

## On the Orientational Properties of Some One-Dimensional Model Systems

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We use the transfer matrix formalism to examine the behavior of some anisotropic hard-core fluids, the centers of whose particles are constrained to a line. At large elongation and pressure, the compressibility factor  $\beta p/\rho$  is higher than that for a system with complete alignment by a factor  $1 + \nu$  that depends upon the molecular geometry. For molecules with a finite radius of curvature, e.g., ellipses,  $\nu = d/2$ , while for objects with flat sides  $\nu = d$ ; here  $d$  is the number of orientational degrees of freedom. A connection is made to some recent studies of hard ellipsoid fluids. We also model the effect of an external field on physical adsorption and show the existence of a phase transition in certain limiting situations.

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**KEY WORDS:** Anisotropic hard-core fluids; one-dimensional models; large elongation.

### 1. INTRODUCTION

In this work, we examine the behavior of some one-dimensional molecular systems with anisotropic hard-core interactions. Specifically, we investigate the effects of increasing elongation and external fields on the thermodynamic and structural properties. These studies were prompted by the computer simulations of Frenkel *et al.*<sup>(1,2)</sup> and others<sup>(3)</sup> on the phase diagram of hard ellipsoids of revolution. We were particularly motivated by an interesting theoretical paper of Frenkel<sup>(4)</sup> investigating the relationship between the melting of *extremely* prolate (or oblate) ellipsoids of revolution and the solid–fluid transition of hard spheres.

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Frenkel obtained an approximate expression for the free energy of such an elongated ellipsoidal system considered as a function of  $\eta = \rho v_0$  and  $e$ , where  $v_0$  is the volume of a single ellipsoid and  $e$  is the elongation (height/width). It follows from this expression that in the limit  $e \rightarrow \infty$  the difference between the pressure of the ellipsoids and that of the corresponding hard-sphere systems does not vanish (Lebowitz and Perram<sup>(5)</sup> showed that the translational partition function of a system of perfectly aligned ellipsoids is the same as for hard spheres with the same  $\eta$ ). An intriguing question is whether Frenkel's result is exact, and how it applies to other objects, e.g., spherocylinders. We find indeed that such behavior is typical of the dimensionally constrained molecular systems examined: although they are compelled to line up under high elongation or high pressure, their limiting equations of state are *not* those of the corresponding fully aligned systems.

The simple analytic models that we propose have a further interesting application when an external field is applied. Recent computer simulations of nitrogen absorbed on a graphite surface<sup>(6)</sup> yielded some intriguing results for the orientational distribution function, i.e., the distribution of the angle between the intramolecular axis vector and the graphite surface. At low densities, the molecular substrate interaction is dominant and one observes that nearly all the molecules lie parallel to the surface. With increasing density the orientational distribution becomes bimodal, that is, a second minimum appears and a significant fraction of the molecules are almost perpendicular to the surface. Our model is able to reproduce this effect, appearing as a phase transition in the infinite elongation limit, which results from the competition between the field of the substrate and the molecule-molecule interactions.

## 2. GENERAL THEORY

We imagine  $N$  identical molecules with their centers of symmetry restricted to lie on a line. We consider a nearest neighbor hard-core interaction which depends on the relative orientation of a pair of molecules. In this situation a transfer operator analysis is possible. To further simplify matters, consider first the case where the molecules are assumed to have a single rotational degree of freedom, i.e., they rotate in the plane containing the line through the centers. The configurational partition function for this system in the isobaric ensemble is (periodic boundary conditions are imposed such that  $x_{N+1} = x_1$ ).

$$\text{Tr } Z_p^N = \int_{-\pi}^{\pi} d\theta Z_p^N(\theta, \theta)$$

Here  $Z_p(\theta, \theta')$  is the transfer operator, defined as

$$Z_p(\theta, \theta') = \int_0^\infty \exp[-\beta\phi(x; \theta, \theta')] \exp(-\beta px) dx \quad (1)$$

where  $\phi(x; \theta, \theta')$  is the potential between a pair of molecules separated by a distance  $x$  with orientations  $\theta$  and  $\theta'$  (measured with respect to some fixed space axis: conveniently the normal to the line of molecular centers; Fig. 1). A more complete description of the transfer matrix theory applied to molecules with an orientational degree of freedom is given in the paper of Casey and Runnels.<sup>(7)</sup> For hard-core interactions,

$$\phi(x; \theta, \theta') = \begin{cases} \infty, & x < \sigma(\theta, \theta') \\ 0, & x > \sigma(\theta, \theta') \end{cases}$$

where the hard-core diameter  $\sigma(\theta, \theta') = \sigma(\theta', \theta)$  is the closest distance between a pair of molecules with orientations  $\theta$  and  $\theta'$  such that there is no overlap. With this choice, the transfer operator becomes

$$Z_p(\theta, \theta') = (1/\beta p) \exp[-\beta p \sigma(\theta, \theta')] \quad (2)$$

