Free energy of a system of hard spherocylinders serving as a simple model for liquid crystals*

Robert L. Coldwell

*Department of Physics, Northwestern University, Evanston, Illinois 60201
and Department of Physics, University of Florida, Gainesville, Florida 32611* [†]

Thomas P. Henry

Engineering Sciences Department, Northwestern University, Evanston, Illinois 60201

Chia-Wei Woo

*Department of Physics, Northwestern University, Evanston, Illinois 60201
and Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

The free energy for a system of hard spherocylinders with midpoints constrained to random motion in a plane, serving as a zeroth-order approximation to one layer of a smectic liquid crystal or a two-dimensional nematic liquid crystal, has been calculated for spherocylinders with a length-to-width ratio of 5. For ρ, the number density measured in fractions of close-packed density, less than 0.22, the partition function itself is evaluated by means of a Monte Carlo scheme employing 22 500 mesh points and 82 possible angles for 25 particles with periodic boundary conditions. For all ρ the liquid-crystal free energy is calculated by minimizing a function of the hard-disk free energy plus the orientational free energy of a "liquid crystal." The low-density Monte Carlo free energy is found to lie below the liquid-crystal free energy, but can be extrapolated to cross it at $\rho = 0.23 \pm 0.01$. Maxwell construction yields a phase-change region for $0.19 \pm 0.01 < \rho < 0.29 \pm 0.01$. A spline polynominal fit to the entire free energy, which interpolates across the phase-change region, does not give strictly constant pressure, but does imply a phase-change region of $0.20 \pm 0.01 < \rho < 0.30 \pm 0.01$ with $PA'/NkT = 1.38 \pm 0.03$, A' being the cross-sectional area of a close-packed system of N rods.

I. DESCRIPTION OF THE MODEL SYSTEM

The model system consists of hard spherocylinders: rods with hemispherical ends. Their centers of mass are constrained to a plane. The rods are free to move in the two dimensions of the plane, and to point in any direction. The only interaction $u(r_{ij})$ between a pair of rods i and j is an infinite repulsion when they overlap, so that the Boltzmann factor $\exp[-\sum_{i<j} u(r_{ij})/kT]$ is either 0 or 1 independent of the temperature T, making the partition function and hence the free energy a function of the density alone. Since there is no attractive part to the potential, one would not expect to find a distinction between a gas and a liquid phase. However, as the density slowly increases from zero towards close packing, it is obvious that the rods must align in order to reach some of the higher densities. For this reason one suspects that a phase change should occur in which the rods switch from random orientation to alignment in a direction normal to the plane. If one continues to increase the density beyond this point, one would also expect the centers of the rods to fall into a hexagonal crystalline arrangement of more or less long range such as has been found in the hard-disk system.[1]

In this work we concentrate on the orientational or "liquid-crystal" phase change. The rods are first assumed to be extremely stubby, with a length-to-width ratio of 2. No evidence is found in this case for a liquid-crystal phase change. They are then lengthened to a ratio of 5, which gives rise to the results reported here. The two ends of each rod are assumed distinguishable.

In the low-density region the partition function is calculated directly by a minor extension of a method already used for calculating the free energy of a hard-disk system.[2] The two-dimensional integrations are carried out using 22 500 mesh points and midpoint trapezoidal-rule integration, which for the densities considered is far more than enough to remove the need for extrapolating to an infinitely fine mesh. The angular integration is done by dividing the sphere about each particle into 82 equal-area regions and again using midpoint trapezoidal-rule integration. This method fails at about 22% close-packed density, $\rho = 0.22$, where with an orientational order parameter of 0.97 the solid angle associated with pointing straight up, $4\pi/82$, becomes large in proportion to the solid angle actually available for each particle in the emerging liquid crystal.

At higher densities advantage can be taken of the orientational ordering of the system. A fictitious correlation length r_c is introduced which repre-

sents the closest possible approach of a second
particle and also implies the solid angle available
to the first particle. It turns out that the smaller
r_c is, the larger the two-dimensional contribution
to Q becomes, and the smaller the angular contri-
bution becomes. This means that it is possible to
maximize the partition function, or equivalently
minimize the free energy, with respect to r_c to
yield a good estimate for the true free energy in
the high-density region.

