1969

A Model for Correlated Molecular Rotation.

Lanny Max Casey
Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation

Casey, Lanny Max, "A Model for Correlated Molecular Rotation." (1969). *LSU Historical Dissertations and Theses*. 1644.

https://digitalcommons.lsu.edu/gradschool_disstheses/1644

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.

**This dissertation has been
microfilmed exactly as received**

70-9044

**CASEY, Lanny Max, 1943-
A MODEL FOR CORRELATED MOLECULAR
ROTATION.**

**The Louisiana State University and Agricultural
and Mechanical College, Ph.D., 1969
Chemistry, physical**

University Microfilms, Inc., Ann Arbor, Michigan

A MODEL FOR CORRELATED MOLECULAR ROTATION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

Lanny Max Casey
B.S., Harding College, 1965

August, 1969

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to his major professor, Dr. L. K. Runnels, without whose patience and direction this work would not have been accomplished. His ability to offer lucid explanations and examples has been invaluable. Thanks should also be given to the theoretical group for helpful discussions throughout the course of this work. The author also wishes to thank Henry Streiffer for programming assistance.

Financial assistance is gratefully acknowledged from the National Science Foundation in the form of a Traineeship and for assistance during summers under Grant No. GP-6822. The help of the Dr. Charles E. Coates Memorial Fund of the Louisiana State University Foundation donated by George H. Coates is also greatly appreciated.

TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENT	ii
LIST OF TABLES.	iv
LIST OF FIGURES	v
ABSTRACT.	vii
INTRODUCTION.	1
PART ONE: LATTICE GAS MODEL.	3
PART TWO: GENERALIZED MODEL.	21
PART THREE: DISCUSSION	63
APPENDIX I.	66
APPENDIX II	69
APPENDIX III.	71
APPENDIX IV	75
APPENDIX V.	77
BIBLIOGRAPHY.	81
VITA.	83

LIST OF TABLES

<u>TABLE #</u>		<u>PAGE</u>
I	Cusp height as a function of matrix size.	17
II	Convergence of βp^* to βp^{LAT} at $b = a_0$	39
III	Comparison of βp^{ROT} , βp^* , and βp^{LAT} (FC = 10) . . .	42
IV	Comparison of βp^{ROT} , βp^* , and βp^{LAT} (FC = 50) . . .	43
V	Comparison of βp^{ROT} , βp^* , and βp^{LAT} (FC = 100). . .	44

LIST OF FIGURES

<u>FIGURE #</u>		<u>PAGE</u>
1	Defining relations for two adjacent molecules at contact.	5
2	Sample rotational configurations.	6
3	Region of allowed rotations for several values of the lattice parameter a	10
4	Equation of state for the lattice model	15
5	Entropy as a function of density for the lattice model	18
6	Equations of state for the generalized model. . .	28
7	Low temperature convergence of the pressure increment due to rotation	33
8	Rotational pressure increment over an expanded pressure range.	35
9	Clarification of the approach to the lattice limit	36
10	Energy as a function of density for the Sq-S, RS, and SP models at constant $FC = 1.0$	49
11	Energy as a function of density for the Sq-S, RS, and SP models at constant $b = 1.2071$	50
12	Constant pressure heat capacity of the free translator.	53
13	Constant pressure heat capacity for the Sq-S model as a function of density for $b = 1.1$	55
14	Constant pressure heat capacity for the Sq-S model as a function of density for $b = 1.3$	56
15	Entropy of Sq-S and free translator models.	58

16	Entropy as a function of $-\ln \beta p$ for the free translator	60
17	Entropy as a function of $\ln \beta p$ and $-\ln FC$ for the Sq-S model	61

ABSTRACT

Correlated molecular rotations are studied with the aid of models which are representative of more complicated systems. The pertinent thermodynamic properties are calculated in an effort to determine the rotational contributions to these properties.

A lattice-gas model consisting of equally spaced hard molecules, represented by squares and arranged on a linear lattice, is considered first as the simplest model possessing rotational correlations. The molecules are allowed to rotate; the only force present is that due to the infinite potential of the hard core. By use of the canonical partition function the equation of state is calculated, revealing a van der Waals type loop with a sharp cusp at a lattice spacing of $(1 + \sqrt{2})/2$ (in units of the molecular length). With the aid of the Maxwell double tangent construction, the loop is replaced by a tie line connecting two coexisting phases.

A more general model is then considered to explore further the nature of the rotational contributions. The molecules are now allowed to translate while rotating, subject to an additional force attracting neighboring molecules. This model is approached from the standpoint of an isobaric partition function. Thermodynamic properties are calculated numerically for the case of harmonic attractions, indicating that the lattice model transition is no longer present. However, by subtracting out the pressure attributable to non-rotating molecules, the residual pressure does show a region of mechanical instability at low temperatures, and in the limit of zero temperature

is shown to be equivalent to that of the lattice model. Thermal properties, such as energy, heat capacity, and entropy, are also calculated to clarify further the effects of molecular rotation.

INTRODUCTION

Statistical mechanical treatments of interacting systems have taken many forms over the years, from the simple to the extremely difficult. And yet, much the same as in quantum mechanics, there are relatively few examples of exactly soluble systems available. That the large majority of the exactly soluble problems deal with the properties of systems in one dimension is neither gratifying nor surprising. An increase in the dimensionality of a problem always seems to increase the difficulty of arriving at an exact result. To cite a familiar example, Ising¹ solved the model of a one-dimensional ferromagnet in 1925. Not until almost twenty years later was the two-dimensional Ising model solved exactly by Onsager,² and then only in the limit of zero magnetic field.

Needless to say, one-dimensional systems have enjoyed a popularity much the same as that of a winning team in some sport. A comprehensive bibliography of one-dimensional problems solved before Spring, 1965, along with a brief discussion of classical statistical mechanics in one dimension, can be found in a book by Lieb and Mattis.³

The phenomena of phase transitions, such as condensation, is often observed in two- and three-dimensional problems. By choosing the more simple one-dimensional analog, these phenomena are usually ruled out, as has been discussed by several authors.⁴⁻⁶ However, there are some important ideas to be gained from the study of one-dimensional systems. Firstly, one-dimensional models can be useful

as tests of mathematical techniques designed to be used on the more difficult higher dimensional problems. Secondly, though few in nature, there are some real systems which are nearly linear. Adsorption along a polymer chain might be an example of this type problem. Thirdly, phase transitions are presumably possible for certain systems which contain a potential of infinite range,^{7,8} a singular potential,⁹ or a potential which is not a simple sum of finite many-body potentials, such as in the cell cluster model of Fisher.¹⁰

Most such one-dimensional systems studied have dealt with molecules having translational freedom.^{4-8,10-12} In the present work, we will study systems which possess both translational and rotational coordinates, in an attempt to clarify the contributions of the rotational degree of freedom to various thermodynamic properties.

. LATTICE GAS MODEL

Lattice models have been employed frequently as a basis for the description of dense fluids.¹³ Neece¹⁴ has made use of a lattice model to study a system of hard line rotators, conceived as a possible model for nematic liquid crystals.

The model discussed in this section consists of a one-dimensional lattice, each site of which is occupied by a "non- (square) spherical molecule" represented by a square. Each molecule (square) is allowed to rotate about its center, the only interaction present being the (infinitely) hard core potential. This model was chosen because it seemed to be the simplest possible model possessing rotational correlations and many-body effects, even to the exclusion of the translational degree of freedom.

The square edge is set equal to one for convenience, and the lattice separation will be denoted by a . (Hence, all lengths are measured in units of the square edge.) The canonical ensemble partition function then is

$$Q(N,L,T) = \Lambda^{-N} \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} \exp(-\epsilon/kT) d\theta_1 \dots d\theta_N, \quad (1-1)$$

where $\Lambda = h/(2\pi I kT)^{1/2}$, I being the moment of inertia, and the energy, ϵ , is defined by

$$\epsilon = \begin{cases} 0 & \text{if no molecules overlap} \\ \infty & \text{if any molecules overlap.} \end{cases}$$

As usual, k is the Boltzmann constant, h is Planck's constant, and T is the absolute temperature; L is the length of the system, which for

the lattice model is just proportional to the number N of molecules. Since also the hard core potential does not allow discrimination between different (finite) temperatures, there is only one independent variable, which we take to be the lattice spacing $a = L/N$. The factor of Λ^{-N} in Equation (1-1) results from the integration of the momentum part of the partition function, leaving the configurational part to be evaluated. In this case we are dealing with angular momentum due to the rotational nature of the model under study. The limits, $(-\pi/4 \text{ to } \pi/4)$, define the domain of distinguishable rotations of the molecules. The rotations are indicated by θ_i , as shown in Figure 1. The direction of positive rotation is taken as being counterclockwise. In Figure 2, we show three possible configurations for the system where the middle configuration is for the case, $a = [1 + (2)^{\frac{1}{2}}]/2$, which will be denoted by a_0 .

The integrand, $\exp(-\epsilon/kT)$, may be written as $\prod_{i=1}^{N-1} K(\theta_i, \theta_{i+1}, a)$

where

$$K(\theta_i, \theta_{i+1}, a) = \begin{cases} 0 & \text{if molecule } i \text{ and } i+1 \text{ overlap} \\ 1 & \text{otherwise.} \end{cases}$$

This particular factorization is peculiar to systems of hard molecules and is a principal reason for their study. It can also be of use in dealing with the high temperature limit of real systems when attractive forces are of little importance. A related sort of factorization occurs whenever the forces are pairwise additive.

If periodic boundary conditions are imposed (essentially the cylinder convention in one dimension, or $N + 1 \equiv 1$), the partition function can be evaluated by taking the trace of the N^{th} iterate

Figure 1. Defining relations for two adjacent molecules at contact.
As shown, θ_2 is positive and θ_1 negative. In the text,
the pair (θ_1, θ_2) is often replaced by (θ, φ) .

Figure 2. Sample rotational configurations. The top configuration is for $a > a_0$, the middle one for $a = a_0$, and the bottom one for $a < a_0$. As indicated by the middle diagram, $a_0 = (1 + \sqrt{2})/2$.

of the symmetric kernel K . (See Appendix I for further details.)

We have

$$\begin{aligned}\Lambda^N Q(N, L, T) &= \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} K(\theta_1, \theta_2; a) K(\theta_2, \theta_3; a) \dots K(\theta_N, \theta_1; a) d(1, N) \\ &= \int K^{(N)}(\theta_1, \theta_1) d\theta_1 \\ &= \text{tr} K^{(N)}.\end{aligned}\tag{1-2}$$

We shall use the abbreviation $d(1, N)$ to stand for $d\theta_1, d\theta_2, \dots, d\theta_N$.

By taking the limit of the trace as N approaches infinity, we obtain the expression

$$\lim_{N \rightarrow \infty} (\text{tr} K^{(N)})^{1/N} = \lambda, \tag{1-3}$$

where λ is the dominant (largest) eigenvalue of the integral equation

$$\lambda u(\theta) = \int_{-\pi/4}^{\pi/4} K(\theta, \varphi) u(\varphi) d\varphi. \tag{1-4}$$

We can express the partition function as

$$\lim_{N \rightarrow \infty} [\Lambda^N Q(N, L, T)]^{1/N} = \lambda = e^{-\beta A/N},$$

where $\beta = 1/kT$. Solving for the Helmholtz free energy we get

$$A = -NkT \ln \lambda. \tag{1-5}$$

We will suppress the momentum contributions to the thermodynamic functions (given by Λ) and always interpret the symbols to refer to the configurational part. The fundamental thermodynamic relationship

$$dA = -SdT - pdL + \mu dN$$

yields three useful representations of further thermodynamic properties:

$$S = -(\partial A / \partial T)_{L,N}; \quad p = -(\partial A / \partial L)_{T,N}; \quad \mu = (\partial A / \partial N)_{T,L} \quad (1-6a)$$

From Equations (1-5) and (1-6a) we obtain

$$\begin{aligned} S/Nk &= +\ell n \lambda, \\ p/kT &= d\ell n \lambda / da, \end{aligned} \quad (1-6b)$$

and

$$\mu/kT = -S/Nk + p/kT a,$$

which gives us a working set of equations.

We must concentrate on finding the dominant eigenvalue λ and its derivative; the latter, as we shall see, will require that we also compute the corresponding dominant eigenvector. These are both determined by the properties of the symmetric kernel $K(\theta, \varphi)$.