In order to obtain information about the thermodynamic and structural properties, one has to solve the integral equation

$$\int_{-\pi}^{\pi} Z_p(\theta, \theta') \psi(\theta') d\theta' = \lambda \psi(\theta) \quad (3)$$

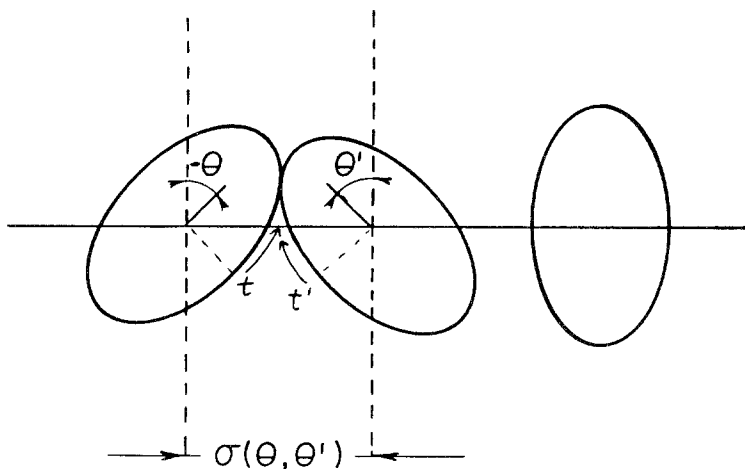


Fig. 1. A diagram illustrating the angles specifying the orientation of two planar convex molecules. The diagram also shows the separation of centers at contact  $\sigma(\theta, \theta')$  and the boundary parameters  $t$  and  $t'$  of Sec. 5.

In the thermodynamic limit  $N \rightarrow \infty$ , the square of the eigenfunction  $\psi(\theta)$  corresponding to the unique maximum eigenvalue  $\lambda$  is proportional to the angular distribution function  $w(\theta)$ , i.e., the probability that a molecule has an orientation between  $\theta$  and  $\theta + d\theta$ . The eigenvalue is simply related to the chemical potential  $\mu$ :  $\ln \lambda = -\beta\mu$  (up to a constant) and thus provides a link to thermodynamics through the relation (in the thermodynamic limit)

$$\frac{1}{\rho} = -\frac{1}{\beta} \frac{\partial \ln \lambda}{\partial p} \quad (4)$$

Analytic solution of Eqs. (2) and (3) is in general not feasible, but limiting solutions can be quite instructive. In particular, let us consider the closed-packed, high-pressure, limit. For general hard convex objects, we note that the important contribution to  $\lambda$  will then come from the vicinity of the minimum value of  $\sigma(\theta, \theta')$ . We assume that this occurs for  $\theta = \theta' = 0$  and that  $\sigma(\theta, \theta')$  can be written for  $\theta, \theta' \sim 0$  as

$$\sigma(\theta, \theta') = a + (A|\theta + \theta'|^\gamma + B|\theta - \theta'|^\gamma)[1 - o(\theta, \theta')] \quad (5)$$

where  $O(\theta, \theta') \rightarrow 0$  as  $\theta, \theta' \rightarrow 0$  and  $a$  is the minimum diameter. We have  $\gamma = 1$  for objects with straight edges, like rectangles, and  $\gamma = 2$  for bodies with a finite radius of curvature at the minimum contact diameter, like ellipses. In the high-pressure limit, the integral equation (3) becomes approximately

$$\frac{\exp(-a\beta p)}{\beta p} \int_{-\infty}^{\infty} \exp[-\beta p(A|\theta + \theta'|^\gamma + B|\theta - \theta'|^\gamma)] \psi(\theta') d\theta' = \lambda \psi(\theta)$$