II. LOW-DENSITY FLUID REGION

The partition function is given by

$$Z(N, A) = \frac{1}{N!} \int_A \cdots \int_A \int_{4\pi} \cdots$$
$$\times \int_{4\pi} d^2 r_1 \cdots d^2 r_N \, d\Omega_1 \cdots d\Omega_N \, e^{-U(\vec{r}, \vec{\Omega})}$$

$$(1)$$

with

$$U(\vec{r}, \vec{\Omega}) \equiv \sum_{i<j} u(r_{ij})/kT,$$

where $\vec{r} = (\vec{r}_1, ..., \vec{r}_N)$ and $\vec{\Omega} = (\Omega_1, ..., \Omega_N)$. Clearly
$U = 0$ if no two rods overlap, and $U = \infty$ if any two
rods overlap. A denotes the area available to the
system. The integral in Eq. (1) can be evaluated
with a midpoint trapezoidal rule using N_r mesh
points in the two-dimensional plane and N_Ω in the
angular part so that

$$Z(N, A) \cong \frac{1}{N!} \left(\frac{A}{N_r} \right)^N \left(\frac{4\pi}{N} \right)^N$$
$$\times \sum_{r_1=1}^{N_r} \cdots \sum_{r_N=1}^{N_r} \sum_{\Omega_1=1}^{N_\Omega} \cdots \sum_{\Omega_N=1}^{N_\Omega} e^{-U(\vec{r}, \vec{\Omega})}, \quad (2)$$

where $\vec{r}$ and $\vec{\Omega}$ are constrained to the mesh of trap-
ezoidal-rule points in the expression for Z. The
sum can now be evaluated by a Monte Carlo meth-
od previously used for the hard-disk system.[2]
A value for $\vec{r}_1$ is first chosen randomly from the
set E_1 of N_r possible values. Those values which
would obviously result in two rods overlapping are
next removed from the set E_1 to form the set E_2
from which $\vec{r}_2$ is randomly chosen. Similarly,
points are then removed from E_2 to form the set
E_3, and so on. With all of the $\vec{r}_i$'s determined, Ω_1
for the first rod is now chosen from the set $F_1 = N_\Omega$.
The second rod may conceivably intersect the
first if it is allowed to take on any arbitrary orien-
tation. So certain angles are removed from the
set F_1 to form the set F_2 from which Ω_2 is chosen.
A similar procedure is used to form the set F_3 for
picking Ω_3, and so on until all Ω_i have been chosen.
The final result of all of this is hopefully a single
configuration in which $\vec{r}$ and $\vec{\Omega}$ are such that $U = 0$.

The number of possible choices in the sets
$E_1, ..., E_N, F_1, ..., F_n$ gives the probability ω_t of hav-
ing chosen t out of all available configurations. The
method for using this information exactly parallels
that discussed in more detail in the earlier paper.[2]

The probability w_t of having made a definite
choice of $(\vec{r}, \vec{\Omega})$ *in the specified order* in a given
trial is given by

$$w_t = \prod_{i=1}^{N} \frac{1}{|E_i|} \prod_{j=1}^{N} \frac{1}{|F_j|}. \quad (3)$$

The probability $P(w_t) \, dw_t$ of observing in a given
trial a finite value w_t in the range dw_t is given by
$w_t n(w_t) \, dw_t$, where $n(w_t) dw_t$ denotes the number of
ordered sets $(\vec{r}, \vec{\Omega})$ which give rise to values of w_t
in the range dw_t. Thus we have $n(w) \, dw =$
$P(w)(1/w) \, dw$. The total number of ways of putting
$(\vec{r}, \vec{\Omega})$ onto the trapezoidal-rule sites leaving $U = 0$
is

$$n = \int n(w) \, dw = \int \frac{P(w)}{w} \, dw = \left\langle \frac{1}{w} \right\rangle = \lim_{N_t \to \infty} \sum_{t=1}^{N_t} \frac{1}{w_t}. \quad (4)$$

Therefore, from Eq. (2),

$$Z(N, A) = \frac{1}{N!} \left(\frac{A}{N_r} \right)^N \left(\frac{4\pi}{N_\Omega} \right)^N \left\langle \frac{1}{w} \right\rangle. \quad (5)$$

