λ and ρ, starting from different initial trial configurations. We, indeed, found that: (i) on convergence of the minimization run, the internal energy per particle is identical to that of the lattices identified by $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ for $\rho^* > \rho_c^*(\lambda)$ and $\rho^* < \rho_c^*(\lambda)$, respectively; (ii) depending on the initial configuration used to start the minimization, many different degenerate lattices are obtained; (iii) the matrices $\mathbf{A}'$ of the primitive vectors of these lattices are related to $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ by the transformation (27), i.e., some rotation matrix $\mathbf{R}$ could always be identified such that the matrix $\mathbf{L}$ given by Eq. (28) has integer elements.

This completes our description of the ground state of the aspherical Gaussian potential. In the following, we will discuss in the light of the present analysis the findings of the previous studies of the same system performed by PS[5] and NL.[12]

B. Relation with previous investigations: Prestipino and Saija

1. Ground state

The above conclusions can now be related to the results presented by PS in Ref. 5, where the aspherical Gaussian model considered here was first introduced. We point out that according to PS, the nematic direction $\mathbf{u}$ is identified with the z-axis as here and that in their notation, the asphericity parameter λ is equal to L/D, D and L being the transverse and longitudinal diameters of the particles.

PS surmised that the best candidates for the crystal phases of the model are obtained by deforming the cell of the most common cubic and hexagonal lattices along a given direction by a factor related to λ. This procedure is clearly described by NL in Ref. 12 for a cubic lattice as *"The stretching of the corresponding [*i.e., *bcc, fcc,* etc.*] cubic unit cell along some direction of high crystallographic symmetry by a factor λ in a volume-preserving fashion, and the orientation of the nematics along the stretched axis."* According to PS notation, the vector specifying the direction of stretching is identified by its coordinates along the axes of the conventional cell, and the stretching factor is denoted by α. So, for instance, bcc001(α) is the lattice obtained by deforming by a factor α the bcc lattice along one of the edges of the cubic cell, bcc110(α) is that obtained by deforming it along the diagonal of one of the faces of the cell, and so on.

We observe that in the 001(α) structure, the direction of deformation coincides with that of the nematic axis $\mathbf{u}$, so no rotation to align the two directions is needed. Therefore, the 001(α) lattices coincide with those generated by the matrix $\mathbf{A}$ in Eq. (14), provided α is identified with the asphericity parameter λ, and the non-stretched lattices with those generated by $\mathbf{A}_0$. In particular, the structures $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$, which according to the previous analysis yield the ground state of the model at high and low densities, respectively, correspond in PS notation to the bcc001(λ) and the fcc001(λ) lattices.

This agrees with the findings of PS. Specifically, they selected a number of different deformed cubic and hexagonal lattices and looked for the most stable among them for several values of λ between $\lambda = 1.1$ and $\lambda = 3$. Note that their calculations were performed at fixed pressure P rather than at fixed density so that the most stable structure corresponds to the minimum of the chemical potential μ. The minimum value of μ was always found to be given either by the bcc001(λ) or fcc001(λ), with a fcc-type to bcc-type transition on increasing the pressure. In their Table I, PS report the results obtained by minimizing with respect to α and ρ 11 different structures for $\lambda = 3$ and two different pressures, $P^* = 0.05$ and $P^* = 0.20$. According to Eq. (32), for this value of λ, the fcc–bcc transition density is $\rho_c^*(\lambda = 3) = 0.060$, and the transition pressure obtained by differentiating E/N with respect to $v = 1/\rho$ is found to be $P_c^*(\lambda = 3) = 0.018$, which is lower than both the values above. Hence, in both cases, we expect the bcc001(λ) lattice to prevail, in agreement with PS results. By minimizing μ with respect to ρ at fixed P for the bcc001(λ) via the relation $\mu = E/N + P/\rho$, we obtained $\mu^* = 0.855\,718$ and $\mu^* = 2.093\,693$ for $P^* = 0.05$ and $P^* = 0.20$, respectively, in very close agreement with PS results $\mu^* = 0.855\,724$ and $\mu^* = 2.093\,695$.

