

Theory of Pure r -mers In the Guggenheim Approximation

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Using a nearest-neighbors lattice model and the Guggenheim approximation to the partition function, we present a molecular theory of pure r -mers. The theory is an extension of the Sanchez-Lacombe theory in that the large coordination number, z , limit is not taken. This leads to a new parameter ϕ being introduced, which is the ratio of the fraction of bonded r -mer pairs to the fraction of sites occupied by r -mers. This parameter depends on the lattice coordination number z and vanishes in the large z limit. The theory works well except in the critical region. In particular, a liquid-vapor transition is obtained. Expressions for various thermodynamic properties are presented, together with a comparison with other theories. In particular, it is shown how the "c" parameter of Prigogine's cell model finds its equivalence in the lattice model from two sources: lattice composition, through the fractions of occupied and vacant lattice sites, and lattice structure, through the fraction of nonbonded pairs in the system.

I. Introduction

The calculation of thermodynamic properties of fluids from a few molecular parameters is a major goal of physical chemistry. To be applicable and useful, such a theory should not contain too many parameters and should be functionally simple. Moreover, fluids properties studied by engineers often involve liquid-vapor equilibrium. Many approaches fail in this region. In particular, the "c" parameter introduced by Prigogine¹ to characterize the decrease in the external degrees of freedom attributable to a mer in a polymer chain leads to a failure of Prigogine's theory at low densities and cannot give a liquid-vapor transition. A theory that is successful in the vapor phase was recently presented by Sanchez and Lacombe² (SL). Their model can be characterized as an Ising or lattice fluid which uses a simplified form of Guggenheim³ combinatorial. Their expression for the reduced Gibbs free energy $\tilde{G} = G/Nre^*$ is

$$\tilde{G} = -\bar{p} + \bar{P}\bar{v} + \bar{T} \left[(\bar{v} - 1) \ln(1 - \bar{p}) + \frac{1}{r} \ln(\bar{p}/\omega) \right] \quad (1)$$

and for the equation of state is

$$\bar{p}^2 + \bar{P} + \bar{T} \left[\ln(1 - \bar{p}) + \left(1 - \frac{1}{r}\right) \bar{p} \right] = 0 \quad (2)$$

Here, $\bar{p} = (\bar{v})^{-1}$ is the reduced density; \bar{P} , \bar{T} the reduced pressure and temperature, respectively; $\omega = \delta r / \sigma e^{r-1}$ where δ and σ are a "flexibility parameter" and the symmetry number,² respectively, whose values are of no consequence for the equation of state if they are assumed to be constant. The number of sites occupied by an r -mer is characterized by r and there are N r -mer molecules in the system. Equations 1 and 2 are obtained by SL by treating the lattice coordination number z as large. Although the theory is poor in the critical region, it does describe many properties of the liquid and vapor and predicts trends correctly. Parametrically, the pure fluid is described by a nonbonded interaction (attractive) energy $\epsilon^* = z\epsilon/2$, the close packed volume per mer v^* , and the number of mers

per r -mer r . For mixtures⁴ an additional interaction energy is introduced.

In spite of the success of their theory, an unappealing feature is having r act as an adjustable parameter since specific alkanes have r values which are in disagreement with the philosophy implicit in the assumption of a lattice; that is, a molecule with r carbon atoms must occupy r sites. Representative values of this situation obtained from the SL theory are $r = 4.26$ for CH_4 , $r = 8.37$ for n -hexane, and $r = 11.06$ for n -decane. Moreover, a large z limit would be reasonable if a coordination number z of about 12 (the average generally accepted⁵) leads to r values equal to the fixed chain length. The idea that an r -mer is surrounded by a very large number of nearest neighbors contradicts the belief that a molecule in the liquid state has an average finite (~ 12) number of nearest neighbors.