With the changed variable  $\phi = (\beta p)^{1/\gamma} \theta$ , we get

$$\lambda = \bar{\lambda} (e^{-a\beta p} / \beta p) (\beta p)^{-1/\gamma}$$

where  $\bar{\lambda}$  is independent of  $\beta p$ : it is the maximum eigenvalue of the equation

$$\bar{\lambda} f(z) = \int_{-\infty}^{\infty} \exp[-A(z+z')^\gamma - B|z-z'|^\gamma] f(z') dz'$$

From (4), the limiting equation of state is easily shown to have, not the intuitively expected pure hard-rod form  $\beta p_0(\rho) = \rho/(1 - a\rho)$  for strictly parallel alignment, but rather

$$\lim_{\rho \rightarrow \infty} p(\rho)/p_0(\rho) = 1 + 1/\gamma \quad (6)$$

For simple convex objects, this ratio is 1.5 (finite curvature) or 2 (zero curvature).

At this level of analysis, we can head toward the hard ellipsoidal system considered by Frenkel by permitting the molecules to rotate in three dimensions. For molecules with an axis of symmetry, the orientation is now specified by two angles  $\theta, \phi$ . The centers are still constrained to a line and only nearest neighbor interactions are permitted. The latter condition would be automatically satisfied by disks or more generally by oblate ellipsoids of revolution (“platelets”), but not by prolate ellipsoids of revolution (“roods”). Since the distance of closest approach is clearly invariant with respect to rotation about the line of centers, it depends only upon the difference of the polar angles:  $\sigma(\theta, \theta', \phi - \phi')$ . In the transfer operator formalism, this result immediately implies that the maximal eigenfunction is independent of  $\phi$ ,

$$\int_0^\infty d\phi' \int_0^\pi \sin \theta' d\theta' Z_p(\theta, \theta', \phi - \phi') \psi(\theta') = \lambda \psi(\theta)$$

Inserting a reasonable form for  $\sigma$  in the vicinity of the minimum,

$$\sigma(\theta, \theta', \phi - \phi') = a + A|\theta + \theta'|^\gamma + B|\theta - \theta'|^\gamma + C\theta^{\gamma/2}(\theta')^{\gamma/2} f(\phi - \phi') + \dots$$

leads as in (5) to the limiting equation of state

$$\lim_{p \rightarrow \infty} p(\rho)/p_0(\rho) = 1 + 2/\gamma \tag{7}$$

differing from the previous result by a factor of 2, which is simply a result of the new weight factor  $\sin \theta d\theta$ . Note that for bodies with finite radius of curvature,  $\gamma = 2$ , the limiting pressure is now twice that of the fully aligned situation. This is exactly the result obtained by Frenkel.

### 3. A SOLVABLE MODEL

Another option is that of weakening our insistence on dealing with a system of legitimate hard objects, and instead use models designed to permit ready solvability of the integral equation (3). In particular, where the transfer operator is factorizable, i.e.,  $Z_p(\theta, \theta') = f(\theta) f(\theta')$ , (3) is easily solved:  $\psi(\theta) = f(\theta)$  and  $\lambda = \int |f(\theta)|^2 d\theta$ . For objects with a center of symmetry (true in all cases we consider), we have

$$\begin{aligned} \sigma(\theta, \theta') &= \sigma(-\theta, -\theta') \\ \sigma(\theta + \pi, \theta') &= \sigma(\theta, \theta') = \sigma(\theta, \theta' + \pi) \end{aligned}$$

The simplest nontrivial form of  $\sigma(\theta, \theta')$  that permits factorization of the transfer operator is

$$\sigma(\theta, \theta') = a + \frac{1}{2}\alpha - \frac{1}{4}\alpha(\cos 2\theta + \cos 2\theta') \tag{8}$$

where  $\alpha$  characterizes the elongation of the molecule. The minimum and maximum "contact separations" are  $\sigma(0, 0) = 1$  and  $\sigma(\pi/2, \pi/2) = 1 + \alpha$ , respectively. Although this is not a model of hard objects, the dependence of its thermodynamics on elongation and pressure will bear a close resemblance to that of hard molecules.