Referring to Figure 1, we need to express the allowed and non-allowed rotation angles, θ and φ , as a function of the lattice parameter, a . This is a purely geometrical problem. The equations of the lines through points 1 and 2 and through points 3 and 4 are

$$y_{12} = \frac{1}{2} \text{Csc} \theta - x \text{Cot} \theta$$

and

$$y_{34} = -\frac{1}{2} \text{Csc} \varphi + (a-x) \text{Cot} \varphi$$

respectively. At the point of intersection (molecules just touching) the x -coordinate is obtained by setting y_{12} equal to y_{34} to give

$$x = \frac{a \cot \varphi - \frac{1}{2}(\csc \theta + \csc \varphi)}{\cot \varphi - \cot \theta}.$$

But this abscissa must be the x-coordinate of one of the points 1-4, and this observation leads to the following possible relationships between θ , φ , and a :

$$\begin{aligned} \cos(\theta - \varphi + \pi/4) &\geq (2a \cos \varphi - 1)/\sqrt{2} & |\theta| > |\varphi| & \theta < 0 \\ \cos(\theta - \varphi - \pi/4) &\geq (2a \cos \varphi - 1)/\sqrt{2} & |\theta| > |\varphi| & \theta > 0 \\ \cos(\theta - \varphi + \pi/4) &\geq (2a \cos \theta - 1)/\sqrt{2} & |\theta| < |\varphi| & \varphi > 0 \\ \cos(\theta - \varphi - \pi/4) &\geq (2a \cos \theta - 1)/\sqrt{2} & |\theta| < |\varphi| & \varphi < 0 \end{aligned} \quad (1-7)$$

The inequalities refer to allowed configurations, and the equalities hold when the molecules are exactly touching, so that these expressions delineate the boundary between the regions in which the kernel, $K(\theta, \varphi)$, assumes its two values, zero and one. Boundaries for several values of the lattice parameter are shown in Figure 3.

Unfortunately, an analytic solution of Equation (1-4) has not been discovered, but a numerical solution can be obtained from a corresponding set of linear algebraic equations.¹⁵ Equation (1-4) can be approximated by

$$\lambda u(\theta) \approx \sum_{i=1}^n K(\theta, \varphi_i) u(\varphi_i) \Delta \varphi_i,$$

where the φ_i 's are discrete values of rotation imagined in the range $(-\pi/4, \pi/4)$. They will always be taken to be equally spaced, so that $\Delta \varphi_i = \pi/2n$. Requiring both sides to be equal at the same n points chosen, we obtain a set of n linear equations

Figure 3. Region of allowed rotations for several values of the lattice parameter a . The values of a are 1.02, 1.05, 1.1, 1.15, 1.18, 1.207, 1.23, 1.25, 1.3, 1.35, and 1.4, increasing outward from the origin. For each value of a , the interior region (containing the origin) is the allowed region.

ϕ

θ

$$\lambda^\dagger u(\theta_k) = \sum_{i=1}^n K(\theta_k, \varphi_i) u(\varphi_i), \quad k = 1, 2, \dots, n, \quad (1-8)$$

where $\lambda^\dagger = 2n\lambda/\pi$. Assuming the scheme to be convergent, the approximation is better for larger values of n .

The problem is now reduced to a matrix eigenvalue equation $\lambda^\dagger \underline{u} = \underline{K} \underline{u}$, where the elements $K(\theta_k, \varphi_i) \equiv K_{ki}$ are either one or zero as determined by the inequality relations of Equations (1-7), and u_k is the n -component approximation to $u(\theta_k)$. Physically, the matrix formulation could be considered to correspond to a restriction of molecular orientations to a discrete set, somewhat analogous to the lattice restriction of the translational coordinates.

To calculate $\lambda^\dagger$ and $\underline{u}$ by this scheme, an iterative process¹⁵ is used. An initial guess $\underline{x}^{(1)}$ is made for $\underline{u}$; operating on $\underline{x}^{(1)}$ with the matrix $\underline{K}$ gives

$$\begin{aligned} \underline{K} \underline{x}^{(1)} &= \underline{y}^{(1)} \\ &\cong \lambda^\dagger \underline{x}^{(1)}. \end{aligned}$$

We will repeat this operation, using normalized $\underline{y}^{(1)}$ as the next approximation $\underline{x}^{(2)}$ to $\underline{u}$. As the number of iterations increases, the vector $\underline{x}^{(j)}$ will converge to $\underline{u}$, provided $\underline{x}^{(1)}$ is not orthogonal to $\underline{u}$. The convergence is followed by the differences in the components of successive approximate vectors. When the maximum difference is less in absolute value than a specified tolerance, usually 10^{-7} , the convergence is considered to be complete.

Having, in principle, found the maximum eigenvalue and its corresponding eigenfunction, we will now find the derivative of λ

with respect to a . Returning to general, exact relationships, we can solve for λ from Equation (1-4), provided that we have normalized eigenfunctions, to obtain

$$\lambda = \iint u(\theta) K(\theta, \varphi) u(\varphi) d\theta d\varphi \quad (1-9)$$

(Unless otherwise indicated, all definite integrals are from $-\pi/4$ to $\pi/4$. It should also be understood that K and u are also functions of the parameter a , although this dependence is usually suppressed.)

The derivative is given by

$$\begin{aligned} d\lambda/da = & \iint u'(\theta) K(\theta, \varphi) u(\varphi) d\theta d\varphi + \iint u(\theta) K(\theta, \varphi) u'(\varphi) d\theta d\varphi \\ & + \iint u(\theta) K'(\theta, \varphi) u(\varphi) d\theta d\varphi, \end{aligned}$$

where primes indicate a partial derivative with respect to a at constant angles. Using Equation (1-4) we can write the derivative as

$$\begin{aligned} d\lambda/da = & \lambda \int u'(\theta) u(\theta) d\theta + \lambda \int u(\varphi) u'(\varphi) d\varphi + \iint u(\theta) K'(\theta, \varphi) u(\varphi) d\theta d\varphi \\ = & \lambda d/da [\int u^2(\theta) d\theta] + \iint u(\theta) K'(\theta, \varphi) u(\varphi) d\theta d\varphi. \end{aligned}$$

The first term is zero since the integral is identically one for all a , due to the normalization of the eigenfunctions. The derivative is then given by the one term

$$d\lambda/da = \iint u(\theta) K'(\theta, \varphi) u(\varphi) d\theta d\varphi.$$

We should point out that this result is similar to that of the Hellman-Feynman Theorem of quantum mechanics, relating the rate of change of the energy to the derivative of the Hamiltonian.

This integrand presents something of a problem since there exists a boundary on which $K(\theta, \varphi)$ is discontinuous due to the infinite potential. The boundary is the only place the derivative

will have any non-zero value since $K(\theta, \varphi)$ is constant in the other regions.

However, the problem is not insurmountable. Since $K(\theta, \varphi)$ is either zero or one, λ can be expressed equivalently as

$$\lambda = \frac{Y(a)}{X(a)} \int_{\alpha(\theta, a)}^{\beta(\theta, a)} d\theta \int u(\theta) u(\varphi) d\varphi$$

where $X(a)$ and $Y(a)$ are limits on θ , and $\alpha(\theta, a)$ and $\beta(\theta, a)$ are limits on φ for specified θ , which may be obtained from Equation (1-7). The derivative is

$$\begin{aligned} d\lambda/da &= Y'(a) \int_{\alpha[Y(a), a]}^{\beta[Y(a), a]} u[Y(a)] u(\varphi) d\varphi - X'(a) \int_{\alpha[X(a), a]}^{\beta[X(a), a]} u[X(a)] u(\varphi) d\varphi \\ &+ \int_{X(a)}^{Y(a)} d\theta [\beta'(\theta, a) u(\theta) u\{\beta(\theta, a)\}] - \int_{X(a)}^{Y(a)} d\theta [\alpha'(\theta, a) u(\theta) u\{\alpha(\theta, a)\}] \\ &+ \int_{X(a)}^{Y(a)} d\theta \int_{\alpha(\theta, a)}^{\beta(\theta, a)} d\varphi [u'(\theta) u(\varphi) + u(\theta) u'(\varphi)], \end{aligned}$$

where the primes have the same meaning as before. It should be remembered that the eigenfunctions are implicitly dependent upon a . The first two integrals are $Y'(a) \lambda u^2[Y(a)] - X'(a) \lambda u^2[X(a)]$. Using symmetry, the last integral is

$$\begin{aligned} 2\lambda d/da \int_{X(a)}^{Y(a)} d\theta u(\theta) u'(\theta) &= \lambda \{ d/da \int_{X(a)}^{Y(a)} u^2(\theta) d\theta \\ &- Y'(a) u^2[Y(a)] + X'(a) u^2[X(a)] \} \\ &= -Y'(a) \lambda u^2[Y(a)] + X'(a) \lambda u^2[X(a)] \end{aligned}$$

which exactly cancels the first two integrals. Hence the derivative is

$$\begin{aligned}
d\lambda/da &= \int_{X(a)}^{Y(a)} [\beta'(\theta, a) u(\theta) u\{\beta(\theta, a)\}] d\theta \\
&- \int_{X(a)}^{Y(a)} [\alpha'(\theta, a) u(\theta) u\{\alpha(\theta, a)\}] d\varphi.
\end{aligned} \tag{1-10}$$

From the first of Equations (1-7) α' is given in the indicated region by

$$\alpha' = (2)^{\frac{1}{2}} \cos \varphi / [\sin(\theta - \varphi + \pi/4) + (2)^{\frac{1}{2}} a \sin \varphi],$$

where $\varphi = \alpha(\theta, a)$ is determined implicitly by the same equation. The analytic forms of α' in the other regions, as well as those of β' , are obtained just as simply from the remaining equations.

It is apparent that the final expression for $d\lambda/da$ may be viewed as a line integral around the perimeter of the region for which $K(\theta, \varphi) = 1$. It should also be realized that for $a > a_0$ there is no contribution from the straight boundaries $\theta, \varphi = \pm\pi/4$, since the integrand there vanishes; or equivalently, if configuration space were allowed to be infinite and doubly periodic, these lines would not be boundaries at all.

The integrals of Equation (1-10) are actually evaluated as sums, using the previously determined eigenvector, to obtain the eigenvalue derivative. We now have enough information to calculate the first order thermodynamic properties of the system by way of Equation (1-6b).

The equation of state so obtained is shown in Figure 4 to possess a van der Waals type "loop", including a region of mechanical instability ($\partial p / \partial \rho < 0$). Such behavior is associated with the use of

Figure 4. Equation of state for the lattice model. The cusp is at $a = a_0$, or $(1 + \sqrt{2})/2$. The tie line connects the densities 0.823 and 0.862 (both ± 0.005), at $\beta p = 7.78 \pm 0.05$. The pressure is identically zero for $\rho < 1/\sqrt{2}$ and diverges at $\rho = 1$.

the canonical ensemble and an implicit or explicit restriction of molecular configurations to those with uniform density throughout the system.¹⁶ The cusp indicated in the low density side of the loop appears to occur at a lattice spacing of a_0 . This spacing is the smallest value of a for which a molecule may rotate completely if both neighbors cooperate. The cusp appears to be of finite height since the height increases slightly for increasing matrix size until a slight decrease is observed, as indicated in Table I. The size of the matrix is indicated by n , and βp is the pressure at a_0 .

The entropy versus density curve is shown in Figure 5. The relationship between the entropy and the equation of state should be noted; that is, from the set of Equations (1-6b), we see that

$$p/kT = d(S/Nk)/da.$$

Thus the equation of state can be obtained from the slope of the entropy curve.

The standard remedy for the mechanical instability is to exclude single-phase densities in this range through the construction of a double tangent to the entropy curve. The two points of double tangency define the end points of a tie line connecting two states having different densities but the same chemical potential. The slope of the double tangent corresponds to the common pressure at which the two "phases" coexist. As usual, this construction also excludes metastable densities near the densities of the coexisting phases, as well as the unstable region. We find 7.78 ± 0.05 for the

TABLE I

CUSP HEIGHT AS A FUNCTION OF MATRIX SIZE

Matrix Size	$(p/kT)_{a=1.2071}$
40	9.6827
100	10.1750
200	10.2450
400	10.2420
800	10.2269
1000	10.2143
1200	10.2071
1600	10.2001
2000	10.1941
2400	10.1895
2800	10.1854

Figure 5. Entropy as a function of density for the lattice model.

The pressure may be obtained from the negative slope.

common pressure (divided by kT) of the two equilibrated phases, having densities of 0.823 and 0.862 ± 0.005 , as shown in Figure 4.

It is also possible to construct the tie line by applying the Maxwell Equal Area Theorem¹⁷ which requires equal areas above and below the tie line in the pressure-volume curves.

As indicated in the Introduction, phase separations are ordinarily absent in one-dimensional systems. It might be instructive to outline the features of the present model which are responsible for the anomalous behavior in the pressure-density curve.