In a previous communication,⁶ motivated by the general success of the SL approach, we presented an equation of state for z finite. In this work we examine in more detail the fundamentals upon which the SL theory is based and extend the theory to finite z . This theory gives the reduced free energy as

$$\tilde{G} = \frac{-\bar{p}(1 - \phi)^2}{(1 - \phi\bar{p})} + \bar{P}\bar{v} + \bar{T} \left[\frac{1}{r} \ln(\bar{p}/\omega') + (\bar{v} - 1) \ln(1 - \bar{p}) - \frac{z}{2} \frac{(1 - \phi\bar{p})}{\bar{p}} \ln(1 - \phi\bar{p}) \right] \quad (3)$$

and the equation of state as

$$\left[\frac{\bar{p}(1 - \phi)}{(1 - \phi\bar{p})} \right]^2 + \bar{P} + \bar{T} \left[\ln(1 - \bar{p}) - \frac{z}{2} \ln(1 - \phi\bar{p}) \right] = 0 \quad (4)$$

where

$$\omega' = r\delta/\sigma \quad (5)$$

The parameter ϕ is for straight chain or branched molecules given by

$$\phi = \frac{2}{z} \left(1 - \frac{1}{r} \right) \quad (6)$$

(1) I. Prigogine (with the collaboration of A. Bellemans and V. Mathot), "The Molecular Theory of Solutions", North Holland Publishing Co., Amsterdam, 1957.

(2) (a) I. C. Sanchez and R. H. Lacombe, *Nature (London)*, 252, 381 (1974); (b) I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, 80, 2352 (1976).

(3) E. A. Guggenheim, *Proc. R. Soc. London, Ser. A*, 183, 203 (1944).

(4) R. H. Lacombe and I. C. Sanchez, *J. Phys. Chem.*, 80, 2563 (1976).

(5) H. Tompa, "Polymer Solutions", Butterworths, London, 1956.

(6) M. Costas, H. I. Epstein, B. C. Sanctuary, D. Richon, and H. Renon, *J. Phys. Chem.*, 85, 1264 (1981).

In this work, we reexamine the mean field approach by Guggenheim and find his partition function to be rich in physical content. We therefore take this as our starting point and obtain eq 3 and 4 with no approximation other than using a nearest-neighbor energy interaction. This being so, eq 3 and 4 reflect the full content of Guggenheim partition function. In section II we review his work and discuss some of the physical content. Section III presents the derivation of eq 3 and 4 together with the expressions for various thermodynamics properties and some consequences of the new equation of state. In this derivation we show that the origin of the term $\bar{T}(1 - 1/r)\bar{p}$ in eq 2 differs from that given in the SL theory. Section IV is devoted to a general comparison of cell model theories and the rigid lattice ones. This leads to an interpretation of Prigogine's "c" parameter within a lattice model.

II. Review of Guggenheim Approach

Since the treatment proposed here rests upon the foundations set by Guggenheim, this section is aimed at establishing the notation, reviewing the derivation, and identifying the physical content of his partition function.

The Gibbs free energy and the partition function are given, in the isothermic-isobaric ensemble, by

$$G = -kT \ln Z(T,P) \quad (7)$$

$$Z(T,P) = \sum_{V,E} \Omega(E,V,N) \exp[-(E + PV)/kT] \quad (8)$$

For N straight chain or branched r -mers, and N_0 holes (or solvent molecules), the following well-known relations and definitions are needed:

- (a) The total number of lattice sites

$$N_s = rN + N_0 \quad (9)$$

- (b) The lattice coordination number z .

- (c) The number of sites which are nonbonded nearest neighbors of an r -mer

$$qz = rz - 2r + 2 \quad (10)$$

- (d) The fraction of sites occupied by holes

$$f_0 = N_0/N_s \quad (11)$$

and by r -mers

$$f = rN/N_s \quad (12)$$

- (e) The total number of lattice pairs

$$(z/2)N_s \quad (13)$$

- (f) The total number of nonbonded pairs

$$(z/2)N_q = (z/2)(N_0 + qN) \quad (14)$$

- (g) The total number of bonded mer-mer pairs

$$(z/2)(N_s - N_q) = N(r - 1) \quad (15)$$

- (h) The numbers N_q , N_s , N , and N_0 are related by

$$N_q = N_s \left(1 - \frac{2}{z} \right) + \frac{2}{z}(N + N_0) \quad (16)$$

For a system of N r -mers and N_0 holes, the number of configurations available to the system for a given potential energy E and volume V is $\Omega(E,V,N)$. Obtaining an accurate form for Ω is a fundamental problem. Exact calculation of Ω for a three-dimensional lattice so far has defined a full solution. Guggenheim,³ in his calculation of Ω , by using a mean field approach in fact builds in more than nearest-neighbor statistics in his lattice model. An essential feature of his work is that "the arrangements of the