With this choice of  $\sigma(\theta, \theta')$  we readily obtain

$$\begin{aligned}\psi(\theta) &= [\exp(\beta p \alpha \cos 2\theta)] / [\pi I_0(2\beta p \alpha)]^{1/2} \\ \lambda &= (\pi/\beta p) I_0(\frac{1}{2}\beta p \alpha) \exp[-\beta p(a + \frac{1}{2}\alpha)]\end{aligned}\quad (9)$$

and so from (4) the equation of state can be written as

$$\frac{p(\rho)}{p_0(\rho)} = 1 + \frac{1}{2} \beta p \alpha \left( 1 - \frac{I_1(\frac{1}{2}\beta p \alpha)}{I_0(\frac{1}{2}\beta p \alpha)} \right) \quad (10)$$

Here

$$I_0(x) = \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} \exp(x \cos 2\theta) d\theta, \quad I_1(x) = I_0(x)$$

are modified Bessel functions. When  $\alpha = 0$ , (10) reduces to the usual equation of state of hard rods on a line. In this model, only the combination  $\beta p \alpha$  enters [true in general whenever  $\sigma(\theta, \theta')$  is linear in the elongation  $\alpha$ ], so that high pressure and large elongation are interchangeable. From (10), we find for large  $\beta p \alpha$ , i.e., either high  $\alpha$  or high  $p$ ,

$$\frac{p(\rho)}{p_0(\rho)} = \frac{3}{2} + \frac{9}{32} \frac{1}{\beta p \alpha} + O\left(\frac{1}{(\beta p \alpha)^2}\right)$$

which is precisely the form (6) that corresponds to true hard, finite-curvature objects at high pressure. The angular distribution function  $w(\theta) = |f(\theta)|^2$  in this limit is of course a delta function centered on  $\theta = 0$ , but we can also obtain the "rescaled" limiting angular distribution by setting  $\theta = \phi/(\beta p \alpha)^{1/2}$  and then letting  $\beta p \alpha \rightarrow \infty$ . This yields

$$\bar{w}(\phi) = (4/\pi)^{1/2} \exp(-4\phi^2)$$

It is not more difficult to consider the effect of an external field acting to orient the molecules perpendicular to the line of centers. Let the interaction between this field and a molecule with orientation  $\theta$  be  $-h(\theta)$ . The transfer operator is now

$$Z_p(\theta, \theta') = (1/\beta p) \exp[-\beta p \sigma(\theta, \theta')] \exp[\frac{1}{2}\beta h(\theta)] \exp[\frac{1}{2}\beta h(\theta')] \quad (11)$$

and for the form of  $\sigma(\theta, \theta')$  given by (8), the eigenfunction is

$$\psi(\theta) = \exp\left[\frac{1}{4}\beta p\alpha \cos 2\theta + \frac{1}{2}\beta h(\theta)\right] \tag{12}$$

to within normalization. For the specific choice  $h(\theta) = E \cos \theta$ , the equation of state is

$$\frac{1}{\rho} = a + \frac{a}{2} + \frac{1}{\beta p} - \frac{1}{\beta} \frac{\partial \ln F}{\partial p} \tag{13}$$

$$F = \int_{-\pi}^{\pi} \exp\left(\frac{1}{2}\beta p\alpha \cos 2\theta + \beta E \cos \theta\right) d\theta$$

If  $p \rightarrow \infty$  or  $\alpha \rightarrow \infty$  at constant  $E$ , the result  $p(\rho)/p_0(\rho) = 3/2$  is of course recovered. But suppose that  $E > 0$  and  $E \rightarrow \infty$  at fixed  $E/\alpha$ . Then (13) can be expanded around the preferred direction,  $\theta = 0$ , giving

$$\frac{1}{\rho} = a + \frac{1}{\beta p} + \frac{1/2}{\beta p + \beta E/2\alpha} \tag{14}$$

In particular, if  $\alpha/E \rightarrow 0$ , the orientational degree of freedom “freezes out” and the molecules obey the hard-rod equation of state  $p(\rho) = p_0(\rho)$ .