Most general theorems regarding the behavior of eigenvalues and eigenfunctions of integral operators such as K are based on the assumption that the operator is at least a continuous function of its main arguments (θ and φ), as well as of any parameters present $[a]$. Since K is clearly discontinuous in its dependence on these variables, such theorems are not applicable and do not provide any information about the existence or absence of thermodynamic singularities. We cannot conclude, for example, that the eigenvalue λ (and hence, p/kT) is a single-valued analytic function of the distance parameter a .

Such analyticity in fact does not appear to be present for our model. At the expense of mathematical rigor we can gain an accurate qualitative understanding of the behavior to be expected from the solution of Equation (1-4) by viewing the eigenvalue $\lambda(a)$ as the (weighted) area of the region in which $K = 1$, as shown by Equation (1-9). In the same way we regard $p/kT = \lambda^{-1} d\lambda/da$ as the (weighted) ratio of perimeter to area of this region, as indicated

by Equation (1-10). Since both perimeter and area change continuously with the length parameter a , we would expect the pressure to be a continuous function of a . The divergence of pressure as a approaches one corresponds to the fact that the perimeter-to-area ratio of a region becomes boundless as the size shrinks to zero.

The rate of change of this ratio, however, must be expected to behave singularly at a_0 , when the expanding region just touches the boundary $|\theta|, |\varphi| = \pi/4$. Thus the pressure should be a differentiable function of a , except at a_0 .

We should point out that the pressure as here defined is not the same as that computed in usual lattice gas calculations because of the manner in which it is obtained, by varying the lattice parameter a . In fact, at this stage of the study the meaning of the pressure is obscure. Hopefully, in the next section we will be able to understand its significance more clearly.

GENERALIZED MODEL

To introduce translational freedom we allow the lattice restriction to be relaxed to include a general "nearest-neighbor" interaction between the molecules in addition to the hard core. By "nearest-neighbor" interaction, we mean the interaction between adjacent molecules, the distance over which the interaction takes place not necessarily being the same for two different pairs of molecules. No direct interaction exists between a pair of molecules separated by another, regardless of the position of the molecules. Takahashi⁴ has developed the formalism for a non-rotating "nearest-neighbor" gas with a general potential. The treatment which follows will use Takahashi's development as a guideline.

Again we will study a system of N rotating molecules, represented by squares, whose centers lie on a line. If we assume there exists a general nearest-neighbor potential energy, $U(\xi, \theta)$, defined by the positions and rotations of the molecules, the canonical partition function becomes

$$Q(N, L, T) = \Lambda^{-(N-1)} \int_0^L \dots \int_0^L d\xi \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} d\theta \exp[-\beta U(\xi, \theta)],$$

where $\xi_i = x_{i+1} - x_i$. The integrations are subject to the restraint

$$\sum_{i=1}^{N-1} \xi_i = L = x_N - x_1, \quad (2-1)$$

where x_i is the coordinate of the i^{th} molecule; the symbol ξ stands for $\{\xi_1, \xi_2, \dots, \xi_{N-1}\}$, and θ stands for $\{\theta_1, \theta_2, \dots, \theta_{N-1}\}$. The total

length (volume) of the system is L , now a true independent variable, and $\Lambda = h^2/2\pi mkT(mI)^{1/2}$ contains the additional factor of $h/(2\pi mkT)^{1/2}$ from the integration of the rectilinear momentum part of the partition function. It should be recognized that the periodic boundaries imposed in the lattice model are absent here.

By changing from the canonical partition function to an isobaric partition function, the cumbersome restriction, (2-1), is removed. We have

$$\begin{aligned}\Gamma(N, p, T) &= \int_0^\infty Q(N, L, T) \exp(-pL/kT) dL \\ &= \Lambda^{-(N-1)} \int_0^\infty d\xi \int_{-\pi/4}^{\pi/4} d\theta \exp[-\beta U^*(\xi, \theta)],\end{aligned}$$

where

$$U^*(\xi, \theta) = U(\xi, \theta) + p \sum_i \xi_i,$$

and p is the one-dimensional pressure which, as we shall see, is quite different in character from that of the lattice model.

Observing that $U(\xi, \theta)$ can be written as

$$U(\xi, \theta) = \sum_{i=1}^{N-1} u(\xi_i, \theta_i, \theta_{i+1}),$$

we can write the exponential factor $\exp[-\beta U^*(\xi, \theta)]$ as

$$\begin{aligned}\exp[-\beta U^*(\xi, \theta)] &= \prod_{i=1}^{N-1} \exp[-\beta u(\xi_i, \theta_i, \theta_{i+1}) - \beta p \xi_i] \\ &= \prod_{i=1}^{N-1} K(\xi_i, \theta_i, \theta_{i+1}).\end{aligned}$$

The partition function can then be written as

$$\Gamma(N, p, T) = \Lambda^{-(N-1)} \int_0^\infty \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} \prod_{i=1}^{N-1} K(\xi_i, \theta_i, \theta_{i+1}) d\xi_i d\theta_i.$$

If we define

$$\begin{aligned} \tilde{K}_p(\theta_i, \theta_{i+1}) &= \int_0^\infty K(\xi_i, \theta_i, \theta_{i+1}) d\xi_i \\ &= \int_0^\infty K_{\xi}(\theta_i, \theta_{i+1}) \exp[-\beta p \xi] d\xi, \end{aligned} \quad (2-2)$$

where

$$K_{\xi}(\theta_i, \theta_{i+1}) = \exp[-\beta u(\xi, \theta_i, \theta_{i+1})],$$

the partition function becomes

$$\Gamma(N, p, T) = \Lambda^{-(N-1)} \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} \prod_{i=1}^{N-1} \tilde{K}_p(\theta_i, \theta_{i+1}) d\theta_i.$$

For a simple check we will look at the ideal gas where

$K_{\xi}(\theta_i, \theta_{i+1}) \equiv 1$. The partition function is

$$\Gamma(N, p, T) = (2\pi mkT/h^2)^{N/2} (2\pi IkT/h^2)^{N/2} (\pi/2)^N (kT/p)^N$$

The first two terms come from integrating the momentum part of the partition function. The last two come from the configurational part, the latter from integration over ξ and the former from integration over θ .

The characteristic equation for the isobaric partition function is¹⁸

$$dG = -SdT + Ldp + \mu dN, \quad (2-3)$$

where $G = -kT \ln \Gamma$ is the Gibbs free energy. From these two equations, we obtain for L ,

$$\begin{aligned} L &= (\partial G / \partial p)_{T,N} \\ &= -kT (\partial \ln \Gamma / \partial p)_{T,N} \\ &= NkT/p, \end{aligned}$$

which is the ideal equation of state.

For Takahashi's non-rotating "nearest-neighbor" gas we find $K_{\xi} = \exp[-\beta U(\xi)]$. $\tilde{K}_p$ is

$$\tilde{K}_p = \int_0^{\infty} \exp[-\beta\{U(\xi) + p\xi\}] d\xi$$

and

$$L = \frac{N \int_0^{\infty} \xi \exp[-\beta\{U(\xi) + p\xi\}] d\xi}{\int_0^{\infty} \exp[-\beta\{U(\xi) + p\xi\}] d\xi},$$

which is the same expression for L as that obtained by Takahashi.

Tonks¹¹ studied a gas of hard rods free to translate along a line subject to the impenetrable hard core diameter σ , which in one dimension is the length of the rod.

The first model we will describe in this section will be essentially a Tonks' gas with the molecules represented by squares instead of rods. (hereafter referred to as free translator). The molecules are allowed to rotate, thus giving some rotational dependence to the hard core diameter, σ . We might think of σ as being the resultant of two terms, one due to the hard core length of the

molecule (in this case, we will choose one again) and another which is dependent upon the rotational angles of adjacent molecules.

Returning to the series of Equations (2-2) we can write for the free translator

$$K_{\xi}(\theta_i, \theta_{i+1}) = \begin{cases} 1 & \xi_i > \sigma(\theta_i, \theta_{i+1}) \\ 0 & \text{otherwise} \end{cases},$$

which gives rise to the following integral for $\tilde{K}_p(\theta_i, \theta_{i+1})$:

$$\begin{aligned} \tilde{K}_p(\theta_i, \theta_{i+1}) &= \int_{\sigma(\theta_i, \theta_{i+1})}^{\infty} \exp(-\beta p \xi) d\xi \\ &= \exp[-\beta p \sigma(\theta_i, \theta_{i+1})] / \beta p. \end{aligned}$$

The partition function is

$$\Gamma(N, p, T) = \Lambda^{-N} \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} \prod_{i=1}^N \exp[-\beta p \sigma(\theta_i, \theta_{i+1})] / \beta p d\theta_i,$$

where $N-1$ is for convenience replaced by N for large N . The functional form of $\sigma(\theta_i, \theta_{i+1})$ is obtained by solving for σ from one of the set of Equations (1-7). Again we have not been able to evaluate Γ analytically. However, we can apply the same technique used in the last section.

We recall that we can find an asymptotic evaluation of the partition function from the largest eigenvalue of an appropriate integral equation. Providing that we have a normalized eigenvector, the eigenvalue is

$$\lambda = \int_{-\pi/4}^{\pi/4} \dots \int_{-\pi/4}^{\pi/4} u(\theta) \tilde{K}_p(\theta, \varphi) u(\varphi) d\theta d\varphi. \quad (2-4)$$

The only difference between this equation and that of the lattice model is the kernel, $\tilde{K}_p(\theta, \varphi)$. Here we have a somewhat more complex but continuous kernel; whereas in the lattice model the kernel was discontinuous on the boundary.

From Equation (2-3) and the fact that $\partial n\Gamma$ is equal to $N\partial n\lambda$, we obtain our set of working equations:

$$L/N = -kT(\partial n\lambda/\partial p)_T; \quad \mu/kT = -\partial n\lambda, \quad (2-5)$$

where we consider only those contributions which are configurational in origin. Thus, again we need to find the maximum eigenvalue and its derivative, this time with respect to pressure at constant temperature, or equivalently with respect to the variable βp .

Returning to Equation (2-4), the eigenvalue was found by using the matrix approximation as in Part One. The derivative, however, turns out to be simpler. It can be expressed as the double integral

$$(\partial \lambda / \partial p)_T = \int_{-\pi/4}^{\pi/4} \int u(\theta) [\partial \tilde{K}_p(\theta, \varphi) / \partial p]_T u(\varphi) d\theta d\varphi,$$

where the other terms cancel, again because of symmetry and the use of normalized eigenfunctions. The derivative of the kernel is easily determined to be

$$[\partial \tilde{K}_p(\theta, \varphi) / \partial p]_{T,N} = \exp[-\beta p \sigma(\theta, \varphi)] [-\sigma(\theta, \varphi)/p - 1/\beta p^2].$$

The derivative of the eigenvalue then becomes

$$\begin{aligned}
(\partial\lambda/\partial p)_{T,N} &= \int_{-\pi/4}^{\pi/4} \int_{-\pi/4}^{\pi/4} u(\theta) \exp[-\beta p \sigma(\theta, \varphi)] [-\sigma(\theta, \varphi)/p - 1/\beta p^2] u(\varphi) d\theta d\varphi \\
&= -\lambda/p - (1/p) \int_{-\pi/4}^{\pi/4} \int_{-\pi/4}^{\pi/4} u(\theta) \sigma(\theta, \varphi) \exp[-\beta p \sigma(\theta, \varphi)] u(\varphi) d\theta d\varphi.
\end{aligned}$$

Combining this derivative with Equation (2-5), we find for the equation of state,

$$L/N = 1/\beta p + (1/\beta p \lambda) \int_{-\pi/4}^{\pi/4} \int_{-\pi/4}^{\pi/4} u(\theta) \sigma(\theta, \varphi) \exp[-\beta p \sigma(\theta, \varphi)] u(\varphi) d\theta d\varphi,$$

where the double integral is, in fact, to be evaluated as a double sum, using the numerically determined eigenvector of the matrix representing $\tilde{K}_p$.

The equation of state is shown in Figure 6, indicated by the circles in any one of the graphs. The most striking feature of this model is the absence of the phase transition found by the lattice approximation. Further discussion of the properties of the free translator model will be taken up as the high temperature limit of a harmonic model to be considered next.

We have just presented a Tonks' gas with rotational effects included. Koppel¹⁹ has studied a generalized Tonks' gas where the rods were connected with springs. He evaluated the canonical partition function by the elegant but laborious method of steepest descents. Northcote and Potts²⁰ showed later that an equivalent evaluation can be accomplished more simply by transforming to an isobaric partition function as we have just presented. No phase transition was found by either investigation. The following model is treated in essentially

Figure 6. Equations of state for the generalized model. The three diagrams correspond to different values of the parameter b , which locates the position of the minimum of the harmonic potential, and consequently the reciprocal density at low temperatures. Each diagram contains eight isotherms shown as lines, representing temperatures defined by FC values of 0.01, 0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0. The isotherms occur in this order from left to right in the lower part of each diagram; the order becomes inverted, however, at high pressures, as shown most clearly for $b = 1.6$. The high temperature limit is the free translator model for which circles are shown lying near the $FC = 0.01$ isotherm. The low temperature limit would be a vertical line at density b^{-1} .

the same manner as that of Northcote and Potts, extended to accommodate the rotational degree of freedom.