2. Degeneracy

Interestingly, PS also acknowledged the occurrence of degenerate structures. In fact, in their Table I, the bcc001(3), bcc110(3), bcc111(3), sc111(1.5), and fcc001($3/\sqrt{2}$) are all degenerate. The same is true for the sc001(3), sc110(3), and for the fcc110(3), fcc111(3), even though the last two groups do not correspond to the ground state. PS pointed out that *"an emergent aspect of this table is the existence of a rich degeneracy that is only partly a result of the effective identity of crystal structures up to a dilation"* and that *"points in these three lattices* [i.e., bcc001, bcc110, and bcc111] *have different local environments, as can be checked by counting the n*th *order neighbors for n up to 4, yet the three stretched crystals of minimum μ share*

the same U/N" (*E*/*N* in our notation). They also commented *"this fact is an emergent phenomenon whose deep reason remains unclear to us: it should deal with the dependence of u* (the potential Φ in our notation) *on the ratio r*/σ(ϑ), *since the same symmetry holds with a polynomial, rather than Gaussian, dependence."*

The origin of this degeneracy has been identified in Sec. III B. Moreover, we are in a position to explain not only why the degeneracy is there but also why it involves, in particular, the lattices found by PS, as we discuss in detail below.

Let us first consider the structures obtained by deforming the bcc lattice. As observed above, the bcc001(λ) lattice is just that of Eq. (30), which is obtained by identifying $\mathbf{A}_0$ with the matrix of the primitive vectors of the bcc lattice $\mathbf{A}_{0,\mathrm{bcc}}$ and deforming it along the nematic axis by a factor λ. In order to stretch the lattice vectors by a factor α along a generic direction specified by a unit vector $\mathbf{v}$ so as to obtain the bcc$v_xv_yv_z(\alpha)$ structure, one has to multiply by α their components along $\mathbf{v}$ and leave unchanged those orthogonal to $\mathbf{v}$. This amounts to applying to $\mathbf{A}_0$ the matrix $\mathbf{V}$ given by

$$\mathbf{V} = \begin{pmatrix} 1+(\alpha-1)v_x^2 & (\alpha-1)v_xv_y & (\alpha-1)v_xv_z \\ (\alpha-1)v_xv_y & 1+(\alpha-1)v_y^2 & (\alpha-1)v_yv_z \\ (\alpha-1)v_xv_z & (\alpha-1)v_yv_z & 1+(\alpha-1)v_z^2 \end{pmatrix} \tag{33}$$

and adjusting the lattice constant a in $\mathbf{A}_0$ so that at a given density ρ, one has $v_0 = \det \mathbf{A}_0 = 1/(\alpha\rho)$, as discussed in Sec. III A. Obviously, $\mathbf{V}$ is diagonalized by rotating the axis vectors $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ in such a way that one of them, say $\mathbf{e}_z$, is mapped onto $\mathbf{v}$, whereas $\mathbf{e}_x$ and $\mathbf{e}_y$ are mapped onto two orthogonal vectors $\mathbf{v}'$ and $\mathbf{v}''$ lying in the plane orthogonal to $\mathbf{v}$. We have then $\mathbf{D}_\alpha = \mathbf{R}_0\mathbf{V}\mathbf{R}_0^{-1}$, where $\mathbf{D}_\alpha$ is the diagonal matrix of Eq. (16) with λ replaced by α and $\mathbf{R}_0$ is the rotation matrix connecting the old and new axes such that

$$(\mathbf{e}_x|\mathbf{e}_y|\mathbf{e}_z) = (\mathbf{v}|\mathbf{v}'|\mathbf{v}'')\mathbf{R}_0. \tag{34}$$

If $\mathbf{v}$ does not coincide with $\mathbf{e}_z$, in which case of course $\mathbf{V}$ is already diagonal, $\mathbf{R}_0$ can be chosen as

$$\mathbf{R}_0 = \begin{pmatrix} \dfrac{v_y}{\sqrt{1-v_z^2}} & -\dfrac{v_x}{\sqrt{1-v_z^2}} & 0 \\ \dfrac{v_xv_z}{\sqrt{1-v_z^2}} & \dfrac{v_yv_z}{\sqrt{1-v_z^2}} & -\sqrt{1-v_z^2} \\ v_x & v_y & v_z \end{pmatrix}. \tag{35}$$