molecules will be completely random". Then, by invoking a detailed balance argument for evaporation-condensation, Guggenheim restrains the system in such a way that the liquid-vapour transition is guaranteed. Consequently, the equation of state derived directly from his Ω displays the correct low density behavior.

Guggenheim obtained his formula by assuming the above-mentioned randomness and equating chemical potentials for liquid-vapor equilibrium. With the connection to thermodynamics established, it is straightforward to obtain the free energy by direct integration subject to the condition that, in the absence of r -mers, the free energy reduces to that of the pure solvent. In this way he deduced that

$$\Omega(E,V,N) = \left(\frac{\delta}{\sigma} \right)^N \frac{N_s!}{N!N_0!} \left(\frac{N_q!}{N_s!} \right)^{z/2} \quad (17)$$

We shall refer to eq 17 as the full Guggenheim form. To be correct, he did not obtain the factorials upon integration, but rather $\ln \Omega$ was obtained in terms of factors x in $x - x$ which he then equated to $\ln(x!)$. When Stirling's formula is used, eq 17 becomes

$$\Omega(E,V,N) = \left(\frac{\omega'}{f} \right)^N \left(\frac{1}{f_0} \right)^{N_0} N_s^{N(r-1)} \left(\frac{N_q^{N_q}}{N_s^{N_s}} \right)^{z/2} \quad (18)$$

where ω' is given by eq 5. Equation 18 can be converted into a form which is independent of q by using the relation

$$N_q/N_s = (1 - \phi f) \quad (19)$$

where ϕ is given by eq 6. Hence, eq 18 becomes

$$\Omega(E,V,N) = \left(\frac{\omega'}{f} \right)^N \left(\frac{1}{f_0} \right)^{N_0} (1 - \phi f)^{(z/2)N_s - N(r-1)} \quad (20)$$

This expression is exactly equivalent to the full Guggenheim form. The large z limit gives

$$\lim_{z \rightarrow \infty} \Omega(E,V,N) = (\omega/f)^N (1/f_0)^{N_0} \quad (21)$$

which agrees with SL's eq 8b in ref 2b (note that in SL theory $\omega = r\delta/\sigma e^{-1}$ in contrast to eq 5).

The neglect of the $(1 - \phi f)$ term between eq 20 and 21 by taking the large z limit ignores an important contribution to Ω . The first two terms of eq 20 take into account the configurations of r -mers and holes on the lattice, but give no contribution due to neighboring site occupation. The last term does this. Physically, the quantity ϕ , given by eq 6, or by simple manipulation (cf. eq 13 and 14) is

$$\phi = \left[\frac{(z/2)(N_s - N_q)}{(z/2)N_s} \right] / \left(\frac{rN}{N_s} \right) \quad (22)$$

This is, in words, the ratio of the fraction of *bonded* r -mer pairs to the fraction of sites occupied by r -mers. Therefore, it follows that the fraction of *nonbonded* pairs in the system (that is, the hole-hole, hole-mer, and nonbonded mer-mer pairs) denoted by f_{NB} is

$$f_{NB} = \frac{(z/2)N_q}{(z/2)N_s} = (1 - \phi f) \quad (23)$$

As such, f_{NB} gives a measure of the external degrees of freedom of the r -mers. As f_{NB} decreases, the external degrees of freedom of the r -mers decrease. The exponent of this term in eq 20 is simply the number of nonbonded pairs $(z/2)N_q$ (see eq 14 and 15). Hence, an alternative way of expressing Ω is

$$\Omega(E, V, N) = \left(\frac{\omega'}{f}\right)^N \left(\frac{1}{f_0}\right)^{N_0} (f_{NB})^{(z/2)N_q} \quad (24)$$

Using the full Guggenheim form has a fundamental appeal over the large z limit, i.e., it allows explicit inclusion of the effects of nonbonded pairs. The mean field approach used to obtain Guggenheim's partition function clearly does more than count the number of configurations of r -mers on the lattice. It includes some effects of external flexibility and size in the liquid and vapor via f_{NB} .