For the free translator model, the "nearest-neighbor" potential was zero unless the molecules were bumping into each other. We will now consider a model which replaces the zero part of the free translator potential with the potential of a Hooke's Law spring of force constant f (hereafter referred to as square-springs model). If we let b be the distance between adjacent molecules at their potential energy minimum, the "nearest-neighbor" potential takes the following form:

$$u(\xi_i, \theta_i, \theta_{i+1}) = \begin{cases} (f/2)(\xi_i - b)^2 & \xi_i > \sigma(\theta_i, \theta_{i+1}) \text{ for all } i \\ \infty & \text{otherwise,} \end{cases}$$

where $\sigma(\theta_i, \theta_{i+1})$ is the same as in the free translator. Then, from Equation (2-2) we have

$$K_{\xi}(\theta_i, \theta_{i+1}) = \begin{cases} \exp[-(\beta f/2)(\xi_i - b)^2] & \xi_i > \sigma(\theta_i, \theta_{i+1}) \\ 0 & \text{otherwise} \end{cases}$$

and

$$\tilde{K}_p(\theta_i, \theta_{i+1}) = \int_{\sigma(\theta_i, \theta_{i+1})}^{\infty} \exp[-\beta\{(f/2)(\xi - b)^2 + p\xi\}] d\xi.$$

This integral can be expressed as the complement of an error function²¹ to give

$$\tilde{K}_p(\theta_i, \theta_{i+1}) = \frac{1}{2}(\pi/FC)^{\frac{1}{2}} \exp[(\beta p)^2/4FC - \beta p b] \operatorname{erfc}[\{2FC(\sigma - b) + \beta p\}/2(FC)^{\frac{1}{2}}],$$

where

$$\operatorname{erfc}(x) = (2/\sqrt{\pi}) \int_x^{\infty} \exp[-t^2] dt,$$

and FC is our second independent variable,

$$FC \equiv \beta f/2.$$

Evaluation of the partition function is the same as in the free translator case, except for a different form of $\tilde{K}_p(\theta_i, \theta_{i+1})$. Knowing numerically the eigenvalue and the corresponding eigenfunction for the pressure derivative, we can arrive at the equation of state:

$$\begin{aligned} L/N = & -\beta p/2FC + b + (1/2FC\lambda) \int_{-\pi/4}^{\pi/4} \int u(\theta) \\ & \exp[-FC(\sigma - b)^2 - \beta p \sigma] u(\varphi) d\theta d\varphi. \end{aligned} \quad (2-6)$$

Several isotherms for three values of b are presented in Figure 6. We make the following observations:

- a) There appears to be no evidence of a phase transition.
- b) The density obeys the following relationship, which can be proven analytically (see Appendix II):
- c) At low densities the pressure approaches that due to springs alone and can be predicted by

$$-\beta p \cong 2FC(\rho^{-1} - b).$$

(See Appendix IIIB for a description of a model consisting only of springs.) A negative pressure corresponds to stretching the springs apart (positive tension).

- d) The graphs seem to show that as FC increases the density approaches b^{-1} . This is especially evident in the set of graphs where b equals 1.6, and the isotherms are shown crossing each other. (See e) below.) For a proof that the density does in fact approach b^{-1} when FC approaches infinity, see Appendix IV.
- e) In light of d) above, we observe that if the density is less than b^{-1} , then it increases as FC increases. If, however, the pressures are sufficiently large so that the density is greater than b^{-1} , then it decreases as FC increases, reflecting a negative coefficient of thermal expansion. Physically, these two trends are interpreted as a consequence of a search for the potential energy minimum as the temperature decreases.
- f) Finally, we notice that as FC approaches zero, the isotherms approach those of the freely translating model, represented by the circles.

It might be well to point out that an understanding of the trends c) through f) is essential to a subsequent discussion of the thermal properties of this model.

We have already investigated the high temperature limit of the square-springs model as the free translator. We know from observation d) that the equation of state in the low temperature limit of the square-springs model approaches a vertical line at a density of b^{-1} . We will now look at the low temperature limit of an expression which is dependent only upon the rotational effects present.

Rewriting Equation (2-6) in the following way,

$$\beta p = (1/\lambda) \iint u(\theta) \exp[-FC(\sigma-b)^2 - \beta p \sigma] u(\varphi) d\theta d\varphi - 2FC(L/N-b),$$

we have an expression for the pressure in which the first term on the right results primarily from the short-range repulsive forces. The second term is the harmonic contribution which we can easily understand. We want to look more closely at the behavior of the first term, since it contains the rotational contributions to the pressure.

If we define βp^* as

$$\beta p^* \equiv \beta p + 2FC(L/N - b),$$

we can show that (see Appendix VA for proof)

$$\beta p^* \xrightarrow{FC \rightarrow \infty} \beta p^{LAT},$$

where βp^{LAT} is the pressure obtained in the lattice model with the parameter a set equal to b . It should be recognized that this pressure βp^* in general depends on both the temperature (FC) and the total pressure (βp).

That βp^* should approach βp^{LAT} is intuitively obvious since with very low temperature the system becomes more and more lattice-like. We should also admit that the present treatment is not really correct in this limit, since at low temperatures the vibrations should be treated quantum mechanically instead of classically.

We have calculated βp^* for increasing FC (decreasing temperature) and a few values of b . Figure 7 shows βp^* plotted against density for FC equal to 1, 5, 10, 20, 50, 100, 500, and 1000, where the range of βp is the same for each FC . Notice that as FC increases,

Figure 7. Low temperature convergence of the pressure increment due to rotation. The quantity plotted as a function of density is the total pressure less the contribution attributable to the harmonic forces, or βp^* as discussed in the text. The different b values were chosen so that the limiting densities would be representative of the two-phase and one-phase regions of Figure 4. Each line is an isotherm representing the dependence of βp^* on the total pressure βp , which varies from 4 to 12 in each instance. For $b = 1.1$, the FC values from left to right are 1, 5, 10, 20, 50, 100, 500, and 1000. The decreasing sensitivity of βp^* to total pressure should be noted; at the lowest temperatures (FC = 500 and 1000) the calculated points have been omitted altogether for clarity. The isotherms occur in the same order for the other b values, except for the two lowest temperatures in the two-phase region. The limit points approximated by the FC = 1000 isotherms, should be compared with the lattice curve shown in Figure 4.

there is a decrease in the pressure dependence of βp^* . There also seems to be some peculiar behavior in the curves for FC equal to 500 and 1000 for b values in the neighborhood of 1.2 (the phase transition occurred at $a \cong 1.207$ in the lattice model). If we take a closer look at one isotherm ($FC = 1000$, $b = 1.2$) by expanding the scale and the range of βp , we obtain a graph of the type shown in Figure 8. "Van der Waals" loops of this sort may be obtained at sufficiently low temperatures as long as the densities are in the vicinity of the phase transition (0.81-0.85). For moderate pressure ranges, this means a value of b^{-1} in the same range, 0.81-0.85.

The appearance of the graph in Figure 8 is misleading because of the very expanded scale. If we use a more reasonable scale, we obtain a small portion of a larger, more complete graph which spans the entire density range. A few of these small portions are indicated by the points in Figure 9. Referring back to relation (d) discussed earlier, it is easy to see why we are able to get only a small part of the density curve from a single value of b for any large value of FC.

Remembering that we have proved (Appendix VA) that βp^* approaches βp^{LAT} (at $a = b$) with increasing FC, we can obtain βp^* over the full density range more simply by merely varying b . A variation of b amounts to changing the shape of the intermolecular potential and at first seems decidedly non-physical. However, a further examination of relation (b) will justify this approach.

Relation (b) says that the density at a particular set of variables b , FC , and βp , is equal to the density at a different value

Figure 8. Rotational pressure increment over an expanded pressure range. To obtain curves of this sort, two requirements must be met: the temperature must be low enough to localize the molecules and the pressure must be extreme enough to produce a significant variation in density. Here, the total pressure p_p for the points shown varies from 0 to 54.

Figure 9. Clarification of the approach to the lattice limit. The lines represent the variation of βp^* produced by changes in the parameter b ; in each case, the total pressure βp is zero. The three temperatures shown in order of increasing structure are for $FC = 100, 500$, and $10,000$. The circles all belong to another low temperature, $FC = 1000$, and reflect the dependence of βp^* on total pressure with fixed parameter b . Three b values are illustrated by sets of circles ($1.3, 1.2$, and 1.1 from left to right), although in principle one b value would suffice to map the entire isotherm. Computational difficulties attending the extreme pressures required render this approach unfeasible. For comparison, the lattice curve from Figure 4 is included but displaced vertically for clarity.

of b , same FC , and the original β_p plus a correction. All that we need show is that β_p^* is the same in either case. By definition, β_p^* for the original set of conditions is

$$\beta_p^* = \beta_p + 2FC(L/N-b).$$

For the second set of conditions, we have

$$\begin{aligned}\beta_p^* &= \beta_p - 2FC(b-b') + 2FC(L/N-b') \\ &= \beta_p + 2FC(L/N-b).\end{aligned}$$

Thus β_p^* is the same for both sets of conditions and should best be considered as a function of FC and L/N . We have shown then that a variation of b is equivalent to a change of pressure. Since the full density range is numerically more easily obtained by a variation of b , we will adopt that procedure to study the convergence of β_p^* to β_p^{LAT} .

The results of such calculations for $FC = 100, 500$, and $10,000$, are shown in Figure 9 as lines along with those of the lattice model for comparison. The lattice model curve has been displaced upward for the sake of clarity. The points, indicated by the circles, calculated by varying β_p for $FC = 1000$ would fall on the corresponding line obtained by varying b if it had been plotted. The agreement between β_p^{LAT} and β_p^* appears to be good except for the region near the transition. However, the loop does begin to form as the temperature decreases. We estimate the "critical temperature" to be about $FC = 500$, above which the isotherms have no region of instability.

The asymptotic convergence of βp^* to βp^{LAT} is especially slow at $b = a_0$. In Table II, we show various calculated values of βp^* as FC was increased to extremely large values.

Still trying to gain a better physical insight as to exactly what βp^* represents, we suggest the following procedure. Observing that βp^{LAT} should be the pressure due to rotation, we might intuitively suggest a factorization of the partition function such as

$$\Gamma^{\text{Sq-S}}(N, p, T) \cong \Gamma^{\text{RS}}(N, p, T) Q^{\text{ROT}}(N, p, T),$$

where RS stands for a rods and springs model. The RS model is essentially Koppel's model¹⁹ and is equivalent to the square-springs model without any rotational freedom. Thus, $\sigma(\theta_i, \theta_{i+1})$, the distance of closest approach of adjacent molecules, is a constant, namely the length of the molecule. A complete description of the RS model can be found in Appendix IIIA. The translational partition function is Γ^{RS} , and Q^{ROT} is the rotational partition function.

Assuming the factorization is meaningful, we have

$$\beta p^{\text{Sq-S}} = \beta p^{\text{RS}} + \beta p^{\text{ROT}}.$$

Intuitively again we could suggest that

$$Q^{\text{ROT}}(N, p, T) \cong Q^{\text{LAT}}(a = \rho_{\text{RS}}^{-1}),$$

where ρ_{RS} is the density determined by Γ^{RS} at (N, p, T) . We hope to show then that $\beta p^{\text{ROT}} \cong \beta p^{\text{LAT}}$.

From Appendix IIIA we see that ρ^{RS} can be calculated rather simply. Thus, βp^{ROT} is most easily determined by calculating ρ_{RS} with very small βp^{RS} increments and then matching ρ_{RS} with $\rho_{\text{Sq-S}}$

TABLE II
CONVERGENCE OF βp^* to βp^{LAT} AT $b = a_0$ ^a

βp^*	ρ	FC	n ^b
7.508	0.83707	10^2	40
7.169	0.83037	5×10^2	40
7.397	0.82905	10^3	40
8.086	0.82870	5×10^3	40
8.373	0.82849	10^4	40
8.936	0.82843	5×10^4	80
9.113	0.82843	10^5	80
9.358	0.82843	5×10^5	80
9.417	0.82843	10^6	80
9.745	0.82850	5×10^6	200
9.894	0.82850	10^7	200

- a. See Table I for lattice model values.
b. The choice of matrix size is dependent upon both economy and accuracy.

as closely as possible. By definition, βp^{ROT} is equal to the difference between the Sq-S and RS pressures when the densities are equal.