After stretching the lattice, thus obtaining the matrix $\mathbf{V}\mathbf{A}_0$ of the stretched lattice vectors, the above described PS recipe requires that the nematic axis be aligned with $\mathbf{v}$. In the present notation, the nematic axis coincides with $\mathbf{e}_z$, and this is aligned with $\mathbf{v}$ via the rotation (34). The matrix of the primitive vectors $\mathbf{A}_{\mathrm{PS}}$, which identifies the bcc$v_xv_yv_z(\alpha)$ lattice, is then

$$\mathbf{A}_{\mathrm{PS}} = \mathbf{R}_0\mathbf{V}\mathbf{A}_0 = \mathbf{R}_0\mathbf{R}_0^{-1}\mathbf{D}_\alpha\mathbf{R}_0\mathbf{A}_0 = \mathbf{D}_\alpha\mathbf{R}_0\mathbf{A}_0. \tag{36}$$

If $\mathbf{A}_0$ is expressed via Eq. (14) by the matrix $\mathbf{A}$ [whose explicit expression is $\mathbf{A}_{\mathrm{bcc},\lambda}$ of Eq. (30) for the specific case of the bcc lattice], one gets

$$\mathbf{A}_{\mathrm{PS}} = \mathbf{D}_\alpha\mathbf{R}_0\mathbf{D}_\lambda^{-1}\mathbf{A}. \tag{37}$$

For $\alpha = \lambda$, Eq. (37) is the same as Eq. (22) relating degenerate structures $\mathbf{A}$ and $\mathbf{A}'$ when the rotation matrix $\mathbf{R}$ is identified with $\mathbf{R}_0$. Therefore, the bcc001(λ), bcc110(λ), and bcc111(λ) are degenerate for arbitrary λ. By the same token, this is still true if $\mathbf{A}_0$ is the matrix of a generic Bravais lattice other than the bcc, irrespective of whether the corresponding matrix $\mathbf{A}_{\mathrm{PS}}$, obtained by setting $\alpha = \lambda$ in Eq. (36), corresponds to the ground state or not. So, for instance, the sc001(λ) and sc110(λ) are degenerate, as well as the fcc(110)(λ) and fcc(111)(λ), as pointed out above. Besides, it is not even necessary that $\mathbf{v}$ corresponds to some "special" direction of high symmetry such as those considered by PS: according to Eq. (22), *any* direction goes so that the degeneracy is actually infinite, as discussed in Sec. III B.

In addition, Table I in Ref. 5 shows that deforming the sc or fcc lattices can again give the ground state, even though in that case, the stretching factor α does not coincide with λ. As stated above, this happens for the sc111(1.5) and fcc001($3/\sqrt{2}$) lattices. Such an occurrence can also be explained by the present analysis.

The matrix $\mathbf{A}_{\mathrm{PS}}^{\mathrm{sc111}(\alpha)}$ of the sc111(α) lattice is obtained from Eq. (36) when $\mathbf{A}_0$ is chosen as the unit cell $\mathbf{A}_{0,\mathrm{sc}}$ of the sc lattice and $\mathbf{R}_0$ is the rotation matrix of Eq. (35) corresponding to the 111 direction, i.e., to $u_x = u_y = u_z = 1/\sqrt{3}$. This gives

$$\mathbf{A}_{\mathrm{PS}}^{\mathrm{sc111}(\alpha)} = \frac{\ell_{\mathrm{sc}}}{\sqrt{3}} \begin{pmatrix} \sqrt{\dfrac{3}{2}} & -\sqrt{\dfrac{3}{2}} & 0 \\ \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & -\sqrt{2} \\ \alpha & \alpha & \alpha \end{pmatrix}, \tag{38}$$

where the edge ℓ_{sc} of the cell is given by Eq. (21) with λ replaced by α. In order for this lattice to have the same energy as the bcc001(λ), a sufficient condition is that the matrix $\mathbf{A}_{\mathrm{PS}}^{\mathrm{sc111}(\alpha)}$ and the matrix $\mathbf{A}_{\mathrm{bcc},\lambda}$ given by Eq. (30) fulfill Eq. (22). Using the relation $\mathbf{A}_{0,\mathrm{bcc}} = \mathbf{D}_\lambda^{-1}\mathbf{A}_{\mathrm{bcc},\lambda}$, this amounts to requiring that there exists some rotation matrix $\mathbf{R}$ such that