It should be noted that the average comes from
taking the observed probability $P(w_t)$ over the cal-
culated probability w_t. This gives rise to the
number of ways of arranging $(\vec{r}, \vec{\Omega})$ which must ex-
ist to account for our having observed these calcu-
lated probabilities as often as we did. It is worth
noting at this point that the function $\exp[-U(\vec{r}, \vec{\Omega})]$
is rather unique in that it is unity for every al-
lowed configuration. For a function f which is not
always unity, e.g., $(\sum_i \cos^2 \theta_i) \exp[-U(\vec{r}, \vec{\Omega})]$,
something which we shall need later for calculating
the orientational order parameter of the system,
it is necessary to include the value of f in $n(f, w)$
so that the probability $P(f_t, w_t) \, df_t \, dw_t$ in the range
$dw_t \, df_t$ becomes $w_t n(f_t, w_t) \, dw_t \, df_t$. The expecta-
tion value of f is then

$$\langle f \rangle = \frac{\int n(f, w) f \, df \, dw}{\int n(f, w) \, df \, dw} = \frac{\int [P(f, w)/w] f \, df \, dw}{\int [P(f, w)/w] \, df \, dw}$$
$$= \lim_{N_t \to \infty} \sum_{t=1}^{N_t} \frac{f_t}{w_t} \Big/ \lim_{N_t \to \infty} \sum_{t=1}^{N_t} \frac{1}{w_t}. \quad (6)$$

$P(w_t)$ is frequently zero for a given trial, since
it may happen that after choosing the first I $\vec{r}_i$'s
(or Ω_i's), the set E_{I+1} (or F_{I+1}) from which $\vec{r}_{I+1}$
(or Ω_{I+1}) is to be chosen becomes the null set.
Conceptually this causes no problem since $w_t \to \infty$
and $1/w_t \to 0$, leaving the above relations, which
are exact, correct as they stand. Practically and

numerically it leads to difficulties because at suf-
ficiently high densities it is almost always the case
that $1/w_t$ vanishes unless the selection method is
a little more biased than the completely honest one
described above.

The whole purpose of constructing the sets E_i
and F_i is to avoid making choices in which the rods
are certain to overlap. The same argument can
now be extended to restrict E_i and F_i even further
to reduce the possibility of choosing configurations
with vanishing $1/w_t$. There is a tradeoff: smaller
E_i's give rise to larger w_t's and hence to smaller
estimates of $n(w_t) = 1/w_t$, but they also lead to
fewer zeros and therefore better statistics. In
principle of course the average of a host of such
small numbers should be the same as the average
of one large number and a host of zeros. In prac-
tice, however, we have a problem. While the num-
ber of trials is on the order of a few hundred, the
variations in $1/w_t$ are on the order of 10^5. In the
hard-disk paper this was treated by establishing
orthogonal ways of choosing $\bar{r}$ and then summing
over these ways. However, even there it was
found better to compromise by accepting a small
number of large $1/w_t$'s than to try to go strictly
along the orthogonal choice route.[2] Here a more
cavalier attitude has been adopted, which is that
of making one category account for *almost* every-
thing. Restrictions are used so that the E_i's and
F_i's are small enough to allow an acceptable num-
ber of nonzero $1/w_t$'s to be encountered in each
set of trial runs conducted under a different re-
striction. Obviously some acceptable $(\bar{r}, \vec{\Omega})$ are
missed in any given set of runs, which means that
the $n(w_t)$ calculated within the Monte Carlo error
will result in a lower bound to the true $n(w_t)$. That
restriction which leads to the largest value of $n(w_t)$
will therefore yield a lower bound on $Z(N, A)$.

Two types of restrictions are imposed, one in
the plane and the other on the solid angles. The
restriction in the plane consists of introducing a
core of radius r_c greater than twice the radius of
the rods and requiring that no two $\bar{r}_i$'s are chosen
within a distance less than r_c. For each value of
r_c employed, the angular restrictions are deter-
mined after all the $\bar{r}_i$'s have been picked. The
closest pair of rods are first identified. If one of
the pair is permitted to take on *any* direction Ω_1,
it may become nearly impossible to find a direc-
tion Ω_2 for the other rod. Thus one of the two rods
must have its direction restricted to some finite
range of solid angles. Next, a third rod closest to
the pair is identified. A similar consideration for
Ω_3 results in the restriction of the *second* of the
pair to some finite range of solid angles. But since
its distance to the third rod is larger than the dis-
tance between the original pair, the restriction

need not be as stringent. This procedure continues
until either all N rods are accounted for, or when
an overlap becomes unavoidable. The former
gives us a success, the latter a failure. It is to
the credit of this procedure that a reasonable suc-
cess rate, like 5 out of 100, can be collected to
give rise to sets of $(\bar{r}, \vec{\Omega})$ with $U(\bar{r}, \vec{\Omega}) = 0$.