We need to compare βp^{ROT} with βp^* . From our previous definitions of βp^* and βp^{ROT} , we have

$$\beta p^* = \beta p^{\text{Sq-S}} + 2FC(\rho^{-1}-b)$$

and

$$\beta p^{\text{ROT}} = \beta p^{\text{Sq-S}} - \beta p^{\text{RS}},$$

where the densities are the same for each model. By eliminating $\beta p^{\text{Sq-S}}$ from these two equations, we obtain

$$\beta p^* = \beta p^{\text{ROT}} + \beta p^{\text{RS}} + 2FC(\rho^{-1}-b). \quad (2-7)$$

Substituting the expression for βp^{RS} developed in Appendix VB into Equation (2-7) results in the explicit relationship between the two "pressures",

$$\beta p^* = \beta p^{\text{ROT}} + \frac{2(FC)^{\frac{1}{2}} \exp[-FC(1-b)^2 - \beta p]}{(\pi)^{\frac{1}{2}} \exp[(\beta p)^2/4FC - \beta p b] \operatorname{erfc}[\{2FC(1-b) + \beta p\}/2(FC)^{\frac{1}{2}}]}.$$

It is also shown in Appendix VB that the last term in this equation approaches zero as FC approaches infinity, which enables us to write the limiting equation,

$$\beta p^* \xrightarrow{FC \rightarrow \infty} \beta p^{\text{ROT}}.$$

This term in question, however, is precisely the pressure contribution from the hard core (diameter one) of a non-rotating molecule. There was no such contribution to the pressure in the lattice model, which suggests that βp^{ROT} should converge more rapidly than

βp^* to βp^{LAT} . Furthermore, since the contribution of the hard core term should be more important at high densities, we should expect better agreement between βp^* and βp^{ROT} in the low density region.

In Tables III, IV, and V, βp^* and βp^{ROT} are compared at FC values of 10, 50, and 100, respectively. The values of βp^{LAT} corresponding to the indicated densities are also tabulated, having been obtained by graphical interpolation. The tables indicate that βp^{ROT} is indeed a better approximation to βp^{LAT} than is βp^* . We also see that βp^* does approach βp^{ROT} more rapidly at lower densities.

The usefulness of βp^{ROT} is somewhat masked by the fact that βp^* has essentially converged to βp^{ROT} before the approximate "critical temperature" of $FC = 500$ is reached. Since βp^* is also more easily computed than βp^{ROT} , most correlations have been based on βp^* . However, the fact that βp^{ROT} is in better agreement with βp^{LAT} than is βp^* , especially at the lower values of FC, does strengthen our interpretation of the significance of the pressure calculated by the lattice model technique; namely, this pressure should be regarded as the pressure increment due to molecular rotations.

The implied singular behavior of the square-springs model as $FC \rightarrow \infty$ is of interest in connection with the general theory of phase transitions. Unlike the kernel considered in connection with the lattice model, the present kernel is analytic in its dependence on the configuration variables θ and φ as well as on the thermodynamic parameters βp and FC. It therefore falls into the category of analytic, strictly positive, kernels such as considered by Kac.²² As with most one-dimensional assemblies, then, the generalized model now under

TABLE III
COMPARISON OF βP^{ROT} , βP^* , AND βP^{LAT}

FC = 10

βP^{ROT^a}	βP^{*^a}	βP^{LAT^b}	ρ
1.8	2.2	0.2	.709
2.5	3.2	0.9	.736
3.3	4.3	1.6	.760
4.1	5.6	2.4	.783
5.0	6.9	3.9	.803
5.8	8.3	8.5	.823
6.5	9.8	7.5	.842
7.3	11.3	7.8	.857
8.0	12.9	8.3	.872
8.8	14.6	8.9	.884
9.5	16.3	9.6	.895
10.3	18.1	10.4	.904
11.0	19.9	11.2	.912
11.8	21.8	12.2	.919
12.5	23.6	13.2	.925

a. Computed with matrix size $n = 40$.

b. Computed with matrix size $n = 200$.

TABLE IV
COMPARISON OF βP^{ROT} , βP^* , AND βP^{LAT}

FC = 50

βP^{ROT^a}	βP^{*^a}	βP^{LAT^b}	ρ
0.3	0.3	0.0	.674
0.9	0.9	0.2	.710
1.5	1.5	0.7	.727
2.2	2.2	1.1	.745
2.6	2.6	1.4	.745
3.1	3.1	1.6	.763
4.1	4.2	2.3	.780
5.1	5.3	3.4	.798
6.2	6.5	5.6	.816
7.2	7.8	7.8	.834
8.1	9.3	7.7	.853
9.1	11.0	8.3	.870
10.1	12.9	9.0	.885
11.1	15.2	10.0	.899
12.3	17.7	11.1	.911
13.5	20.5	12.5	.921

a. n = 40.

b. n = 200.

TABLE V
COMPARISON OF β_P^{ROT} , β_P^* , AND β_P^{LAT}

FC = 100

$\beta_P^{\text{ROT}^a}$	$\beta_P^{*^a}$	$\beta_P^{\text{LAT}^b}$	ρ
0.8	0.8	0.5	.717
1.0	1.0	0.7	.727
1.4	1.4	0.9	.737
1.8	1.8	1.2	.747
2.3	2.3	1.4	.757
2.8	2.8	1.8	.767
3.5	3.5	2.1	.777
4.1	4.2	2.6	.787
4.9	4.9	3.3	.797
5.6	5.6	4.4	.808
6.3	6.3	6.4	.819
7.0	7.1	8.2	.830
7.6	7.8	7.5	.842
8.2	8.5	7.7	.853
8.9	9.4	8.0	.864
9.6	10.5	8.5	.875
10.4	11.7	9.1	.886
11.2	13.2	9.7	.896
12.2	14.9	10.5	.905
13.2	16.9	11.5	.914

a. n = 40.

b. n = 200.

consideration should not exhibit any singularities or phase separations at any finite values of the thermodynamic parameters. Anomalous behavior is not precluded, however, as the parameters become infinitely large ($p \rightarrow \infty$ or $T \rightarrow 0$).

The discussion so far has been limited largely to the mechanical properties of the system. We would also like to investigate some of the thermal properties such as energy, entropy, and heat capacity. To do this, we will have to develop some additional thermodynamic equations.

As stated earlier, Equation (2-3), the Gibbs free energy is related to the dominant eigenvalue of the appropriate kernel by

$$G = -NkT \ln \lambda;$$

this relationship, together with the general thermodynamic equations

$$E = G + TS - pL$$

and

$$dG = -SdT + Ldp + \mu dN,$$

suffice to determine all other thermodynamic properties. We can thus express the energy as

$$E = -NkT \ln \lambda + TS - pL, \quad (2-8)$$

the entropy as

$$S = -(\partial G / \partial T)_{p,N},$$

and the length as

$$L = (\partial G / \partial p)_{T,N}.$$

The expression for energy now becomes

$$E = -NkT\ell\lambda + NkT\ell\lambda + NkT^2(\partial\ell\lambda/\partial T)_{p,N} + pNkT(\partial\ell\lambda/\partial p)_{T,N},$$

or

$$E/NkT = T(\partial\ell\lambda/\partial T)_{p,N} + p(\partial\ell\lambda/\partial p)_{T,N}.$$

For convenience, we will write these partial derivatives in terms of our canonical variables βp and FC instead of p and T . Using the chain rule for differentiation, we have

$$\begin{aligned} E/NkT &= T[(\partial\ell\lambda/\partial FC)_{\beta p}(-FC/T) + (\partial\ell\lambda/\partial\beta p)_{FC}(-\beta p/T)] \\ &\quad + p[(\partial\ell\lambda/\partial\beta p)_{FC}(\beta)] \\ &= -FC(\partial\ell\lambda/\partial FC)_{\beta p}. \end{aligned} \tag{2-9}$$

Now that we have an expression for energy, we can easily calculate the entropy from Equation (2-8) as

$$S/Nk = E/NkT + pL/NkT + \ell\lambda, \tag{2-10}$$

where $L/N = \rho^{-1}$ is given by Equation (2-5).

We can choose two routes for developing an expression for the heat capacity, one by way of the entropy and one by way of the enthalpy. We choose to take the latter path, returning to the entropy route later as a check on the calculated heat capacities.

Since enthalpy is

$$H = E + pL,$$

by means of Equations (2-5) and (2-9) we can immediately write

$$H/NkT = -FC(\partial\ell\lambda/\partial FC)_{\beta p} - \beta p(\partial\ell\lambda/\partial\beta p)_{FC}.$$

Dividing through by FC, we obtain

$$\tilde{H} = -(\partial \ln \lambda / \partial FC)_{\beta p} - (\beta p / FC)(\partial \ln \lambda / \partial \beta p)_{FC},$$

where $\tilde{H} \equiv 2H/Nf$. To calculate the constant pressure heat capacity, we take the partial derivative of $\tilde{H}$ with respect to T at constant pressure and convert to canonical variables, arriving at

$$\begin{aligned} 2C_p / Nf &= (\partial \tilde{H} / \partial T)_p \\ &= (\partial \tilde{H} / \partial FC)_{\beta p} (dFC/dT) + (\partial \tilde{H} / \partial \beta p)_{FC} (\partial \beta p / \partial T)_p \\ &= -(FC/T)(\partial \tilde{H} / \partial FC)_{\beta p} - (\beta p / T)(\partial \tilde{H} / \partial \beta p)_{FC}, \end{aligned}$$

which can be rearranged to yield

$$C_p / Nk = -(FC)^2 (\partial \tilde{H} / \partial FC)_{\beta p} - (FC)(\beta p)(\partial \tilde{H} / \partial \beta p)_{FC}. \quad (2-11)$$

Performing the appropriate derivatives, we obtain

$$\begin{aligned} C_p / Nk &= (FC)^2 [\partial^2 \ln \lambda / \partial (FC)^2]_{\beta p} + 2(FC)(\beta p) [\partial^2 \ln \lambda / \partial \beta p \partial FC] \\ &\quad + (\beta p)^2 [\partial^2 \ln \lambda / \partial (\beta p)^2]_{FC}. \end{aligned}$$

This last expression for C_p / Nk is not easily evaluated because of the second derivatives of the eigenvalue. In terms of bra-ket notation, the eigenvalue λ and its first derivative are

$$\lambda = \langle u | K | u \rangle$$

and

$$\lambda' = \langle u | K' | u \rangle,$$

respectively. The second derivative contains terms such as $\langle u' | K' | u \rangle$ which do not vanish and are not cancelled by other terms. To evaluate these terms requires a knowledge of the implicit

dependence of the eigenfunction on the variables FC and βp . We can, however, perform the derivatives of Equation (2-11) numerically and evaluate the heat capacity by adding the two results together.

We have calculated energies for the three models, Sq-S, RS, and one which consists only of springs. The latter model treats molecules as mass points and so has no hard core. We will refer to this model as SP (see Appendix IIIB for a further description). It should be remembered that we are discussing only the configurational contributions to the energy; the momenta would contribute an additional $NkT/2$ (from the equipartition theorem) for the RS and SP models and NkT for the Sq-S model.

Using Equation (2-9) and the appropriate expression for λ , the energy equations for the three models are

$$(E/NkT)_{Sq-S} = \frac{1}{2} + (\beta p)^2/4FC + (1/2\lambda) \iint u(\theta) [-\beta p/2FC + \sigma - b] \exp[-FC(\sigma-b)^2 - \beta p\sigma] u(\varphi) d\theta d\varphi,$$

$$(E/NkT)_{RS} = \frac{1}{2} + (\beta p)^2/4FC + (1/2\tilde{K}_p^{RS})(1 - b - \beta p/2FC) \exp[-FC(1-b)^2 - \beta p],$$

and

$$(E/NkT)_{SP} = \frac{1}{2} + (\beta p)^2/4FC.$$

The results of the energy calculations are shown in Figures 10 and 11, plotted against density. There are three sets of curves on each graph. On the first graph, each set of curves consists of one curve for each model at a particular value of b . On the second graph, each set consists of a curve for each model at a particular value of FC.

Figure 10. Energy as a function of density for the Sq-S, RS, and SP models at constant $FC = 1.0$. Each set of three curves from left to right is for $b = 1.6$, 1.2071 , and 1.1 .

Figure 11. Energy as a function of density for the Sq-S, RS, and SP models at constant $b = 1.2071$. Each set of three curves from left to right is for $FC = 0.5, 1.0$, and 2.0 .