III. Derivation of the Equation of State and Thermodynamic Properties

The lattice energy is assumed to depend only on nearest-neighbor interaction. There are four types of these pairs: hole-hole, hole-mer, bonded mer-mer, and nonbonded mer-mer. Following the usual procedures, the interaction energy is taken to be nonzero only for the nonbonded mer-mer pairs. The lattice energy is

$$E = \frac{-(qN)^2 \epsilon^*}{N_q} \quad (25)$$

or, in reduced form

$$\tilde{E} = \frac{E}{Nr\epsilon^*} = \frac{-f(1-\phi)^2}{(1-\phi f)} \quad (26)$$

which follow from eq 12 and 19. Substitution of E and eq 20 into the expression for the Gibbs free energy, eq 7, gives eq 3. The reduced-state variables are

$$\begin{aligned} \tilde{T} &= T/T^* & T^* &= \epsilon^*/k \\ \tilde{P} &= P/P^* & P^* &= \epsilon^* r N / V^* \\ f &= \bar{p} = 1/\bar{v} = V^*/V & f_0 &= 1-f = 1-\bar{p} \end{aligned} \quad (27)$$

where V^* is the molar closed packed volume of N r -mers equal to Nrv^* , with v^* the closed packed volume of a single mer; v^* is also the volume of a lattice site, so a hole has assigned a volume equal to v^* . Since we do not consider r as an adjustable parameter, we prefer to use V^* rather than v^* in the definitions (eq 27). Hence, \tilde{T} , \tilde{P} , and \bar{v} depend on three adjustable parameters ϵ^* , V^* , and ϕ with z determining ϕ for fixed r .

It is worthwhile to pinpoint exactly where the various terms in eq 3 and 4 arise, and to contrast the use of large z combinatorial eq 21 as used by SL. To show this, eq 20 is written

$$\begin{aligned} -\frac{1}{Nr\epsilon^*} \ln \Omega(E, V, N) = \\ \frac{1}{r} \ln (\bar{p}/\omega') + (\bar{v} - 1) \ln (1 - \bar{p}) - \frac{z}{2} \frac{(1 - \phi \bar{p})}{\bar{p}} \ln (1 - \phi \bar{p}) \end{aligned} \quad (28)$$

In SL's work, only the first two terms in eq 28 arise. Differentiation of eq 28 obtains the equation of state

$$\begin{aligned} \left(\frac{\partial \tilde{G}}{\partial \bar{v}}\right)_{\tilde{T}, \tilde{P}} = 0 = \left(\frac{\bar{p}(1-\phi)}{1-\phi\bar{p}}\right)^2 + \tilde{P} + \\ \tilde{T} \left[\ln (1 - \bar{p}) + \left(1 - \frac{1}{r}\right) \bar{p} - \frac{z}{2} \ln (1 - \phi \bar{p}) - \left(1 - \frac{1}{r}\right) \bar{p} \right] \end{aligned} \quad (29)$$

where the first two terms in the square brackets arise from the first two terms in eq 20 or the complete eq 21. These are the ones retained in the SL theory. However, if the full Guggenheim form is used by retaining all terms in eq 20, there arises a term from the third part which exactly

cancels the term obtained by SL in eq 2 (see eq 29).

The reason for the cancellation lies in the way Ω is broken up going from eq 18 to eq 21 in the large z approximation: namely, a term $N_s^{N(r-1)}$, which (cf. eq 15) is proportional to the number of pairs raised to the power of the number of bonded pairs, is factored out when the large z limit used by SL is taken, viz.

$$\begin{aligned} \Omega(E, V, N) = \left[\left(\frac{\delta}{\rho}\right)^N \frac{N_s!}{N_0! N! N_s^{N(r-1)}} \right] \times \\ \left[N_s^{N(r-1)} \left(\frac{N_q!}{N_s!}\right)^{z/2} \right] = \left[\left(\frac{\omega'}{f}\right)^N \left(\frac{1}{f_0}\right)^{N_0} \right] f_{NB}^{(z/2)N_q} \end{aligned} \quad (30)$$

The limit $z \rightarrow \infty$ of $(f_{NB})^{(z/2)N_q}$ is $e^{-(r-1)N}$.

