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Cell theory for the phase diagram of hard spherocylinders

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Abstract A cell theory is proposed to obtain the full phase diagram of hard spherocylinders involving isotropic, nematic, smectic as well as plastic and aligned crystalline phases. Despite its conceptual and numerical simplicity this free-volume theory yields the correct topology of the phase diagram

in semi-quantitative agreement with recent computer simulations.

Key words Hard spherocylinders – phase transitions – cell theory

Hard spherocylinders with an orientational degree of freedom represent a standard model for liquid crystals [1] which has the advantage to be simple since the only parameters characterizing the system are the number density ρ and the aspect ratio $p = L/D$. Here, L is the length of the cylindrical part and D is the sphere and cylinder diameter. The density can suitably be scaled by the closed packed density ρ_{CP} leading to the dimensionless quantity $\rho^* = \rho/\rho_{CP}$, $0 \leq \rho^* \leq 1$. A further advantage is that, for $p = 0$, the well-known system of (isotropic) spheres is recovered and that the opposite limit $p \rightarrow \infty$ leads to the analytical Onsager solution for the isotropic-nematic transition. Recently, the full phase diagram in the whole parameter space spanned by ρ^* and p was obtained by computer simulation [2]; parts of it were known from former work [3, 4]. The resulting phase diagram has a pretty rich topology involving isotropic, nematic, smectic and plastic crystalline phases as well as aligned crystals with different stacking sequences.

The aim of this paper is to propose a cell theory for the full phase diagram of hard spherocylinders. This theory is similar in spirit to the free-volume approach of ref. [5] where a system of completely aligned spherocylinders was studied. However, as an essential part of our theory, we also incorporate the orientational degrees of freedom by assuming an effective shape of the particles gained from an orientational average. Our theory gives, for the first time,

a stable plastic crystal (rotator solid) and an AAA-stacked solid whose stabilities were not investigated in previous density functional calculations [6]. It has the further advantage of being conceptionally and numerically simpler than sophisticated and basically uncontrolled density functional approximations. Surprisingly, our cell approach gives the correct topology of the phase diagram in semi-quantitative agreement with the simulation data [2].

Let us now briefly describe our theory. In order to locate phase coexistence we have to know the Helmholtz free energy f per particle in any phase which is under consideration. For the *isotropic* (fluid) phase we use the well-known analytical expression of scaled particle theory [7]. In the remaining phases we approximately split the system into cells containing one particle. The cell size is chosen in such a way that the particles do not feel the interaction with their neighbours. In this case, the total free energy f splits naturally into a part f_{rot} stemming from the orientational degrees of freedom and another part f_{cm} resulting from the motion of the centre-of-mass coordinate: $f = f_{rot} + f_{cm}$.

Calculating f_{rot} we consider the angular distribution function $g(\omega)$ which is rotational symmetric around a fixed director ω_0 . Here, ω and ω_0 are unit vectors. Particularly, we use a Maier–Saupe form for $g(\omega)$, i.e., $g(\omega) = (1/\mathcal{N}) \exp[\alpha P_2(\omega \cdot \omega_0)]$, where $P_2(x) = (3x^2 - 1)/2$ is the

second Legendre polynomial, \mathcal{N} is to guarantee correct normalization $\int f(\omega) d^2\omega = 1$ and α is a variational parameter which is yet to be determined. Then the rotational free energy per particle reads $f_{\text{rot}} = \int d^2\omega g(\omega) \ln[g(\omega)]$.

The key idea for calculating f_{cm} is to map the system onto *completely oriented* particles with an *effective shape* which in general differs from the original spherocylindric shape. This effective shape should depend on the angular distribution function $g(\omega)$ in order to take orientational correlations between nearest neighbours roughly into account. We then estimate the centre-of-mass part f_{cm} by assuming a cell model for the solid part and a scaled-particle approach for the fluid part of the different phases [5] in this substitute system. Finally, the choice of effective shape is optimized by choosing the variational parameter α such that the total free energy f becomes minimal with respect to α .

Let us now describe the mapping in more detail. We define a mean distance \bar{R} by averaging over the orientational distribution function g as

$$\bar{R}(\theta, [f]) = D/2 + L/2 \int d^2\omega' g(\omega') |\omega \cdot \omega'|. \quad (1)$$