We notice the following trend for all the graphs at a common density:

$$E_{SP} > E_{RS} > E_{Sq-S}.$$

This trend can be readily explained. The energy is actually an average potential energy. We are using a Hooke's Law potential, so the average potential energy can be written as

$$\langle \text{potential energy} \rangle \propto \langle (\xi-b)^2 \rangle,$$

where $\langle \text{----} \rangle$ indicates an average property. Thus, $\langle (\xi-b)^2 \rangle$ is the average of the square of the distance between neighboring molecules. The trend in energies given above then implies

$$\langle (\xi-b)^2 \rangle_{SP} > \langle (\xi-b)^2 \rangle_{RS} > \langle (\xi-b)^2 \rangle_{Sq-S}$$

even though the densities, $\langle \xi-b \rangle$, are equal. These trends are in the reverse order of the hard core effects of the different models. The hard core effects are greatest in the Sq-S model, less in the RS model, and nonexistent in the SP model. Thus, we can conclude that as the hard core effects are increased, the density fluctuations decrease and result in the energy trends shown in the graphs.

The difference in the energies of the Sq-S and RS models is a result of the reduced density fluctuations in the Sq-S model, which has an effective hard core diameter greater than one because of the rotations present. As in the pressure studies, the difference between these two models best points up the thermodynamic significance of the molecular rotations. In this instance, we see that providing a mechanism for an increase in the effective range of the

repulsive part of the intermolecular potential actually results in a statistical lowering of the collective potential energy of all the molecules.

Although the analogy cannot be pushed too far, the present results do call to mind the first order condensation of a fluid of hard spheres to a more dense solid state. This condensation may be visualized as resulting from a statistical attraction between nearby hard molecules.

The configurational heat capacities have been obtained from Equation (2-11) by a numerical differentiation using the method of finite differences²³ for the free translator and square-springs models.

The free translator heat capacity is shown in Figure 12. The configurational part of the energy is identically zero, and so the enthalpy is simply the pL term which has the ideal value NkT at low densities. Thus, the heat capacity is very nearly one at low density. It increases as the density increases, goes through a slight maximum at a density of approximately 0.89, and then approaches two at higher densities. The maximum was investigated to re-examine the possibility of a phase transition missed in the study of the mechanical properties. There appears to be no discontinuity in either the heat capacity or its derivative with respect to $1/\beta p$. The height of the maximum remains relatively constant as the matrix approximation is improved by increasing n , the size of the matrix. The slight maximum is presumably a vestige of the transition present in the lattice model.

Figure 12. Constant pressure heat capacity of the free translator.

The branches at high density are shown to illustrate the convergence with increasing matrix size. From top to bottom, the matrix size n is 40, 120, and 200. The actual calculated values are shown as a magnification to the left of the curves.

The heat capacities for the square-springs model are shown in Figures 13 and 14 for b values of 1.1 and 1.3, respectively. Each curve is at constant βp with FC varying.

In Figure 13 we notice that there is a hump in the heat capacity in the same region as that of the free translator for the smaller values of βp . However, as βp increases, the small maximum is no longer observed. The disappearance can be explained by an intuitive observation that the heat capacity of the square-springs model must approach that of the free translator at the same βp as FC approaches zero (high temperature). The limiting values for selected constant βp lines are shown as filled triangles. As βp changes from small positive values to larger values, the limiting value of the heat capacity increases. Thus, the heat capacity corresponding to higher βp values increases sharply with a decrease in density, and we fail to observe the small maximum.

We notice a different behavior of the graphs corresponding to zero and negative pressures. They, too, show the maximum but have a different limiting value as FC decreases. The free translator model has no corresponding zero or negative pressure. For these pressures the limiting value of the heat capacity should approach that of the springs model (Appendix IIIB). The heat capacity of the springs model is trivially one-half at any pressure. The graphs indicate this is the proper limit.

In Figure 14 we have changed the value of b . We notice that we have no maximum as before. This is easily understood by observing that the density is not in the right neighborhood (approximately

Figure 13. Constant pressure heat capacity for the Sq-S model as a function of density for $b = 1.1$. Each line represents constant βp and varying FC. For some values of βp the calculated values are given as circles to indicate the uncertainty inherent in the calculation. The filled triangles indicate the limiting value ($FC \rightarrow 0$) for the selected values of βp .

Figure 14. Constant pressure heat capacity for the Sq-S model as a function of density for $b = 1.3$. Each line represents constant β_p and varying FC. For some values of β_p the calculated values are given as circles to indicate the uncertainty inherent in the calculation. The filled triangles indicate the limiting value ($FC \rightarrow 0$) for the selected values of β_p .

0.85) to obtain the maximum. We observe the same limiting conditions as in the previous graph.

At this point it might be informative to point out a possible application of first-order perturbation theory to the basic integral equation problem.

All of our calculations depend upon the derivatives of the eigenvalue. Since we cannot write down an analytic expression for λ or its eigenfunction, we have resorted to numerical methods. First order thermodynamic properties can be satisfactorily obtained by the iterative matrix technique. However, the second order properties, such as heat capacity, are much less accessible because they require a derivative of the eigenfunction.

In certain limiting cases involving small values of βp and FC , we should certainly be able to write down a first-order correction to the zero-order eigenvalue since we would be required to know only the zero-order eigenfunction. Here we are using the term "order" in the perturbation theory sense; thus, if the zero-order state is $\beta p = FC = 0$, the zero-order eigenfunction is simply a constant.

Returning to the discussion of the thermal properties, we have computed entropies for the free translator and square-springs models by use of Equation (2-10). Results of these computations are shown plotted against density in Figure 15. Each curve was obtained by varying βp over approximately the same range, showing the reduced density range for higher FC . We observe the normal entropy relationship that as temperature increases (FC decreases), the entropy increases until in the limit of infinite temperature it reaches the free translator value.

Figure 15. Entropy of Sq-S and free translator models. Circles are shown for the Sq-S model at the indicated value of FC. The free translator is indicated by the triangles.

As we mentioned earlier, entropy can be used to calculate heat capacities just the same as enthalpy. An equivalent thermodynamic expression for heat capacity is

$$C_p = T(\partial S / \partial T)_p.$$

If we change variables to βp and FC , we obtain

$$C_p = -FC(\partial S / \partial FC)_{\beta p} - \beta p(\partial S / \partial \beta p)_{FC},$$

or equivalently

$$C_p / Nk = [\partial(S/Nk) / \partial \ln(1/FC)]_{\beta p} - [\partial(S/Nk) / \partial (\ln \beta p)]_{FC}. \quad (2-12)$$

For the free translator, only the second term exists. If we were to make a plot of the entropy versus $\ln \beta p$, the slope would be equal to the heat capacity. Such a plot is shown in Figure 16 where we have used $\ln(1/\beta p)$ instead of $\ln \beta p$ which changes the sign of the slope. For large βp we obtain a straight line with slope equal to 1.989 with a standard deviation of 0.003. We conclude from this that the heat capacity in the limit of high density is two (compare Figure 12).

For the Sq-S model, two plots must be made, one for each derivative in Equation (2-12), for each heat capacity value in question. A sample graph is given in Figure 17, where the upper portion is for constant FC and the lower portion for constant βp .

Two trends should be observed from these graphs:

- (1) At constant FC , the slope of the curve increases as βp increases, and

Figure 16. Entropy as a function of $-\ln p$ for the free translator.
The slope is equal to the heat capacity at constant pressure.

Figure 17. Entropy as a function of $\ln \beta_p$ and $-\ln \beta_C$ for the Sq-S model. The constant pressure heat capacity is obtained by adding the two slopes together.

(2) at constant βp , the slope decreases as FC decreases. Both of these trends indicate that the derivative with respect to $\ln \beta p$ in Equation (2-12) becomes the dominant term of the heat capacity for both limits, $p \rightarrow \infty$ and $FC \rightarrow 0$. Trend (2) indicates what we have intuitively observed before, that the heat capacity must approach the free translator value in the limit of infinite temperature.

The disappearance of the hump in Figure 13 as βp is increased can be explained in the following way. At small βp , the limiting value of the heat capacity as $FC \rightarrow 0$ occurs at low density. As βp is increased, the limiting value increases and also occurs at higher density. When this density passes through the density region in which the hump occurs, the limiting process completely obscures the maximum.

In going from the lattice model to the generalized model, we introduced temperature as a real thermodynamic variable. As we have seen earlier, our variable FC had to be taken to (extremely) high values to achieve relatively good agreement between βp^* and βp^{LAT} , the convergence being much better away from the transition region. We have also just seen that the Sq-S model approaches the free translator as $FC \rightarrow 0$. The convergence is again slow as we have to use very small values of FC in order to obtain satisfactory agreement.

DISCUSSION

It is difficult to escape the comparison of the lattice model with cell models of liquids.¹³ In such models, the assumption that cell centers form a regular lattice structure is commonly made. When considering the motion of a central molecule, an additional approximation which restricts the cage of neighboring molecules to their cell centers is made in the more elementary models. This restriction of motion neglects the correlations between neighboring molecules. However, it is precisely these correlations which are of the utmost importance in our model.

Cell models in general have been shown to be more descriptive of the solid state rather than the liquid state. More likely than not, this is the case with the lattice model. The two phases in equilibrium with each other could be looked upon as two distinct solid state phases. As a matter of fact, the lattice model was indeed conceived, at least initially, as a very simple description of a solid state phase known as the rotator phase.²⁴ At some temperature below the melting point, some substances exhibit a first order phase transition which corresponds to the onset of hindered molecular rotations. Methane, methyl alcohol, and cyclohexane are examples. Thus, we might postulate that the high density phase corresponds to a strict solid phase and the low density phase to a rotating solid phase.

At the end of the lattice model section, we commented that the pressure βp^{LAT} was different from ordinary lattice-gas calculations.

In the generalized model section we tried to determine the nature of this pressure. We have shown that βp^{LAT} is actually better defined as a pressure increment due to rotation.

We might think of the pressure as being made up of two parts, one of a rotational nature having its origin in the non-spherical part of the molecules, and one of a translational nature arising from the spherical part of the molecules. The natural question to ask is what are the relative contributions of each type.

One fairly safe conclusion can be made. Since the rotations are dependent upon the asymmetry of the molecules, we can say that the more asymmetric molecules will, in general, have a larger rotational contribution to the pressure. The models we have considered possess a relatively high asymmetry as far as rotations are concerned, and we have observed a large contribution to the total pressure. Ordinarily, the rotational contributions should probably be small, though by no means insignificant, compared to the translational contributions. The relative importance of the rotational contributions would also seem to be the greatest when the rotations are neither terribly difficult nor ridiculously easy.

The models considered in this work will hopefully spur further effort to obtain more descriptive models of physical systems. One extension of this work which should be possible, but admittedly difficult, is the analogous two-dimensional problem. With some modification, the two-dimensional model could be a good description for liquid crystalline systems. We would need to introduce a new variable to allow for interactions between molecules in different rows. Most

important would be an additional length parameter to allow for rod-like molecules since liquid crystals are usually long and slender molecules.

APPENDIX I

EVALUATION OF THE TRACE OF THE Nth ITERATE OF

$K(\theta, \varphi)$ BY WAY OF THE DOMINANT EIGENVALUE²⁵

Referring back to Equation (1-3), we would like to prove the limit,

$$\lim_{N \rightarrow \infty} (\text{tr} K^{(N)})^{1/N} = \lambda,$$

which arose in connection with the integral equation,

$$\lambda u(\theta) = \int_a^b K(\theta, \varphi) u(\varphi) d\varphi,$$

where $K(\theta, \varphi)$ is a symmetric kernel. By symmetric kernel we mean that

$$K(\theta, \varphi) = K(\varphi, \theta).$$

We will assume the equation has solutions $u_1(\theta), u_2(\theta), \dots, u_n(\theta), \dots$, which correspond to the eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_n, \dots$, so that we have

$$\lambda_n u_n(\theta) = \int_a^b K(\theta, \varphi) u_n(\varphi) d\varphi. \quad (\text{I-1})$$

Without loss of generality we may assume that $\{u_n(\theta)\}$ is an orthonormal set of functions.