The cancellation of the two terms in eq 29 is reasonable since it is the part depending upon the fraction of *bonded* pairs, namely

$$\left(1 - \frac{1}{r}\right) \bar{p} = \frac{z}{2} \phi \bar{p} \quad (31)$$

which drops out (cf. eq 6 and 22) while physically it is the *nonbonded* pairs contribution which should contribute to Ω . However, interestingly and, to the authors, fortuitously, in the large z limit it happens

$$\lim_{z \rightarrow \infty} \left[-\frac{z}{2} \ln (1 - \phi \bar{p}) \right] = \left(1 - \frac{1}{r}\right) \bar{p} \quad (32)$$

so that eq 2 of SL is the correct large z limit of eq 6 even though the origin of the $(1 - 1/r)\bar{p}$ factor is different.

When the new equation of state, eq 4, is used, a liquid-vapor transition is predicted similar to SL theory.² A numerical technique⁷ such as a fixed-point iteration method can be used to show this. From eq 4 the equation

$$\begin{aligned} \bar{p} = h(\bar{p}) = \\ 1 - \exp \left[-\frac{1}{\tilde{T}} \left[\left(\frac{\bar{p}(1-\phi)}{1-\phi\bar{p}}\right)^2 + \tilde{P} \right] + \frac{z}{2} \ln (1 - \phi \bar{p}) \right] \end{aligned} \quad (33)$$

defines the value of \bar{p} at a given (\tilde{T}, \tilde{P}) that minimizes the Gibbs free energy. Equation 33 has, in general, three solutions: the lowest and highest values of \bar{p} correspond to minima in the Gibbs function while the intermediate solution corresponds to a maximum in G . Since at a given pressure and temperature two minima appear, the higher free-energy minimum corresponds to a metastable state. The metastability limit (spinodal) is defined by the locus of the pressures and temperatures $(\tilde{P}_s, \tilde{T}_s)$, which, using the spinodal condition $(\partial h(\bar{p})/\partial \bar{p})_{\tilde{T}, \tilde{P}} = 1$, are

$$\tilde{T}_s = \frac{2\bar{p}_s(1-\phi)^2}{(1-\phi\bar{p}_s)^3} \left[\frac{1}{1-\bar{p}_s} - \frac{z}{2} \phi \frac{1}{(1-\phi\bar{p}_s)} \right]^{-1} \quad (34)$$

$$\begin{aligned} \tilde{P}_s = - \left[\frac{\bar{p}_s(1-\phi)}{1-\phi\bar{p}_s} \right]^2 \times \\ \left[1 + \frac{2(1-\bar{p}_s) \left[\ln (1 - \bar{p}_s) - \frac{z}{2} \ln (1 - \phi \bar{p}_s) \right]}{\bar{p}_s \left[(1 - \phi \bar{p}_s) - \frac{z}{2} \phi (1 - \bar{p}_s) \right]} \right] \end{aligned} \quad (35)$$

which reduce to SL's expressions in the large z limit.

(7) S. D. Conte and C. de Boor, "Elementary Numerical Analysis", 2nd ed, McGraw-Hill, New York, 1972.

At a given pressure, there is a unique temperature such that the two free-energy minima are equal. This set of temperatures and pressures define the coexistence liquid-vapor line, i.e., the model undergoes a liquid-vapor phase transition. In this way, in a \bar{P} vs. \bar{T} diagram, eq 4 provides three regions: (i) stable liquid only, (ii) stable vapor only (in both cases eq 33 has only one solution), and (iii) metastability region (three solutions of eq 33) whose limits are given by eq 34 and 35. As in SL case, the present model does not obey a corresponding states principle.

In the following, some consequences of eq 4 are discussed. In this work, only general comments are made regarding the functional forms. Specific data are not discussed and the parameters V^* , ϵ^* , and ϕ are not, at this stage, fit to experiment.