The successes give us lower bounds on $Z(N, A)$.
Among several hundred trials run with a typical
value of r_c and a typical set of rules for restrict-
ing angular directions, the highest estimates on Z
range from say e^{235} to e^{238}. Since what we want is
the Helmholtz free energy F which goes as
$-kT \ln Z$, such a range of Z represents an uncer-
tainty of just 1–2% in F. But in calculating the ori-
entational order parameter, i.e., the mean value
of $\cos^2 \theta$, no logarithm is taken. The $\cos^2 \theta$ which
corresponds to the largest weight $1/w_t$ will domi-
nate the averaging process [see Eq. (6)], causing
the result to emerge from a single trial. This
statistical deficiency can be circumvented by as-
signing the same weight to the five or so top values
of $1/w_t$, the rationale being that values of $1/w_t$
close to its peak value represent the same type of
$(\bar{r}, \vec{\Omega})$ to within the coarse accuracy needed for de-
termining the order parameter.

After the above has been carried out at one cho-
sen value of r_c, a new r_c is picked and the process
repeated. By varying r_c over a wide range of rea-
sonable values, an optimum value will emerge to
give us a maximum among the lower bounds. *That*
we identify as $Z(N, A)$.

This all works quite well as ρ increases from 0
to about 0.22, at which the order parameter

$$\sigma \equiv \langle \tfrac{1}{2}(3 \cos^2 \theta - 1) \rangle \qquad (7)$$

reaches 0.97. Beyond 0.22, the rods are practi-
cally all aligned vertically. The solid angle of
$4\pi/41$ ($4\pi/82$ up and $4\pi/82$ down) assigned to the
vertical direction by our coarse grid becomes
larger than the solid angle available to each rod,
which now finds itself in close proximity with many
others. $Z(N, A)$ calculated in the fashion described
in this section becomes overestimated. It now
equals the hard-disk result plus a constant from
the angular integration. This gives us a clue as to
how to proceed to still higher densities in which
the rods can be assumed to be upright in a "liquid-
crystal" ordering.

III. LIQUID-CRYSTAL REGION

The restrictions of the preceding section are
illustrated in Fig. 1. The restriction in the plane
first results in no two rods being closer than r_c,
as is shown. Rods 1 and 2 are placed with angular
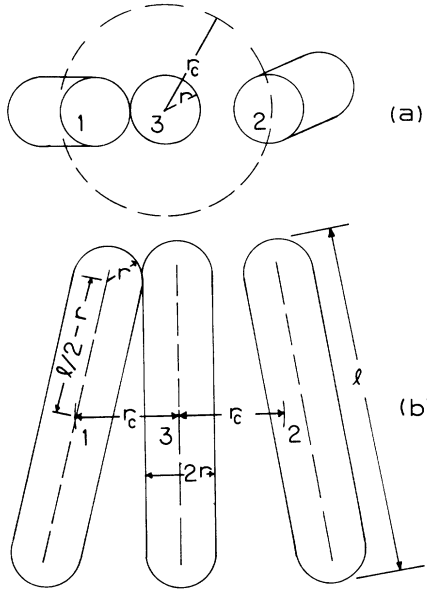restrictions such as to guarantee that rod 3 could

FIG. 1. A typical view of a section of the system about rod 3 in which the rods are shown to scale and r_c is illustrated. (a) View looking down on the plane; (b) side view seen in a direction along the plane.

be introduced in *some* direction. There is one and only one truly sweeping way to guarantee that rod 3 will be able to squeeze in, given the presence of all the other rods, namely to restrict the polar angles θ_i to values less than

$$\theta_m = \sin^{-1}\left(\frac{r_c - 2r}{\frac{1}{2}l - r}\right),\tag{8}$$

where r denotes the radius of the rods and l their length. Under this condition, rod 3 will always find it possible to be introduced into the configuration, at least vertically, no matter how the other rods are oriented. Such a restriction makes every trial a success. While it is too stringent for the gaseous phase because the rods can actually flop around a lot more there, it is a realistic condition to employ in the liquid-crystalline phase since the rods are essentially vertically oriented anyway. The error brought upon by such a restriction is small.