If we also assume that the kernel, $K(\theta, \varphi)$, can be expressed as a convergent expansion in terms of the 'dyads' $u_n(\theta)u_n(\varphi)$, we have

$$K(\theta, \varphi) = \sum_n u_n(\theta) u_n(\varphi) \lambda_n.$$

Replacing φ by α in the above equation, multiplying through by $K(\alpha, \varphi)$, and integrating over α yields

$$\int_a^b K(\theta, \alpha) K(\alpha, \varphi) d\alpha = \int_a^b K(\alpha, \varphi) \sum_n u_n(\theta) u_n(\alpha) \lambda_n d\alpha.$$

The left hand side of this last equation is called the first iterated kernel and is denoted by $K^{(2)}(\theta, \varphi)$. By using Equation (I-1) and the orthogonality of the eigenfunctions, we can write $K^{(2)}(\theta, \varphi)$ as

$$K^{(2)}(\theta, \varphi) = \sum_n \lambda_n^2 u_n(\theta) u_n(\varphi).$$

Applying the same procedure to the above equation,

$$\int_a^b K(\alpha, \varphi) K^{(2)}(\theta, \alpha) d\alpha = \int_a^b K(\alpha, \varphi) \sum_n \lambda_n^2 u_n(\theta) u_n(\alpha) d\alpha,$$

we obtain the second iterated kernel,

$$K^{(3)}(\theta, \varphi) = \sum_n \lambda_n^3 u_n(\theta) u_n(\varphi).$$

By repeated application of this process, we could obtain in general

$$K^{(m)}(\theta, \varphi) = \sum_n \lambda_n^m u_n(\theta) u_n(\varphi).$$

We can write this last equation as

$$K^{(m)}(\theta, \varphi) / \lambda_1^m = u_1(\theta) u_1(\varphi) + \sum_{n \geq 2} (\lambda_n / \lambda_1)^m u_n(\theta) u_n(\varphi).$$

If the eigenvalues are ordered according to decreasing value, meaning especially that λ_1 is non-degenerate and greater than all other λ_n , then for very large m we can write as an asymptotic expression for $K^{(m)}(\theta, \varphi)$,

$$K^{(m)}(\theta, \varphi) \cong \lambda_1^m u_1(\theta) u_1(\varphi).$$

Taking the trace of this $(m-1)^{st}$ iterate of $K(\theta, \varphi)$, we find

$$\begin{aligned} \lambda_1^m &\cong \int_a^b K^{(m)}(\theta, \theta) d\theta / \int_a^b u_1^2(\theta) d\theta \\ &\equiv \text{tr } K^{(m)}, \end{aligned}$$

or equivalently

$$\lim_{m \rightarrow \infty} (\text{tr } K^{(m)})^{1/m} = \lambda_1.$$

We should point out that the use of subscripts with λ and u has been suppressed everywhere except in this Appendix. In the text, λ and u are used to refer to the dominant eigenvalue and its corresponding eigenfunction.

APPENDIX II

DENSITY DEPENDENCE ON THE PARAMETER b

We wish to prove the following relationship:

$$\rho(b, FC, \beta p) = \rho[b', FC, \beta p - 2FC(b - b')],$$

where b and b' are two different values of the length parameter occurring in Equation (2-6).

Equation (2-6) gives the inverse density in terms of the dominant eigenfunction $u(\theta)$ as

$$\rho^{-1} = -\beta p / 2FC + b + (1/2FC\lambda) \iint u(\theta) \exp[(-FC(\sigma - b))^2 - \beta p \sigma] u(\varphi) d\theta d\varphi,$$

where

$$\lambda = \frac{1}{2} \iint u(\theta) \left(\pi / FC \right)^{\frac{1}{2}} \exp\left[(\beta p)^2 / 4FC - \beta p b \right] \\ \operatorname{erfc}\left[\{2FC(\sigma - b) + \beta p\} / 2(FC)^{\frac{1}{2}} \right] u(\varphi) d\theta d\varphi,$$

and $\sigma(\theta, \varphi)$ is given by solving for a in Equation (1-7). The error function complement erfc is defined on page 30. We will simply substitute b' for b and $\beta p - 2FC(b - b')$ for βp into the expression for inverse density and show that an identity results.

Making the above substitutions, we find

$$\rho[b', FC, \beta p - 2FC(b - b')] = -\beta p / 2FC + b - b' + \\ (1/2FC\lambda') \iint u(\theta) \operatorname{NUM} u(\varphi) d\theta d\varphi, \quad (\text{II-1})$$

where

$$\operatorname{NUM} = \exp[-\beta p \sigma + 2FC\sigma(b - b') - FC(\sigma - b')^2]$$

and

$$\lambda' = \iint u(\theta) \frac{1}{2} \left(\pi / FC \right)^{\frac{1}{2}} \exp\left[\{\beta p - 2FC(b - b')\}^2 / 4FC - \beta p b' + 2FCbb' - 2FCb'^2 \right] \\ \operatorname{erfc}\left[\{2FC(\sigma - b') + \beta p - 2FCb + 2FCb'\} / 2(FC)^{\frac{1}{2}} \right] u(\varphi) d\theta d\varphi.$$

Algebraic simplification of these expressions for NUM and λ' gives

$$\text{NUM} = \exp(-\beta p \sigma + 2FC\sigma b - FC\sigma^2 - FCb'^2)$$

and

$$\lambda' = 2FC \exp(-FCb'^2 + FCb^2) \lambda.$$

Substituting these expressions back into Equation (II-1) gives

$$\begin{aligned} \rho[b', FC, \beta p - 2FC(b - b')] &= -\beta p / 2FC + b + (1/2FC\lambda) \iint u(\theta) \\ &\quad \exp[-FC(\sigma - b)^2 - \beta p \sigma] u(\varphi) d\theta d\varphi \\ &\equiv \rho(b, FC, \beta p) \end{aligned}$$

APPENDIX III

DESCRIPTION OF ADDITIONAL MODELS

A. Rods and Springs Model (RS)

As mentioned in the text, this model is exactly the one studied by Koppel.¹⁹ The descriptive technique is essentially that proposed by Northcote and Potts.²⁰

Referring back to the series of Equations (2-2), we are able to write $\tilde{K}_p$ for the RS model as

$$\tilde{K}_p^{RS} = \int_1^{\infty} \exp[-(\beta f/2)(\xi-b)^2 - \beta p \xi] d\xi. \quad (\text{III-1})$$

There is no angle dependence in $\tilde{K}_p^{RS}$ since rotations are not allowed in this model. Thus, the lower limit of the above integral is equal to the hard core length of one.

If we change variables by setting $y = \beta p(\xi-1)$, $\tilde{K}_p^{RS}$ is transformed into the standard form:

$$\tilde{K}_p^{RS} = (1/\beta p) \int_0^{\infty} \exp(-ay^2 + 2by + c) dy,$$

where

$$\begin{aligned} a &= FC/(\beta p)^2, \\ b &= FC/\beta p - FCb/\beta p + \frac{1}{2}, \\ c &= FC - 2FCb + \beta p + FCb^2, \end{aligned}$$

and FC is defined as

$$FC \equiv \beta f/2.$$

In this form, $\tilde{K}_p^{RS}$ may be expressed in terms of the error function complement:²¹

$$\tilde{K}_p^{RS} = \frac{1}{2}(\pi/FC)^{\frac{1}{2}} \exp[(\beta p)^2/4FC - \beta p b] \cdot \operatorname{erfc}[\{2FC(1-b) + \beta p\}/2(FC)^{\frac{1}{2}}].$$

We recall from Equation (2-5) that the density can be obtained from the partial derivative

$$\rho^{-1} = -(\partial \ln \lambda / \partial \beta p)_T$$

which, in this case, reduces to

$$\rho_{RS}^{-1} = -(\partial \ln \tilde{K}_p^{RS} / \partial \beta p)_T \quad (\text{III-2})$$

since λ is here proportional to $\tilde{K}_p^{RS}$. Performing this derivative of $\tilde{K}_p^{RS}$ to obtain the density gives

$$\rho_{RS}^{-1} = -\beta p / 2FC + b + \frac{\exp[-FC(1-b)^2 - \beta p]}{(\pi FC)^{\frac{1}{2}} \exp[(\beta p)^2/4FC - \beta p b] \operatorname{erfc}[\{2FC(1-b) + \beta p\}/2(FC)^{\frac{1}{2}}]}.$$

It may be seen that the description of the RS model may be obtained formally from that of the more general Sq-S model by considering the distance of closest approach σ to be constant and equal to one. Hence the difference between the two is precisely the rotational effects present in the Sq-S model. Qualitatively the RS model would be just as informative as far as translational or hard core effects are concerned.

B. Springs Model (SP)

In the springs model we treat the molecules as point masses, and thus we have no hard core repulsions present.

The equation corresponding to Equation (III-1) for the springs model is

$$\begin{aligned}
\tilde{K}_p^{SP} &= \int_{-\infty}^{\infty} \exp[-(\beta f/2)(\xi-b)^2 - \beta p \xi] d\xi \\
&= \int_{-\infty}^{\infty} \exp[-FC\xi^2 - (\beta p - 2bFC)\xi - FCb^2] d\xi.
\end{aligned}$$

Completing the square, we obtain

$$\tilde{K}_p^{SP} = \exp[(\beta p)^2/4FC - \beta p b] \int_{-\infty}^{\infty} \exp[-FC(\xi + \beta p/2FC - b)^2] d\xi,$$

where the integral is the standard form:

$$\int_{-\infty}^{\infty} \exp(-a^2 x^2) dx = (\pi)^{1/2}/a.$$

Thus, we obtain

$$\tilde{K}_p^{SP} = \exp[(\beta p)^2/4FC - \beta p b] (\pi/a)^{1/2}.$$

Taking the appropriate derivative, Equation (III-2), we arrive at the expression for the density,

$$\rho_{SP}^{-1} = -\beta p/2FC + b.$$

We would like to point out the following characteristics of this rather simple model:

- (a) The description of the SP model may be obtained formally from the Sq-S model by considering σ to be equal to $-\infty$.
- (b) Of the models considered, this is the only one completely describable in closed form and in terms of elementary functions.
- (c) A model of this type, generally described as an array of N harmonic oscillators, is usually treated with a canonical ensemble approach with $\beta p = 0$. The approach is much more cumbersome since it requires a normal mode analysis.

- (d) The coefficient of thermal expansion is zero, a general property of harmonic systems.

APPENDIX IV

LOW TEMPERATURE LIMIT OF THE DENSITY

We would like to prove relationship (d) of the discussion of the square-springs model. This relationship postulated that

$$\rho^{-1} \xrightarrow{FC \rightarrow \infty} b.$$

From Equation (2-6) the density expression is

$$\rho^{-1} = -\beta p / 2FC + b + (1/2FC) \iint u(\theta) \exp[-FC(\sigma-b)^2 - \beta p \sigma] u(\varphi) d\theta d\varphi,$$

where

$$\lambda = \iint u(\theta) \tilde{K}_p u(\varphi) d\theta d\varphi \quad (IV-1)$$

and

$$\tilde{K}_p = \frac{1}{2}(\pi/FC)^{\frac{1}{2}} \exp[(\beta p)^2 / 4FC - \beta p b] \operatorname{erfc}[\{\beta p + 2FC(\sigma-b)\} / 2(FC)^{\frac{1}{2}}].$$

The complement of the error function is defined as

$$\operatorname{erfc}(x) \equiv 2/(\pi)^{\frac{1}{2}} \int_x^{\infty} \exp(-t^2) dt.$$

If we look at limiting cases of $\operatorname{erfc}(x)$, we see that

$$\operatorname{erfc}(x) \xrightarrow{x \rightarrow \infty} 0$$

and

$$\operatorname{erfc}(x) \xrightarrow{x \rightarrow -\infty} 2,$$

so that we have for $\tilde{K}_p$,

$$\tilde{K}_p \xrightarrow{FC \rightarrow \infty} \begin{cases} 0 & b < \sigma \\ (\pi/FC)^{\frac{1}{2}} \exp[(\beta p)^2 / 4FC - \beta p b] & b > \sigma. \end{cases}$$

Returning to Equation (IV-1), we can write the limit of λ

as

$$\lambda \xrightarrow{FC \rightarrow \infty} (\pi/FC)^{\frac{1}{2}} \exp[(\beta p)^2 / 4FC - \beta p b] \iint u(\theta) u(\varphi) d\theta d\varphi,$$

the integration being over the region satisfying $\sigma(\theta, \varphi) < b$. Further, since the kernel $\tilde{K}_p$ becomes constant in this region, the eigenfunction $u(\theta)$ must reduce to the lattice model eigenfunction (for $a = b$). In particular, $u(\theta)$ becomes independent of FC in the low temperature limit, $FC \rightarrow \infty$.

Finally, the density limit may now be written as

$$\rho^{-1} \xrightarrow{FC \rightarrow \infty} -\beta p / 2FC + b + \frac{\iint u(\theta) \exp[-FC(\sigma-b)^2 - \beta p \sigma] u(\varphi) d\theta d\varphi}{2(\pi FC)^{\frac{1}{2}} \exp[(\beta p)^2 / 4FC - \beta p b] \iint u(\theta) u(\varphi) d\theta d\varphi}.$$

The last term on the right-hand side approaches zero, using the temperature independence of $u(\theta)$; of course, the first term also vanishes, leaving

$$\rho^{-1} \xrightarrow{FC \rightarrow \infty} b,$$

which is the relationship we set out to prove.