(a) *Critical Values*. The critical point must satisfy not only the spinodal condition, but also $(\partial^2 h(\bar{p})/\partial \bar{p}^2)_{\bar{T}, \bar{P}} = 0$. These conditions lead to a cubic equation for the reduced critical density \bar{p}_c

$$\phi \bar{p}_c^3 + (1 - 2\phi) \bar{p}_c^2 + \frac{2 - \phi}{r \left(1 - \frac{1}{r} - \phi\right)} \bar{p}_c - \frac{1}{r \left(1 - \frac{1}{r} - \phi\right)} = 0 \quad (36)$$

For $z \rightarrow \infty$ this equation reduces to a quadratic with a positive root of $\bar{p}_c = (1 + r^{1/2})^{-1}$ in agreement with SL. The analytic expression for the roots of eq 36 does not display a simple form. Numerically, for decreasing ϕ there are three real roots, which change to one real positive and a complex conjugate pair. One root is always positive and this root, together with eq 34 and 35 (evaluated at \bar{p}_c) give values for the critical compressibility factor $Z_c = P_c V_c / RT_c = r \bar{P}_c \bar{v}_c / \bar{T}_c$ that are bigger than 0.3, while experimentally Z_c of most simple molecules is less than this value. Thus, as with SL case, eq 4 is unsatisfactory near the critical point.

(b) *Virial Expansion*. By expanding eq 4 in powers of the reduced density, the virial expansion is found to be

$$\frac{PV}{RT} = \frac{\bar{P}\bar{v}}{\bar{T}} = 1 + B_2(\bar{T})\bar{p} + B_3(\bar{T})\bar{p}^2 + \dots \quad (37)$$

where

$$B_n(\bar{T}) = r \left[\frac{1}{n} \left(1 - \left(1 - \frac{1}{r} \right) (\phi)^{n-1} \right) - \frac{n-1}{\bar{T}} (\phi-1)^2 (\phi)^{n-2} \right] \quad (38)$$

The correct ideal gas-phase limit is found. Moreover, the theory predicts the correct functional form for the second virial coefficient as well as a similar temperature dependence for all the higher coefficients. This is an improvement over the vdW's model and SL theory where $B_3(T)$ = constant.

Equating the second virial coefficient to zero, the reduced Boyle temperature is easily found

$$\bar{T}_B = \frac{2(\phi-1)^2}{(1 - (z/2)\phi^2)} \quad (39)$$

For the vdW equation, the ratio of T_B to the critical temperature T_c is $T_B/T_c = 3.375$. For a dimer SL obtained 2.91, while from our theory we obtain 2.68 at a value of $r = 2$ and $z = 12$. Experimentally, the ratio is Ne, 2.70; Ar, 2.73; N₂, 2.59; CO, 2.60; CH₄, 2.58.

(c) *The Energy and the Entropy of the Lattice*. In the large z limit approximation, the lattice energy (attractive) is

$$E_{SL} = \frac{-z\epsilon^* N_s V^{*2}}{2V^2} \quad (40)$$

while for finite z , the lattice energy becomes

$$E = \frac{-z\epsilon^* N_s V^{*2} (1 - \phi)^2}{2(V^2 - \phi V V^*)} \quad (41)$$

Comparison between eq 40 and 41 shows that $E_{SL} < E$. Since the full Guggenheim form is considered better than the large z limit approximation, the effect of using the large z approximation is that of overestimating the number of effective interactions in the system. As a result, the attractive lattice energy is lower than it should be. These two lattice energies give rise to different "energy parts" of the respective equations of state (first term in eq 2 and 4). We believe that the first term in eq 4, if not simpler than in the SL case, gives a better estimation of the "energy part" of the equation of state.