The formalism developed above has an interesting application to physical adsorption. Even though the model is highly idealized, it nevertheless contains some of the important physical effects. In physical adsorption, the molecules of the adsorbant are attracted to the substrate by weak dispersion forces (9). The electronic structure is not greatly disturbed, and one can think of the molecules as being in an external field that favors a lining up of molecules parallel to the surface,  $\theta = \pm\pi/2$  in our notation. However, as surface density increases, the hard-core interaction becomes increasingly important, so that a fraction of molecules will orient perpendicular to the surface, an effect that has been observed in molecular dynamics simulations of nitrogen adsorbed on graphite.<sup>(6)</sup> Our model has similar behavior. Suppose that

$$h(\theta) = a_1 \exp(-a_2 \cos 2\theta), \quad a_1, a_2 > 0$$

indicative of a strong preference<sup>(6,9)</sup> for parallel orientation. The distribution function  $w(\theta) = \psi(\theta)^2$  of (12) always has a maximum at  $\theta = \pm\pi/2$ . But at  $\theta = 0$ , which is also a stationary point, we have

$$(\ln w)''(0) = 2\beta(a_1 a_2 e^{-a_2} - \alpha p)$$

and hence a new maximum also appears at  $\theta = 0$  when

$$\alpha p > a_1 a_2 e^{-a_2} \tag{15}$$

These results are indicated pictorially in Fig. 2.

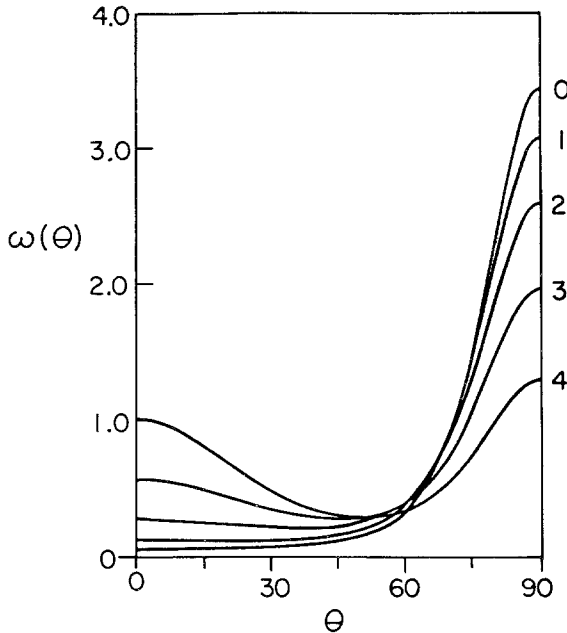


Fig. 2. The angular distribution function for the adsorption model. The external field is  $h(\theta) = \exp(-1.5 \cos 2\theta)$ , and the curves are labeled by  $\beta p$ . At high pressure, the angular distribution function becomes bimodal.

#### 4. NUMERICAL RESULTS

For realistic shapes, it appears difficult to obtain an analytic solution to the integral equation (3) for general elongations. It is, however, easy to examine the behavior numerically. There are two problems: first, that of obtaining  $\sigma(\theta, \theta')$ , the distance of closest approach, and second, that of solving the integral equation. The form of  $\sigma(\theta, \theta')$  is in general sufficiently complicated that a numerical approach is not amiss. Suppose we approximate a convex body  $C$  by a set of  $n_c$  straight line segments determined by the vectors  $\{\mathbf{c}_i, i = 1, \dots, n_c\}$  from the center of  $C$  to each vertex. Consider a congruent convex body  $D$  whose center is a distance  $r$  from that of  $C$ . The condition for a corner of  $C$  to touch one of the line segments defining body  $D$  is

$$\mathbf{c}_i = r\mathbf{e}_x + (1 - \mu)\mathbf{d}_j + \mu\mathbf{d}_{j+1}$$

where  $i = 1, \dots, n_c$ ,  $j = 1, \dots, n_D$ , and  $\mathbf{d}_{n_D+1} = \mathbf{d}_1$  with  $0 < \mu < 1$ ;  $\mathbf{e}_x$  is the



$x$ -directed unit vector. Similarly, for a corner of  $D$  to touch a line segment of  $C$ ,

$$\mathbf{d}_j = -r\mathbf{e}_x + (1 - \mu)\mathbf{c}_i + \mu\mathbf{c}_{i+1} \tag{16}$$

The computational procedure, e.g., for (15), is as follows. Calculate  $\mu$  for all combinations of  $i$  and  $j$ ,

$$\mu_{ij} = \frac{c_{iy} - d_{jy}}{d_{j+1,y} - d_{jy}} \tag{17}$$

If  $\mu_{ij} \notin (0, 1)$ , then the vertex  $\mathbf{c}_i$  cannot touch the side defined by  $\mathbf{d}_j, \mathbf{d}_{j+1}$ ; if  $\mu_{ij} \in (0, 1)$ , it will, and so we calculate

$$\sigma = \max_{\{i,j|\mu_{ij} \in (0,1)\}} c_{ix} - (1 - \mu) d_{jx} - \mu d_{j+1,x} \tag{18}$$