APPENDIX V

LOW TEMPERATURE LIMITS OF βp^* AND βp^{ROT}

A. Proof of the relationship $\beta p^* \xrightarrow{FC \rightarrow \infty} \beta p^{\text{LAT}}$.

From Equation (2-6) the density is again,

$$\rho^{-1} = -\beta p / 2FC + b + (1/2FC\lambda) \iint u(\theta) \exp[-FC(\sigma-b)^2 - \beta p \sigma] u(\varphi) d\theta d\varphi,$$

where

$$\lambda = \frac{1}{2}(\pi/FC)^{\frac{1}{2}} \iint u(\theta) \exp[(\beta p)^2/4FC - \beta p b] \operatorname{erfc}[\{\beta p + 2FC(\sigma-b)\}/2(FC)^{\frac{1}{2}}] u(\varphi) d\theta d\varphi.$$

As before, we will define βp^* as

$$\begin{aligned} \beta p^* &= \beta p + 2FC(\rho^{-1} - b) \\ &= (1/\lambda) \iint u(\theta) \exp[-\beta p \sigma - FC(\sigma-b)^2] u(\varphi) d\theta d\varphi \\ &\equiv \text{NUM}/\lambda^*, \end{aligned}$$

where

$$\text{NUM} = \iint u(\theta) (FC/\pi)^{\frac{1}{2}} \exp[-\beta p \sigma - FC(\sigma-b)^2] u(\varphi) d\theta d\varphi$$

and

$$\lambda^* = \frac{1}{2} \exp[(\beta p)^2/4FC - \beta p b] \iint u(\theta) \operatorname{erfc}[\{\beta p + 2FC(\sigma-b)\}/2(FC)^{\frac{1}{2}}] u(\varphi) d\theta d\varphi.$$

First, we will investigate the limiting expressions of λ^* as FC approaches infinity.

We have already used the limiting values of the λ^* integrand in Appendix IV. We found that, due to the behavior of erfc , the only region contributing to the total integral was that for which $\sigma(\theta, \varphi) < b$. Then we can write the limit of λ^* as

$$\lambda^* \xrightarrow{FC \rightarrow \infty} \exp(-\beta p b) \int_{\sigma < b} u(\theta) u(\varphi) d\theta d\varphi = \exp(-\beta p b) \lambda_{(b)}^{\text{LAT}},$$

where $\lambda_{(b)}^{\text{LAT}}$ is the eigenvalue of the lattice model at the lattice parameter a equal to b .

In the limit of FC approaching infinity, the only values of $\sigma(\theta, \varphi)$ that contribute to any extent to the integral in NUM are those close to b ; therefore, we can write

$$\text{NUM} \xrightarrow{FC \rightarrow \infty} \exp(-\beta p b) \int_{-\pi/4}^{\pi/4} u(\theta) d\theta \left[\int_{-\pi/4}^{\pi/4} u(\varphi) (FC/\pi)^{\frac{1}{2}} \exp[-FC\{\sigma(\theta, \varphi) - b\}^2] d\varphi \right].$$

The closest approach parameter $\sigma(\theta, \varphi)$, hereafter indicated by σ' , is not a monotonic function of the integration variable φ . Hence, we must split the integral over φ occurring in square brackets above into two parts as

$$[] = (FC/\pi)^{\frac{1}{2}} \left[\underbrace{\int_{-\pi/4}^0 u(\varphi) \exp[-FC(\sigma' - b)^2] d\varphi}_I + \underbrace{\int_0^{\pi/4} u(\varphi) \exp[-FC(\sigma' - b)^2] d\varphi}_{II} \right].$$

In integral I $\sigma(\theta, \varphi)$ is a monotone decreasing function of φ and in integral II is a monotone increasing function of φ . For a given θ , we will let $\varphi(\theta, \sigma')$ and $\bar{\varphi}(\theta, \sigma')$ be the positive and negative solutions of Equation (1-7) in terms of σ' and θ , respectively. Thus, in terms of previous notation occurring in Equation (1-10), we have the correspondence $\varphi(\theta, \sigma') \equiv \beta(\theta, \sigma')$ and $\bar{\varphi}(\theta, \sigma') \equiv \alpha(\theta, \sigma')$. Transforming I into an integral over σ' , we have

$$I = \int_{\sigma(\theta, \pi/4)}^{\sigma(\theta, 0)} u\{\bar{\varphi}(\theta, \sigma')\} \exp[-FC(\sigma' - b)^2] \left(\frac{\partial \bar{\varphi}}{\partial \sigma'} \right)_{\theta} d\sigma'$$

and in the limit

$$\begin{aligned}
I &\approx \int_{-\infty}^{\infty} (\text{same integrand}) d\sigma' \\
&= - \int_{-\infty}^{\infty} (\text{same integrand}) d\sigma' \\
&\approx -u\{\bar{\varphi}(\theta, b)\}(\partial\bar{\varphi}/\partial\sigma')_{\theta, \sigma'=b} \int_{-\infty}^{\infty} \exp[-FC(\sigma'-b)]^2 d\sigma' \\
&\equiv -u\{\alpha(\theta, b)\}\alpha'(\theta, b)(\pi/FC)^{\frac{1}{2}}
\end{aligned}$$

assuming b is in the range $[\sigma(\theta, 0), \sigma(\theta, -\pi/4)]$.

Similarly, for II we have

$$\begin{aligned}
II &= \int_{\sigma(\theta, 0)}^{\sigma(\theta, \pi/4)} u\{\varphi(\theta, \sigma')\} \exp[-FC(\sigma'-b)^2] (\partial\varphi/\partial\sigma')_{\theta} d\sigma' \\
&\approx \int_{-\infty}^{\infty} (\text{same integrand}) d\sigma' \\
&\approx u\{\varphi(\theta, b)\}(\partial\varphi/\partial\sigma')_{\theta, \sigma'=b} \int_{-\infty}^{\infty} \exp[-FC(\sigma'-b)]^2 d\sigma' \\
&\equiv u\{\beta(\theta, b)\}\beta'(\theta, b)(\pi/FC)^{\frac{1}{2}}
\end{aligned}$$

assuming b is in the range $[\sigma(\theta, 0), \sigma(\theta, \pi/4)]$.

Both I and II are approximately equal to zero if $\sigma(\theta, 0) > b$, i.e., if $|\theta| > Y(b)$, in terms of the notation of Equation (1-10). Thus, we have

$$\begin{aligned}
NUM &= \exp(-\beta p b) \left[\int_{X(b)}^{Y(b)} u(\theta) u\{\beta(\theta, b)\} \beta'(\theta, b) d\theta \right. \\
&\quad \left. - \int_{X(b)}^{Y(b)} u(\theta) u\{\alpha(\theta, b)\} \alpha'(\theta, b) d\theta \right] \\
&\equiv \exp(-\beta p b) [d\lambda_{(a)}^{LAT}/da]_{a=b},
\end{aligned}$$

and

$$\begin{aligned}
\beta p^* &\xrightarrow{FC \rightarrow \infty} \{[d\lambda_{(a)}^{LAT}/da]/\lambda_{(a)}^{LAT}\}_{a=b} \\
&= \beta p^{LAT}.
\end{aligned}$$

It should be noted that the proof assumes that b is in the physically interesting range $[1, (2)^{\frac{1}{2}}]$.

B. Proof of the relationship $\beta p^* \xrightarrow{FC \rightarrow \infty} \beta p^{ROT}$.

From Equation (2-7) the expression relating βp^* and βp^{ROT} is

$$\beta p^* = \beta p^{ROT} + \beta p^{RS} + 2FC(\rho^{-1} - b), \quad (V-1)$$

where βp^{RS} is obtained from the density expression for the RS model developed in Appendix IIIA as

$$\beta p^{RS} \equiv 2FC(b - \rho^{-1}) + \frac{2(FC)^{\frac{1}{2}} \exp[-FC(1-b)^2 \beta p]}{(\pi)^{\frac{1}{2}} \exp[(\beta p)^2 / 4FC - \beta p b] \operatorname{erfc}[\{2FC(1-b) + \beta p\} / 2(FC)^{\frac{1}{2}}]}.$$

Substituting this relation for βp^{RS} into Equation (V-1), we see that the difference between βp^* and βp^{ROT} is asymptotically ($FC \rightarrow \infty$) equal to

$$\beta p^* - \beta p^{ROT} \xrightarrow{FC \rightarrow \infty} 2(FC)^{\frac{1}{2}} \exp[-FC(1-b)^2 - \beta p] / (\pi)^{\frac{1}{2}} \exp(-\beta p b) \operatorname{erfc}(-\infty),$$

assuming $b > 1$. Since $\operatorname{erfc}(-\infty)$ is equal to two, the denominator is bounded away from zero while the numerator approaches zero. Hence, the term approaches zero, and in the limit as FC approaches infinity we have

$$\beta p^* \xrightarrow{FC \rightarrow \infty} \beta p^{ROT}.$$

We should notice also that the term expressing the difference between βp^* and βp^{ROT} also approaches zero as βp approaches $-\infty$ for constant finite FC . This behavior is related to the better agreement between βp^* and βp^{ROT} at low density than at high density as discussed on pages 40 and 41.

BIBLIOGRAPHY

1. E. Ising, Z. Physik. 31, 253 (1925).
2. L. Onsager, Phys. Rev. 65, 117 (1944).
3. E. W. Lieb and D. C. Mattis, Mathematical Physics in One Dimension (Academic Press, New York, 1966).
4. H. Takahashi, Proc. Phys.-Math. Soc. Japan, 24, 60 (1942).
5. G. Rushbrooke and H. Ursell, Proc. Cambridge Phil. Soc. 44, 263 (1948).
6. L. Van Hove, Physica 16, 137 (1950).
7. M. Kac, G. Uhlenbeck, and P. Hemmer, J. Math. Phys. 4, 216 (1963); J. Math. Phys. 4, 229 (1963); J. Math. Phys. (5), 60 (1964). G. Baker, Phys. Rev. 122, 1477 (1961); Phys. Rev. 126, 2071 (1962).
8. H. A. Gersch, Phys. Fluids 6, 599 (1963).
9. M. Baur and L. Nosanow, J. Chem. Phys. 37, 153 (1962).
10. M. Fisher, Proc. Centennial Conf. Phase Transformation, Kentucky, 1965.
11. L. Tonks, Phys. Rev. 50, 955 (1936).
12. F. Gursey, Proc. Cambridge Phil. Soc. 46, 182 (1950). T. Nagamiya, Proc. Phys.-Math. Soc. Japan, 22, 705 (1940); Proc. Phys.-Math Soc. Japan, 22, 1034 (1940).
13. J. A. Barker, Lattice Theories of the Liquid State (Pergamon, New York, 1963).
14. G. Neece, Dissertation, Duke University, 1964.
15. F. B. Hildebrand, Methods of Applied Mathematics (Prentice-Hall, Englewood Cliffs, 1965).
16. T. L. Hill, Statistical Mechanics (McGraw-Hill, New York, 1959), Appendix 9.
17. C. Maxwell, Collected Works (Dover, New York, 1952), Vol. II, p. 425.

18. T. L. Hill, Introduction to Statistical Thermodynamics (Addison-Wesley, Reading, 1960), Chap. 13.
19. D. Koppel, Phys. Fluids 6, 609 (1963).
20. R. Northcote and R. Potts, Phys. Fluids 7, 475 (1964).
21. W. Gautschi, "Error Function and Fresnel Integrals", in Handbook of Mathematical Functions, edited by M. Abramowitz and S. A. Stegun (National Bureau of Standards Applied Mathematics Series, Washington, D. C., 1964), No. 55, p. 295.
22. M. Kac, Phys. Fluids 2, 8 (1959).
23. H. Margenau and G. Murphy, The Mathematics of Physics and Chemistry (Van Nostrand, Princeton, 1956), p. 472.
24. J. Phys. Chem. Solids 18, 1961, No. 1.
25. L. P. Smith, Mathematical Methods for Scientists and Engineers (Dover, New York, 1953), p. 390.

VITA

Lanny Max Casey was born in Searcy, Arkansas on September 18, 1943. He attended Harding Academy in Searcy, Arkansas for his elementary and secondary education and was graduated in May, 1961. He received his B.S. in Chemistry from Harding College in June, 1965. He entered the Graduate School of Louisiana State University in September, 1965, where he is currently a candidate for the Doctor of Philosophy Degree.

EXAMINATION AND THESIS REPORT

Candidate: Lanny Max Casey

Major Field: Chemistry

Title of Thesis: A Model for Correlated Molecular Rotation

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 18, 1969