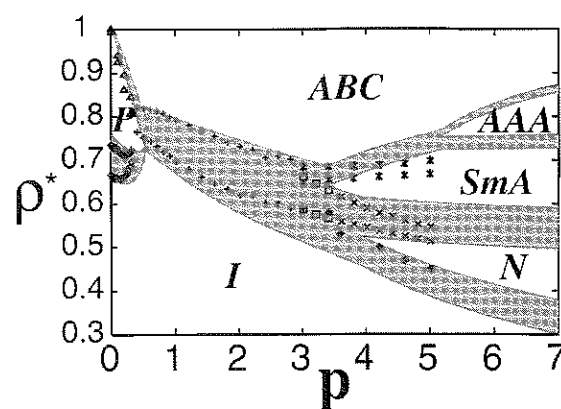
Clearly, \bar{R} is a functional of g and only depends on the angle θ defined via $\cos\theta = \omega_0 \cdot \omega$. The actual effective shape is now obtained as a Legendre transform of \bar{R} with respect to θ . Equivalently, the effective shape is the envelope of all planes which have a distance $\bar{R}(\theta, [f])$ from the centre-of-mass of the spherocylinder and whose normal forms an angle θ with the director ω_0 . It is instructive to consider two special cases: For fully aligned spherocylinders, we have $g(\omega) = \delta(\omega - \omega_0)$ and the effective shape coincides with the original spherocylindric shape. Second, for an isotropic distribution $g(\omega) = 1/4\pi$, we get $\bar{R} = D/2 + L/4 = \text{const}$. The Legendre transform is again a sphere of the same radius $R_{\text{mean}} = D/2 + L/4$ and the resulting effective shape is a sphere of radius R_{mean} . Note that – by construction – this is the *mean radius* R_{mean} of the spherocylinder which is obviously smaller than its *maximal* radius, $R_{\text{max}} = D/2 + L/2$. Therefore, the volume corresponding to the effective shape is in general smaller than $4\pi R_{\text{max}}^3/3$ as resulting from a fully rotated spherocylinder, hence taking roughly orientation correlation effects between nearest neighbour into account.

We finally propose a variational principle for the free energy. In the original version of the cell model [8], the free energy per particle is bounded from above by $-k_B T \ln(V_{\text{cell}})$ where V_{cell} is the free cell volume in suitable units. Hence, the best upper bound is achieved by maximizing V_{cell} within the given constraints of fixed average density and geometry [9]. Of course, since we invoke scaled particle approximations and work with an ef-

fective shape, our results are no longer true upper bounds to the exact free energy. As a further approximation, we carry over the variational principle in order to optimize the actual free energy values in the different phases.

Let us now describe the theoretical treatment of the different phases in more detail. The *plastic crystal* is a rotator solid with positional but without orientational order. In this case, the distribution function $g(\omega)$ is constant. As we demonstrated above, the effective system consists of spheres of radius R_{mean} and the cell theory reduces to that of spheres. The *aligned solid with ABC stacking* has both positional and orientational order, exhibiting a distorted fcc-structure. The free-volume cell is estimated to be a rhombic dodecahedron corresponding to an undistorted fcc hard sphere crystal. In the *aligned solid with AAA stacking*, on the other hand, the free-volume cell is a hexagonal prism. In the *smectic-A phase* the free energy splits into a contribution of a one-dimensional cell model for a rod of length $2\bar{R}(\theta = 0, [g])$ and the scaled particle contribution of a two-dimensional liquid of hard discs with diameter $2\bar{R}(\theta = \pi/2, [g])$. Note that the total free energy is then minimized with respect to the layer spacing and the orientation distribution. Finally, the scaled particle free energy of parallel hard spherocylinders [10] of diameter $D_n^* = 2\bar{R}(\theta = \pi/2, [g])$ and length $L_n^* = 2\bar{R}(\theta = 0, [f]) - D_n^*$ is used to calculate f_{cm} of the *nematic phase*. In order to compensate lack of configuration space in the cell approach we add a constant of $-1.8k_B T$ to

Fig. 1 Phase diagram of hard spherocylinders in the $(p-p^*)$ -plane. The shaded area is the coexistence region calculated within our theory and the dots are the simulation data [2]. There is an aligned ABC-solid, an aligned AAA-solid, a plastic crystal (P), an isotropic fluid (I) and a nematic (N) and smectic-A (SmA) phase. The meaning of the symbols for the simulation data are: (+) I-ABC transition, (\circ) I-P transition, (\square) I-SmA transition, (\blacklozenge) I-N transition, (\times) N-SmA transition, (\ast) SmA-ABC transition, (\blacktriangle) P-ABC transition



f_{cm} in the plastic crystal and in the aligned solids and consistently a third of this constant in the smectic-A phase. A second constant of $-2.25k_B T$ is added in the nematic phase. These two constants can be regarded as fitting parameters.

The results for the phase diagram are shown in Fig. 1 in the range of $0 \leq p \leq 7$ and compared against the simulation data [2]. The theory predicts correctly

all the stabilities of the different phases, exhibits all qualitative trends and is in semiquantitative agreement with the exact data although the density jumps are overestimated.

We are at present calculating the phase diagram of spherocylinders in an external field coupling to the orientational degrees of freedom. Here, we obtained critical points between phases of same geometry.

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