Any symmetry present can be used to reduce the number of calculations. The simplest example of (18) is that in which  $C$  and  $D$  are two “needles” of length  $l$  at respective angles  $\theta$  and  $\theta'$ . Then one finds

$$\sigma(\theta, \theta') = \frac{l}{2} \frac{\sin |\theta - \theta'|}{\cos(\min |\theta|, |\theta'|)} \tag{19}$$

where  $|\theta|, |\theta'| < \pi/2$ . Note that at high density, so that  $|\theta|, |\theta'| \sim 0$ , one has

$$\sigma(\theta, \theta') \sim \frac{1}{2}l |\theta - \theta'|$$

which is the prototypical case of  $\gamma = 1$  in (5).

Given  $\sigma(\theta, \theta')$ , the numerical procedure is direct. For a discrete set of  $n$  angles  $\theta_i = i\pi/n$ , the integral equation becomes a matrix eigenvalue problem

$$\sum_1^n M_{ij} x_j = \lambda' x_i$$

where  $M_{ij} = Z_p(\theta_i, \theta_j)$ ,  $x_i = \psi(\theta_i)$ , and  $\lambda' = n\lambda/\pi$ . Following standard procedures, the eigenvalues and eigenvectors are obtained by iteration. The reciprocal density is then given by

$$\frac{1}{\rho} = \frac{1}{\beta p} + \frac{1}{\lambda'} \sum_{i,j=1}^n \sigma(\theta_i, \theta_j) x_i M_{ij} x_j$$

The number of divisions  $n$  of the angular range required to effect an accurate solution depends to a large extent on the elongation, but  $n = 80-160$  was found to be satisfactory for the situations we considered.

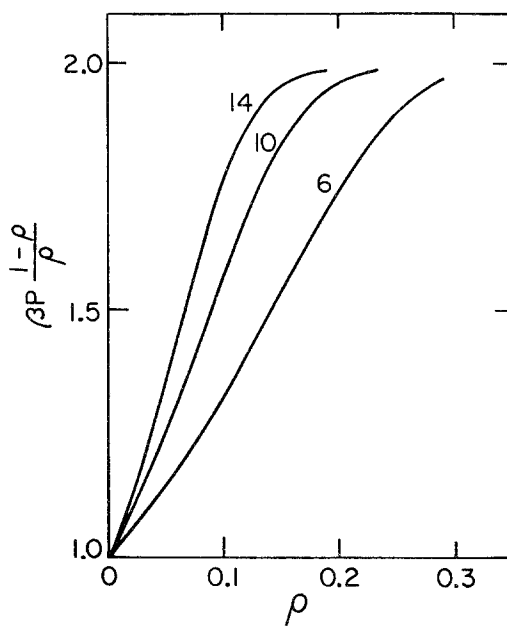


Fig. 3. The ratio of the pressure for rectangular molecules to that of a one-dimensional hard-rod gas at the same density. The numbers refer to the length of the rectangle (width = 1).

Figure 3 shows results for rectangles of different elongation. The limiting behavior is clearly illustrated by the plot, which shows  $p(\rho)/p_0(\rho)$  as a function of  $\rho$ . The plot visually confirms the limiting ratio of 2 at high pressure.

## 5. ANALYSIS AT HIGH ELONGATION

We return to possible analytic solutions. We have seen in the model (8) that the limits of very high pressure and very large elongation have similar effects on the thermodynamics, which is reasonable enough, given that both bias the system toward perpendicular alignment. But the large- $\alpha$  limit, at least as relevant to the experiments we have quoted, is not quite as trivial. Our starting point is an unelongated, perpendicularly oriented, hard, convex molecule, again in two dimensions and again symmetric about the  $x$  and  $y$  axes. It is sufficient to specify the first and fourth quadrant boundary, which we write in the parametric form

$$x = f(t), \quad y = g(t) \quad (20)$$

where

$$t = -dx/dy = -f'(t)/g'(t)$$

Here  $t$  has the range  $(-\infty, \infty)$ ,  $f$  is an even, single-valued function, while  $g$  is odd, and we write  $a = 2f(0)$  as the transverse diameter of the molecule. If we now elongate in the  $y$  direction by a factor  $\alpha$  and rotate counterclockwise by  $\theta$ , the new boundary becomes

$$\begin{aligned} x &= f(t) \cos \theta - \alpha g(t) \sin \theta \\ y &= f(t) \sin \theta + \alpha g(t) \cos \theta \end{aligned} \tag{21}$$