The partition function is then given by

$$Z(N, A) \gtrsim \int \exp\left(-\sum_{i<j} \overline{u}(r_{ij})\right) d^2 r_1 \ldots d^2 r_N \left(\int_{\theta_m} d\Omega\right)^N,\tag{9}$$

with

$$\overline{u}(r) = \begin{cases} 0, & r > r_c, \\ \infty, & r \le r_c. \end{cases}\tag{10}$$

The multidimensional integral is dependent upon r_c. Its maximum occurs at the r_c which manages

the best trade-off between freedom in the plane and in the orientation. It has the same form as the integral that appears in the hard-disk problem. Fortunately, the latter has been evaluated by Hoover and Ree[3] (HR) over a range of densities ρ_e. Since ρ_e for present use is proportional to Nr_c^2/A, and our actual density ρ is proportional to $N(2r)^2/A$, HR's results can be taken over through the relation

$$\rho_e/\rho = r_c^2 /(2r)^2 .\tag{11}$$

A spline fitted to these results reproduces the original table of numbers to within their accuracy for densities below 0.75. And since the highest density considered in this paper is 0.55, which at the optimum r_c corresponds to $\rho_e = 0.672$, the hard-disk data obtained by HR are quite sufficient and no new calculation is required.

The angular integration is straightforward. It is given by

$$\Omega_m \equiv \int_{\theta_m} d\Omega = 2\pi \times 2 \int_0^{\theta_m} \sin\theta \, d\theta$$

$$= 4\pi \left\{1 - \left[1 - \left(\frac{r_c - 2r}{\frac{1}{2}l - r}\right)^2\right]^{1/2}\right\}$$

$$= 4\pi \left\{1 - \left[1 - 4\left(\frac{(\rho_e/\rho)^{1/2} - 1}{l/2r - 1}\right)^2\right]^{1/2}\right\} .$$

$$\tag{12}$$

The factor of 2 comes from the fact that the two ends of each rod are assumed distinguishable.

A few words can be said about the probable error in Z in this region. Let us pick the rods in the sequence $1, 2, \ldots, i, i+1, \ldots, N$. Let Ω_i be the *actual* value (in contrast to the *approximate* value Ω_m) of $\int d\Omega$ for the ith rod and let Z_Ω be the part of Z coming from the angular integrations. We should have

$$\ln(Z_\Omega) = \sum_{i=1}^{N} \ln(\Omega_i) .$$

For small i there are few rods present in the system so that given θ_m there is little error in Ω_i. For i approaching N, however, the neighbors of rod i frequently restrict its flopping to a very small region. The probability of having a neighbor is proportional to i/N. Let the probability of having say four neighbors be given by $a(i/N)^4$, with a being of the order of 10%, and let the integral $\int d\Omega$ drop by a factor of b, with b being of the order of 10. We have

$$\ln(Z_\Omega) = \sum_{i=1}^{N} \ln(\Omega_m) [1 - a(i/N)^4] + \sum_{i=1}^{N} \ln(\Omega_m/b) a(i/N)^4$$

$$= \sum_{i=1}^{N} [\ln(\Omega_m) - a(i/N)^4 \ln(b)] .$$

Switching to $f = i/N$ and from summation to integration, we find

$$\ln(Z_\Omega) = N\ln(\Omega_m) - a\ln(b)\int_0^1 f^4\,df$$

$$\approx N\ln(\Omega_m) - 0.05N.$$

In other words Z could be too high by several percent from this source alone. Next, there is a compensating feature in that θ_m could have been made a function of i/N, which has the effect of driving Z up. Finally, these errors are not random. They are roughly independent of the density.

IV. RESULTS

The partition function is calculated in the low-density region directly by the Monte Carlo method described in Sec. II, and in the liquid-crystal region by maximizing the right-hand side of Eq. (9) as a function of r_c. The angular correlation function, σ of Eq. (7), is also calculated by similar methods. The results of these calculations are given in Table I. Figure 2 is a plot of the liquid-
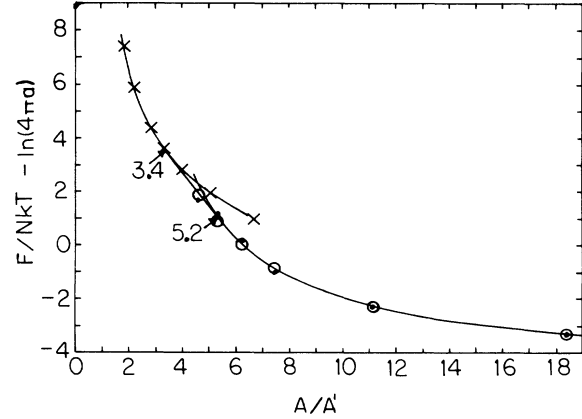