The entropy in SL case is

$$S_{SL} = R[(1 - \bar{v})r \ln(1 - \bar{p}) + \ln \bar{v}] + R \ln(\delta r / \sigma \epsilon^{r-1}) \quad (42)$$

If eq 20 is used, the entropy obtained is

$$S = R[(1 - \bar{v})r \ln(1 - \bar{p}) + \ln \bar{v} + (z/2)r(\bar{v} - \phi) \ln(1 - \phi \bar{p})] + R \ln(\delta r / \sigma) \quad (43)$$

It is straightforward to show from eq 42 and 43 that $S_{SL} > S$. Therefore, neglecting f_{NB} in the Guggenheim combinatory (20) has the effect of increasing the number of configurations and overestimating the entropy. It is interesting to notice that eq 43 shows that the entropy of the present theory depends not only on molecular size through r but on "lattice composition" through f_{NB} .

(d) *Thermodynamic Properties*. From the equation of state (eq 4), all thermodynamic properties can be derived. The thermal expansion coefficient α and the isothermal compressibility β are given by

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = - \frac{1}{T^*} \left. \frac{\partial \ln \bar{p}}{\partial \bar{T}} \right|_P \quad (44a)$$

$$\beta = - \frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T = \frac{1}{P^*} \left. \frac{\partial \ln \bar{p}}{\partial \bar{P}} \right|_T \quad (45a)$$

$$\alpha T = \bar{\alpha} \bar{T} = \frac{(1 - \phi)^2 + \bar{P}(\bar{v} - \phi)^2}{\bar{T}(\bar{v} - \phi) \left[\frac{1 - \phi}{\bar{v} - 1} + \frac{1}{r} \right] - \frac{2(1 - \phi)^2 \bar{v}}{(\bar{v} - \phi)}} \quad (44b)$$

$$\beta P = \bar{\beta} \bar{P} = \frac{\bar{P}(\bar{v} - \phi)^2}{\bar{T}(\bar{v} - \phi) \left[\frac{1 - \phi}{\bar{v} - 1} + \frac{1}{r} \right] - \frac{2(1 - \phi)^2 \bar{v}}{(\bar{v} - \phi)}} \quad (45b)$$

The reduced thermal pressure coefficient $\bar{\gamma} = (T^*/P^*)\gamma = (T^*/P^*)(\alpha/\beta)$ at low pressure ($\bar{P} = 0$) is given by

$$\bar{\gamma} = \frac{(1 - \phi)^2}{\bar{T}(\bar{v} - \phi)^2} \quad (46)$$

which displays the correct inverse \bar{T} and \bar{v} dependence.

It is of interest to compare eq 44-46 with other theories. For this purpose, Figure 1 shows a plot of $(\alpha T)^{-1}$ against $\log T$. Patterson and Bardin⁸ in their test of the Prigogine principle of corresponding states, reported values for $(\alpha T)^{-1}$ against $\log T$ from methane to polymethylene using data reported in the literature. The values shown for n -C₈ and

(8) D. Patterson and J. M. Bardin, *J. Chem. Soc., Faraday Trans. 2*, 66, 321 (1970).

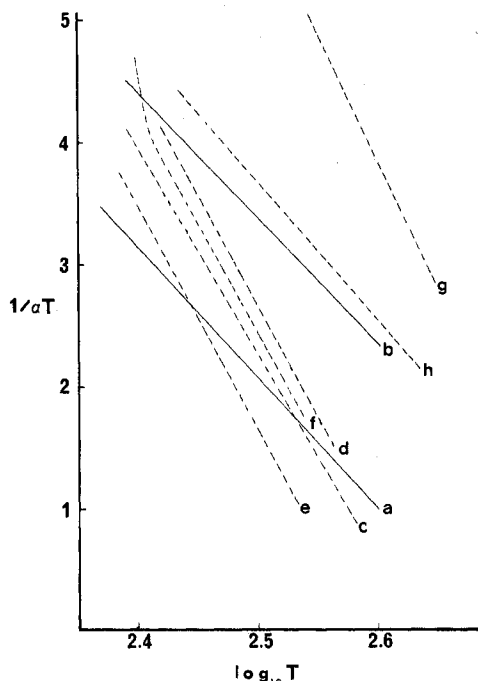


Figure 1. The quantity $(\alpha T)^{-1}$ against $\log T$. Full lines, experimental data: (a) $n\text{-C}_6$, (b) $n\text{-C}_{16}$. Dotted lines: (c) SL equation for $n\text{-C}_6$ ($r = 8.37$); (d) SL equation for $n\text{-C}_{17}$ ($r = 15.83$); (e) eq 44b at $\bar{P} = 0$, $z = 12$, and $r = 6$ ($n\text{-C}_6$); (f) eq 44b at $\bar{P} = 0$, $z = 12$, $r = 16$ ($n\text{-C}_{16}$); (g) Flory-Orwoll-Vrij theory; (h) Simha and Somcynsky hole theory.