Let us consider the interaction between two such molecules. If the first is centered at  $x=0$ , the second at  $x=r$ , and the left-hand side of the second molecule is parametrized as was the right-hand side of the first, the two boundaries are given by

$$\begin{aligned} x_1 &= f(t_1) \cos \theta_1 - \alpha g(t_1) \sin \theta_1 \\ y_1 &= f(t_1) \sin \theta_1 + \alpha g(t_1) \cos \theta_1 \\ x_2 &= r - f(t_2) \cos \theta_2 - \alpha g(t_2) \sin \theta_2 \\ y_2 &= -f(t_2) \sin \theta_2 + \alpha g(t_2) \cos \theta_2 \end{aligned} \tag{22}$$

Contact corresponds to the largest value of  $r$  such that  $x_1 = x_2$ ,  $y_1 = y_2$ ,  $dx_1/dy_1 = dx_2/dy_2$ . If we set

$$\theta_2 = \theta_1 + (1/\alpha)\delta, \quad t_2 = t_1 - (1/\alpha)s$$

these conditions yield, respectively,

$$\begin{aligned} r &= 2f(t_1) \cos \theta_1 + \delta g(t_1) \cos \theta_1 - sg'(t_1) \sin \theta_1 + O(1/\alpha) \\ 0 &= 2f(t_1) \sin \theta_1 + \delta g(t_1) \sin \theta_1 + sg'(t_1) \cos \theta_1 + O(1/\alpha) \\ 0 &= 2f'(t_1) + \delta g'(t_1) + O(1/\alpha) \end{aligned}$$

Since  $r$  is the separation at contact, we conclude, on eliminating  $s$  and using  $f'/g' = -t_1$ , that

$$\sigma(\theta_1, \theta_2) = 2 \sec \theta_1 [f(t_1) + f_1 g(t_1)] + O(1/\alpha)$$

where

$$t_1 = \frac{1}{2}\alpha(\theta_2 - \theta_1) + O(1/\alpha) \tag{23}$$

The eigenvalue equation (3) then reads

$$\begin{aligned} &\frac{1}{2\beta p} \int_{-\infty}^{\infty} \exp \left\{ -2\beta p \sec \theta \left[ f(t) + tg(t) + O\left(\frac{1}{\alpha}\right) \right] \right\} \\ &\quad \times \psi \left( \theta + \frac{2t}{\alpha} + O\left(\frac{1}{\alpha^2}\right) \right) dt \\ &= \lambda \psi(\theta) \end{aligned}$$

Now if  $\alpha \rightarrow \infty$ , the (unscaled) eigenfunctions take the form  $\psi_{\theta_0}(\theta) = \delta(\theta - \theta_0)$ , with

$$\alpha\lambda_{\theta_0} = \frac{2}{\beta p} \int_0^\infty \exp\{-2\beta p \sec \theta_0 [f(t) + tg(t)]\} dt \quad (24)$$

Hence,  $\lambda_{\max}$  occurs at  $\theta_0 = 0$  (perpendicularly aligned molecules) and

$$\alpha\lambda_{\max} = \frac{2}{\beta p} \int_0^\infty \exp\{-2\beta p [f(t) + tg(t)]\} dt \quad (25)$$

The equation of state in the infinite-elongation limit has thus been reduced to quadratures. As an example, consider the case of hard ellipses, described in the version (20) by the unelongated circle

$$x = \frac{1}{2}a/(1+t^2)^{1/2}, \quad y = \frac{1}{2}t/(1+t^2)^{1/2} \quad (26)$$