FIG. 2. A plot of $F/NkT - \ln(4\pi a)$ (a being the hexagonal cross-sectional area of a rod in the plane) vs A/A', the ratio of the total available area to the close-packed area. The Maxwell construction is shown. Solid circles are Monte Carlo data points; open circles, from the spline fit of Table I; crosses, from minimizing the liquid-crystal expression as given in either Eq. (14) or (9).
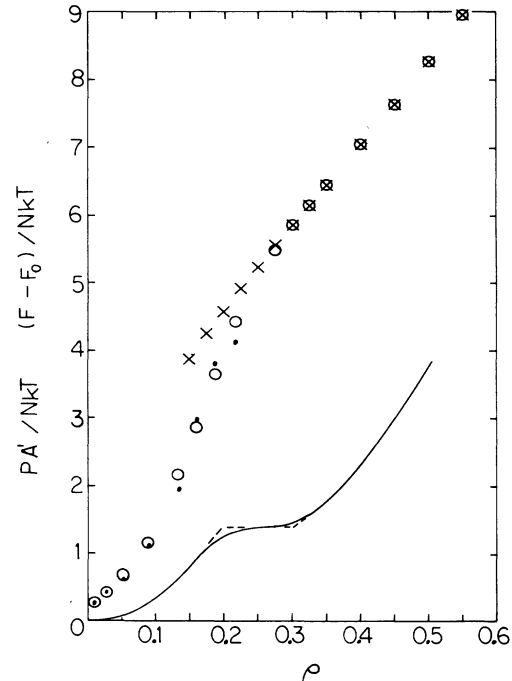
TABLE I. The error estimates on $(F-F_0)/NkT$ are based on the differences between the top value found and the first group of three or four values. The error estimate in the order parameter σ comes from treating the top five $1/w_t$'s as equal and averaging among them. The standard deviation for $\rho = 0.1878$ is low because it was run about 10 times as long as the others, that for $\rho = 0.2178$ because of the impending overestimate of the angular volume. $S(\rho)$ is determined by minimizing $F = x^2 + s$ with $x^2 = \sum_i [S(\rho_i) - (F-F_0)/NkT]^2/\epsilon S_i^2$ and $s = 10^{-5}\sum_j d_j^2$, where d_j is the coefficient of the jth $(\cdots)_+$ in Eq. (16). ϵ_S is used rather than the Monte Carlo error estimates to avoid excessive reliance on the weakest step of the Monte Carlo procedure and along with the smoothing term to allow for interpolation across the phase-change region. F is 61.6 while x^2 is 42.4.

ρ	$(F-F_0)/NkT$	ϵ_S	$S(\rho)$	σ
0.0100	0.27 ± 0.02	0.005	0.268	0.04 ± 0.05
0.0278	0.41 ± 0.03	0.005	0.403	0.06 ± 0.03
0.0544	0.62 ± 0.04	0.06	0.661	0.12 ± 0.04
0.0900	1.13 ± 0.04	0.05	1.166	0.12 ± 0.04
0.1344	1.95 ± 0.13	0.05	2.154	0.29 ± 0.04
0.1600	2.97 ± 0.10	0.05	2.802	0.40 ± 0.05
0.1878	3.80 ± 0.04	0.05	3.651	0.68 ± 0.06
0.2178	4.13 ± 0.05	0.1	4.433	0.97 ± 0.01
0.275	5.550	0.1	5.509	0.967
0.300	5.853	0.005	5.851	0.972
0.325	6.151	0.005	6.154	0.976
0.350	6.445	0.005	6.446	0.980
0.400	7.039	0.005	7.038	0.987
0.450	7.652	0.005	7.650	0.991
0.500	8.290	0.005	8.292	0.994
0.550	8.973	0.005	8.972	0.996