$$\mathbf{A}_{\mathrm{PS}}^{\mathrm{sc111}(\alpha)} = \mathbf{D}_\lambda\mathbf{R}\mathbf{A}_{0,\mathrm{bcc}} \tag{39}$$

or, equivalently,

$$\mathbf{D}_\lambda^{-1}\mathbf{A}_{\mathrm{PS}}^{\mathrm{sc111}(\alpha)}\mathbf{A}_{0,\mathrm{bcc}}^{-1} = \mathbf{R}. \tag{40}$$

It is readily checked that for $\alpha = \lambda/2$, Eq. (40) does give a rotation matrix.

The fcc001(α) lattice is obtained from Eq. (36) by choosing $\mathbf{A}_0$ as the unit cell $\mathbf{A}_{0,\mathrm{fcc}}$ of the fcc lattice and $\mathbf{R}_0$ as the identity. One has then $\mathbf{A}_{\mathrm{PS}}^{\mathrm{fcc001}(\alpha)} = \mathbf{A}_{\mathrm{fcc},\alpha}$, where $\mathbf{A}_{\mathrm{fcc},\alpha}$ is the same as $\mathbf{A}_{\mathrm{fcc},\lambda}$ given by Eq. (31), provided λ is replaced by α.

Unlike $\mathbf{A}_{\mathrm{PS}}^{\mathrm{sc111}(\alpha)}$ with $\alpha = \lambda/2$, $\mathbf{A}_{\mathrm{fcc},\alpha}$ with $\alpha = \lambda/\sqrt{2}$ does *not* satisfy Eq. (40). However, it does satisfy its generalized form Eq. (28), i.e., it can be checked that for $\alpha = \lambda/\sqrt{2}$, there exists a rotation matrix $\mathbf{R}$ such that

$$(\mathbf{D}_\lambda\mathbf{R}\mathbf{A}_{0,\mathrm{bcc}})^{-1}\mathbf{A}_{\mathrm{fcc},\alpha} = \mathbf{L}, \tag{41}$$

where $\mathbf{L}$ is a matrix with integer elements.

It should be noted that, unlike in the case of structures obtained by deforming the same lattice along different directions such as the bcc001(λ), bcc110(λ), and bcc111(λ) discussed above, when comparing structures obtained by deforming different lattices, the direction of stretching $\mathbf{v}$ is, indeed, relevant to the degeneracy: not any direction goes. For instance, while the sc111($\lambda/2$) and the bcc001(λ) are degenerate, the sc001($\lambda/2$) and the bcc001(λ) are not.

In summary, our findings are fully consistent with those of PS at zero temperature: the lattices that correspond to the ground state

include those singled out by PS, which are then found to be degenerate. At the same time, the present analysis provides a rigorous proof of their results and shows that the degeneracy that they observed actually involves infinitely many structures and, as they correctly argued, is not peculiar to the Gaussian potential.

C. Relation with previous investigations: Nikoubashman and Likos

In Ref. 12, NL investigated the ground state of the aspherical Gaussian model using a genetic algorithm (GA) to minimize the internal energy [see Eq. (11)] at a fixed density with respect to the lattice vectors and the direction **u** of the nematic axis. The minimization was performed for densities in the interval $0 < \rho^* < 0.30$ and asphericity parameters λ in the interval $1 < \lambda < 3$. The main conclusions of their study are conveyed by the phase diagram in the (ρ, λ)-plane displayed in their Fig. 5(a) and can be summarized as follows:

(i) GA minimization yields configurations of lower internal energy than those considered by PS. Therefore, PS configurations do not correspond to the ground state. This is displayed in Figs. 4 and 14 of Ref. 12, where the difference between the internal energy per particle of PS bcc001(λ) and fcc001(λ) lattices and that obtained by the GA is plotted as a function of ρ for $\lambda = 1.08$ and $\lambda = 2.0$ and are, indeed, found to be always positive.

(ii) For every λ, a transition takes place which, in the limit $\lambda \to 1$, coincides with the aforementioned fcc–bcc transition of the spherical potential. The transition density $\rho_c(\lambda)$ is empirically found to be accurately represented by Eq. (32).