Thus, (25) becomes  $\alpha\lambda_{\max} = (2/\lambda p) K_1(a\beta p)$ , with the limiting equation of state

$$\frac{1}{\rho} = \frac{1}{\beta p} - a \frac{K_1'(a\beta p)}{K_1(a\beta p)} \quad (27)$$

with the expected high-pressure limit

$$1/\rho = a + \frac{3}{2}\beta p + (15/64)/(\beta p)^2 + \dots$$

as well as the low-pressure form

$$1/\rho = 2/\beta p - \rho p a^2 \ln \beta p a \dots$$

Somewhat less familiar figures lead, however, to simpler closed forms, e.g., the sideways parabola

$$x = \frac{a}{2} \left( 1 - \left| \frac{2y}{a} \right|^{2n} \right), \quad n \geq \frac{1}{2} \quad (28)$$

written as

$$x = \frac{a}{2} \left( 1 - \left| \frac{t}{2n} \right|^{2n/(2n-1)} \right), \quad y = \frac{a}{2} \left| \frac{t}{2n} \right|^{1/(2n-1)} \operatorname{sgn} t$$

gives rise to

$$\alpha\lambda_{\max} = 2a(2n-1)^2 e^{-\beta p a} [\beta p a(2n-1)]^{-(4n-1)/2n} \left( -\frac{1}{2n} \right)!$$

and hence

$$\frac{1}{\rho} = a + \frac{4n-1}{2n} \frac{1}{\beta p} \tag{29}$$

In particular,  $n \rightarrow \infty$  corresponds to rectangular profiles, with  $p(\rho)/p_0(\rho) = 2$ , identical with the  $p \rightarrow \infty$  limit, while  $n \rightarrow 1/2$  produces diamond-shaped profiles, which show no anomaly at all:  $p(\rho)/p_0(\rho) = 1$ .

Finally, let us apply the orienting external potential  $-Eh(\theta)$ . The only modification is that (24) now becomes

$$\alpha \lambda_{\theta_0} = \frac{2}{\beta p} \exp[\beta Eh(\theta_0)] \int_0^\infty \exp\{-2\beta p \sec \theta_0 [f(t) + tg(t)]\} dt \tag{30}$$

Restricting attention to the high-pressure limit at fixed  $p/E$ , we examine the finite-curvature case discussed in Section 2. If the radius of curvature in the vicinity of  $t=0$  is  $R$ , then  $x = \frac{1}{2}a - y^2/2R \dots$ ,  $t = y/R + \dots$ , so that  $f(t) + tg(t) = \frac{1}{2}a + \frac{1}{2}Rt^2$  near  $t=0$ . Hence, (30) reduces to

$$\alpha \lambda_{\theta_0} = \left(\frac{\pi}{R}\right)^{1/2} \exp \beta [Eh(\theta_0) - ap \sec \theta_0] (\beta p)^{-3/2} \cos^{1/2} \theta_0 \tag{31}$$

For analytic malleability, let us choose the surface biasing field

$$h(0) = \sin^2 \theta$$

Then it is easily seen that  $\lambda_{\theta_0}$  is maximum at

$$\theta_0 = \begin{cases} \cos^{-1}(ap/2E)^{1/3} & \text{if } p < 2E/a \\ 0 & \text{if } p > 2E/a \end{cases} \tag{32}$$

and that, correspondingly,

$$\alpha \lambda_{\max} = \left(\frac{\pi}{R}\right)^{1/2} (\beta p)^{-3/2} \begin{cases} (ap/2E)^{1/6} e^{\beta(E-ap)/2} \\ e^{-\beta ap} \end{cases}$$

Thus, there is a limiting first-order phase transition, with

$$\frac{1}{\rho} = \begin{cases} \frac{1}{2}a + \frac{4}{3}\beta p, & p < 2E/a \\ a + \frac{3}{2}\beta p, & p > 2E/a \end{cases} \tag{33}$$

A similar result holds for the zero-curvature case mentioned in Section 2.

## 6. DISCUSSION

We have used the transfer matrix approach to examine the effect of increasing elongation on the properties of some one-dimensional model systems. Our results are basically in agreement with Frenkel's approximate analysis.<sup>(4)</sup> We are further able to examine the influence of geometry on the limiting properties, which at high pressure depend on the behavior of the distance of closest approach  $\sigma(\theta, \theta')$  around its minimum value. Objects with flat sides (at contact) have a higher limiting compressibility factor than those with a finite radius of curvature. The properties of these two classes of objects appear to be quite different. In addition to the present results, we know that a system of perfectly aligned ellipsoids can be transformed to a system of hard spheres, while there appears to be no such transformation for the spherocylinder. Indeed, a recent simulation study indicates that a system of *perfectly aligned* spherocylinders has a nematic-smectic phase transition. It is clear that the corresponding ellipsoidal system will not have such a behavior.

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