FIG. 3. A plot of $(F-F_0)/NkT$ vs ρ and also of PA'/NkT vs ρ as found from Eq. (20) with the spline fit of Table I given in Eq. (16). Solid circles are the Monte Carlo data points; crosses, liquid-crystal results from Eq. (14); open circles, spline fit to the data of Table I. The solid line is PA'/NkT as found, while the dashed segments are the authors' extrapolation to find the phase-change region. Note that $A' = Na$ is the cross-sectional area of a close-packed system of N rods.

crystal free energy, $F/NkT = -\ln(Z)/N$, obtained from maximizing Eq. (9), along with the Monte Carlo free energy at lower densities. Maxwell construction leads to the identification of a phase-change region extending from $\rho = 0.19 \pm 0.01$ to 0.29 ± 0.01 which is remarkably insensitive to details.

In order to be a bit more rigorous it is convenient to work with the ratio of $Z(N, A)$ to

$$Z_0(N, A) \equiv \int d^2 r_1 \cdots d^2 r_N \int d\Omega_1 \cdots d\Omega_N$$

$$= (4\pi)^N A^N, \tag{13}$$

which conveniently removes $\ln \rho$ from F and avoids the difficulties at small ρ. We find then that

$$\frac{F - F_0}{NkT} = \frac{-\ln(Z/Z_0)}{N}$$

in general, and that in the liquid-crystal region

$$\frac{F - F_0}{NkT} \leqslant f(\rho_e) + \ln\left\{ 1 - \left[1 - 4\left(\frac{(\rho_e/\rho)^{1/2} - 1}{l/2r - 1}\right)^2 \right]^{1/2} \right\}, \tag{14}$$

where

$$f(\rho_e) \equiv (F - F_0^*)/NkT \tag{15}$$

represents hard-disk results from HR and F_0^* denotes the free energy of the noninteracting system *without the angular part*. A spline is then fitted to the entire free-energy curve using the Monte Carlo results for $\rho < 0.22$ and the liquid-crystal results for $\rho > 0.275$ with the error assignments given in Table I. The best fit is given by

$$(F - F_0)/NkT = S(\rho)$$

$$= 0.200 + 6.601\rho + 17.162\rho^2 + 320.438\rho^3 - 973.121(\rho - 0.10685)_+^3$$

$$+ 946.700(\rho - 0.21990)_+^3 - 281.829(\rho - 0.33693)_+^3, \tag{16}$$

with

$$(x)_+^3 \equiv \begin{cases} 0, & x < 0 \\ x^3, & x \geqslant 0. \end{cases} \tag{17}$$

The values of the spline for the fitted points are given in Table I and as open circles in Figs. 2 and 3. A single spline with smoothing is used to give as smooth a fit as possible in order to avoid in any way biasing the results in favor of a first-order phase change which seems to be indicated. Less smoothing sharpens the apparent change only a little and does not greatly reduce the χ^2, while more smoothing reduces the apparent phase change a little and increases the χ^2. The results thus seem to be rather independent of the particular spline used.

The surface pressure can now be found as

$$P = \frac{-\partial F}{\partial A} = \left(\frac{Na}{A}\right)^2 \frac{N\ln T}{Na} \frac{\partial(F/NkT)}{\partial(Na/A)} \tag{18}$$

where a is the cross-sectional area of a rod, so that with $A' = Na$ and $\rho = Na/A$,

$$\frac{PA'}{NkT} = \rho^2 \frac{\partial(F/NkT)}{\partial\rho}. \tag{19}$$

Taking into account the part from F_0, we have

$$\frac{PA'}{NkT} = \rho + \rho^2 \frac{\partial}{\partial\rho} S(\rho). \tag{20}$$

The free energy as a function of ρ along with the pressure from Eq. (20) are shown in Fig. 3.

It may well have been anticipated that after all of this the pressure would either give a van der Waals type of loop or miss the phase change altogether. In fact the pressure curve is never perfectly flat. Very little imagination is required to see in Fig. 3 the desired shape. The pressure curve does indeed imply that for $0.20 \pm 0.01 < \rho < 0.30 \pm 0.01$ there is a phase change with a constant pressure in the coexistence region of $PA'/NkT = 1.38 \pm 0.03$.

†Present address.

[1] B. J. Alder and T. E. Wainwright, Phys. Rev. 127, 359 (1962).
[2] R. L. Coldwell, Phys. Rev. A 7, 270 (1973).
[3] W. G. Hoover and F. H. Ree, J. Chem. Phys. 49, 3609 (1968).