(iii) On each side of the $\rho_c(\lambda)$ curve, two distinct phases are present, which are identified by Roman numerals: phases I and III for $\rho < \rho_c(\lambda)$ and phases II and IV for $\rho > \rho_c(\lambda)$. The transition from phase I to phase III and that from phase II to phase IV take place on increasing λ, and in both cases, the values of λ corresponding to the transition are independent of ρ.

(iv) In addition, the bcc phase is found to survive in a small domain for $\rho > \rho_c(\lambda)$ and λ close to 1.

Clearly, point (i) contradicts the findings of the present study and as such must be tackled. The contradiction is all the more surprising, in the light of the fact that point (ii) is instead fully consistent with our analysis, which would in fact provide an explanation for it. In order to clarify this issue, we performed minimization of Eq. (11) for $\lambda = 1.08$ and $\lambda = 1.5$ in the interval $0 < \rho^* < 0.30$ using the GA code employed by NL. As observed above, the value $\lambda = 1.08$ is the same as that considered in Fig. 4 of Ref. 12. The results were compared with those obtained here for the lattices generated by the matrices $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ of Eqs. (30) and (31) for $\rho > \rho_c(\lambda)$ and $\rho < \rho_c(\lambda)$, respectively. We found that at very low density, $\rho^* \lesssim 0.015$, the two procedures gave the same energy within all the significant digits of the GA results. At larger density, the lattices corresponding to $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$ always gave the lower energy, but even in that case, the difference was found to be at most of the order of $\sim 10^{-8}$. This is of the same order of magnitude as the difference obtained for $\lambda = 1$, i.e., the spherical Gaussian potential, between the energy predicted by the GA and that of the bcc or fcc lattices, which are known to give the exact ground state in the spherical case. Therefore, we conclude that the lattice energies predicted by the GA are actually the same as those of the lattices generated by $\mathbf{A}_{\mathrm{bcc},\lambda}$ and $\mathbf{A}_{\mathrm{fcc},\lambda}$, and that the tiny discrepancy is due to small numerical errors of the GA, which are present also in the spherical case, possibly due to round-off. Since, as already discussed in Sec. IV B, these lattices coincide with PS bcc001(λ) and fcc001(λ) lattices, we must similarly conclude that NL energies are the same as those of PS bcc001(λ) or fcc001(λ). This conclusion cannot be reconciled with NL point (i), since the difference between the internal energy per particle of PS lattices and that of NL lattices plotted in their Figs. 4 and 14 is several order of magnitudes larger than the extremely small discrepancy reported above and cannot be traced back to numerical accuracy. Therefore, the only possible explanation left to us is that there must have been some error in the calculation of the internal energies of PS lattices as performed by NL, which prevented them from acknowledging that they actually coincide with those obtained by GA minimization.

If the configurations found by NL and those found here are, indeed, degenerate, then for our picture to be correct, NL lattices must be obtained from ours by the transformation described in Sec. III B. This means that the corresponding matrices have to be related by Eq. (28). In order to perform this check, a preliminary observation must be made: in the present analysis, the axes are chosen in such a way that the nematic direction **u** coincides with the z-axis; in NL calculation, they were instead chosen so that the direction of one of the primitive vectors coincides with the x-axis. Before feeding NL primitive vectors as given by their GA minimization into Eq. (28), we then have to express them on our basis by replacing the original matrix $\mathbf{A}_{\mathrm{NL}}$ of NL primitive vectors with $\mathbf{R}_{\mathrm{NL}}\mathbf{A}_{\mathrm{NL}}$, where $\mathbf{R}_{\mathrm{NL}}$ is the rotation that aligns NL z-axis with **u**. If α and β are the polar and azimuthal angles of **u** with respect to NL axes, $\mathbf{R}_{\mathrm{NL}}$ is given by

$$\mathbf{R}_{\mathrm{NL}} = \begin{pmatrix} \cos\alpha\cos\beta & \cos\alpha\sin\beta & -\sin\alpha \\ -\sin\beta & \cos\beta & 0 \\ \sin\alpha\cos\beta & \sin\alpha\sin\beta & \cos\alpha \end{pmatrix}. \tag{42}$$

Equation (28) then becomes

$$(\mathbf{D}_\lambda \mathbf{R} \mathbf{A}_{0,\mathrm{bcc}})^{-1} \mathbf{R}_{\mathrm{NL}} \mathbf{A}_{\mathrm{NL}} = \mathbf{L} \tag{43}$$

or the similar one with $\mathbf{A}_{0,\mathrm{bcc}}$ replaced by $\mathbf{A}_{0,\mathrm{fcc}}$ depending on whether one has $\rho > \rho_c(\lambda)$ or $\rho < \rho_c(\lambda)$, where $\mathbf{A}_{0,\mathrm{bcc}}$ and $\mathbf{A}_{0,\mathrm{fcc}}$ are as usual the standard matrices of the bcc and fcc lattices, in which the edge of the conventional cubic cell is given by Eqs. (19) and (20), and $\mathbf{A}_{\mathrm{NL}}$ and $\mathbf{R}_{\mathrm{NL}}$ are obtained from the output of the GA minimization.

We did verify that Eq. (43) is always fulfilled, i.e., it was always possible to find some rotation matrix **R** such that **L** would consist of integer elements. This provides compelling evidence that the lattices determined by NL conform to the general picture described in Sec. III B. We can now examine the above points (iii) and (iv) in the light of this conclusion.

As for point (iii), the implication is that phases I and III are necessarily degenerate so that there is not an actual transition between them: both phases are found in the whole region $\rho < \rho_c(\lambda)$, and besides them, infinitely many other degenerate phases exist. The same applies to phases II and IV for $\rho > \rho_c(\lambda)$. We surmise that, while GA always provides a genuine ground state of the system, nothing prevents it from "jumping" from a ground state to another as λ is

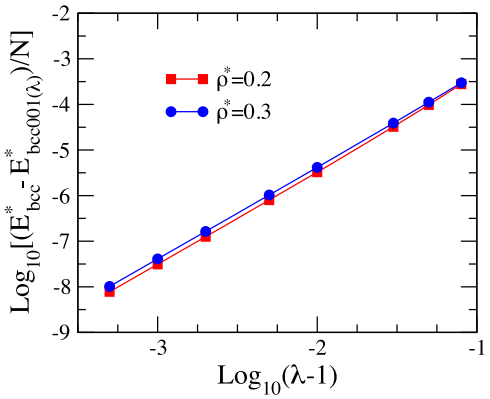

FIG. 2. Log–log plot of the difference between the internal energy per particle of the orientation-optimized bcc lattice and that of the bcc001(λ) lattice of the aspherical Gaussian model for λ close to 1 and $\rho^* = 0.2$ and $\rho^* = 0.3$.

changed. However, these jumps are just a consequence of the degeneracy and do not represent a true phase transition, whereby a state would become favored with respect to the other.

Point (iv) is also at odds with the present picture, according to which the bcc001(λ) must prevail over the non-deformed bcc lattice in the whole region $\rho > \rho_c(\lambda)$. This is, indeed, what happens, as displayed in Fig. 2, where the difference between the internal energy per particle of the bcc lattice optimized with respect to the direction **u** of the nematic axis and that of the bcc001(λ) lattice has been plotted as a function of λ for λ close to 1 at two densities, both of which should lie in the "pocket" of stability of the bcc according to NL. At variance with the NL result, the bcc001(λ) is always found to give the lower energy, even for very small degree of anisotropy. At the same time, the figure shows that in this limit, the energy difference becomes extremely small, and we deem it likely that it simply goes beyond the numerical accuracy of the GA, thereby leading to the incorrect identification of the bcc as the more stable structure.

We may then say that NL results need to be reconsidered in two respects: first, the lattices obtained by their GA-based approach do not have a lower energy than that of the lattices singled out by PS as the best candidates for the ground state: their energy is actually the same as that of PS lattices, and both NL and PS lattices represent true ground states of the model; second, the infinite degeneracy of those structures should be acknowledged. At the same time, the ability of GA minimization to converge on (one of) the lowest-energy structure(s) in a completely unbiased way is one more example of the predictive power of these algorithms.

V. CONCLUSIONS

We have studied the ordered configurations at vanishing temperature of a system of Gaussian core nematics (GCNs), where ellipsoids of revolution (spheroids) with the aspect ratio λ interact via a generalized Gaussian potential such that the directional unit vectors **u** of the particles are oriented in a mutually parallel manner. We showed that, by rescaling the lattice vectors along the direction of **u**, the crystal phases of this system of aspherical particles are mapped onto those of the system of spherical particles with $\lambda = 1$. In the mapping, the energy is conserved, whereas the densities of the systems of aspherical and spherical particles, ρ and ρ_0, are related via $\rho_0 = \lambda\rho$. Since the ordered configurations corresponding to the ground state of the Gaussian fluid of spherical particles are known exactly, this enables one to straightforwardly obtain the ground state of the GCNs.

Based on this mapping and the ensuing conclusions, we could furthermore demonstrate that the ordered configurations of the GCNs must be infinitely degenerate, i.e., there is an infinite number of Bravais lattices, characterized by the same energy. This multitude of configurations is obtained in the following manner: starting from a given Bravais lattice of the *aspherical* potential, one constructs the related Bravais lattice of the *spherical* potential by rescaling the lattice vectors; in a subsequent step, this lattice is rotated via an arbitrary rotation matrix, leading to a Bravais lattice of the same kind as the original one. Transforming these lattice vectors back leads to a new ordered phase of the aspherical particles. As all these steps preserve the internal energy, the resulting ordered phases must be infinitely degenerate. The mechanism leading to the degeneracy was in fact already pointed out by Schiller *et al.* in their investigations of the crystal phases of hard-core spheroids with contact interactions,[17,18] although its relevance to the GCNs has not, to our knowledge, been pointed out before.

With the help of these results, we could elucidate and fully explain the findings of two previous contributions dedicated to the GCNs by Prestipino and Saija (PS)[5] and Nikoubashman and Likos (NL).[12] In particular, we proved that the lattices corresponding to the ground state do include the configurations singled out by PS as their best candidates, explained the origin of the degeneracy that they observed, and showed that it must be actually infinite. Moreover, we could explain the occurrence of the phase transition found by NL on changing the density, as well as the dependence of the transition density on λ empirically found by them. Furthermore, by re-analyzing the data of these studies, we found that some alleged inconsistency between the ground state configurations identified in the two papers is actually not there: the energy of those configurations is rigorously the same, and all of them are obtained by rescaling according to the procedure outlined above either the fcc or the bcc lattice, which provide the ground state of the spherically symmetric Gaussian potential at low and high densities, respectively. The apparent discrepancy must be traced back to some glitch in the calculation of the energy of PS configurations as reported by NL, possibly due to issues of numerical accuracy.

The analysis developed here for ellipsoids of revolution can be straightforwardly extended to aspherical Gaussian particles whose shape is described by a generic ellipsoid, provided the orientation of the ellipsoids remains the same for all particles, as in the present model. Moreover, it is not peculiar to the Gaussian potential and could be equally well applied to different soft-core interactions, including the cluster-forming potentials of the so-called $Q^{\pm}$ class[19] such as the generalized exponential model of order four (GEM-4) considered in Ref. 16, even though the resulting phase diagram will of course be different from that described in this contribution.

The assumption that all particles share the same orientation from the outset is clearly a serious limit of the GCN model. Nevertheless, its phase behavior and the related degeneracy may still have some bearing on that of more realistic models, *if* nematic ordering

is, indeed, preferred in the crystal phases. In their aforementioned study of crystals of parallel hard-core spheroids,[17,18] Schiller *et al.* observed that the existence of an infinite number of different lattices with the same energy can be a source of disorder, hindering the formation of crystals with a specified structure, and their observation is equally relevant to the soft-core model considered here. At the same time, such a feature could also have interesting consequences on the vibrational, elastic, and optical properties of those systems.

A question that comes naturally is whether this infinite degeneracy may survive even at non-vanishing temperature T. For the GCNs, the simulation results obtained by PS[5] indicate that the degeneracy is lifted as soon as one has $T > 0$. However, it is possible that in this respect, the specific form of the interaction may play some role, as seems to be the case, for instance, for the aspherical GEM-4 particles of Ref. 16. We plan to come back to this issue in the near future.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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