$n\text{-C}_{16}$ are taken from Patterson and Bardin's work, which they show are described by the empirical equation

$$(\alpha T)^{-1} = a - b \log T \quad (47)$$

For $n\text{-C}_6$, the parameters are $a = 27.16$ and $b = 10.01$, and for $n\text{-C}_{16}$, $a = 27.98$ and $b = 9.81$. The quantity $\log T = \log(\bar{T}T^*)$ has been calculated by using an arbitrary value of $T^* = 500$. A different value for T^* will shift the lines shown in Figure 1. We have not, at this stage, fit T^* to experiment; hence, we are only interested in comparing the slopes of the lines in Figure 1 against the experimental slope and not against specific experimental values.

Lines c for $n\text{-C}_6$ ($r = 8.37$) and d for $n\text{-C}_{17}$ ($r = 15.83$) were calculated by using SL equation^{2b} for (αT) at $\bar{P} = 0$ (eq 44b with $\phi = 0$ and $\bar{P} = 0$). The data for $n\text{-C}_{17}$ was used instead of $n\text{-C}_{16}$ since SL did not report r for $n\text{-C}_{16}$; this difference should not significantly change the results. The slopes are -16.3 and -17.0 for lines c and d, respectively. Lines e for $n\text{-C}_6$ ($r = 6$) and f for $n\text{-C}_{16}$ ($r = 16$) were calculated by using eq 44b at $\bar{P} = 0$ with a value of $z = 12$. The slopes are -17.3 and -18.5 , respectively. In both cases (SL and eq 4), at a given \bar{T} (values from 0.5 to 0.7 were used) the corresponding equation of state was solved by means of the fixed-point iteration method, in order to obtain the value of $\bar{v} = 1/\bar{p}$ that corresponds to the liquid phase. Line g is given by Flory theory,⁹ its slope is -13.3 at $(\alpha T)^{-1} = 3.0$. Line h represents the Simha and Somcynsky¹⁰ extension of the smoothed potential cell model based on the hole theory of liquids. Here the number of segments $s \rightarrow \infty$, and the flexibility parameter $s/3c \rightarrow 1$ corresponding to free rotation between segments. This model is more satisfactory than the other since the correct slope (-10.0) is found.⁸ Lines g and h, of course, can be shifted to the experimental lines, and they are

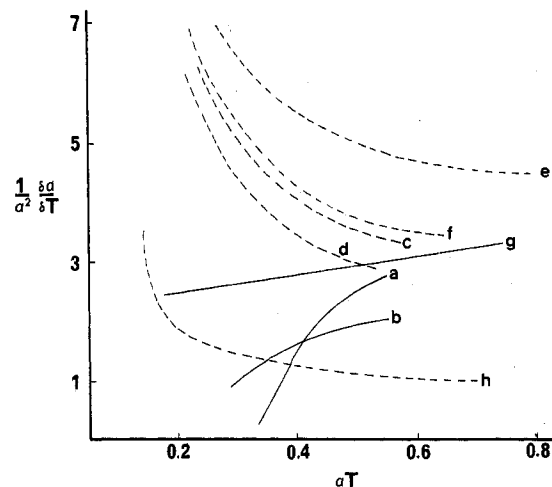


Figure 2. The quantity $\alpha^{-2} \partial \alpha / \partial T$ against αT . Full lines, experimental data: (a) $n\text{-C}_6$, (b) $n\text{-C}_{16}$. Dotted lines: (c) SL eq 48 for $n\text{-C}_6$ ($r = 8.37$); (d) SL eq 48 for $n\text{-C}_{17}$ ($r = 15.83$); (e) eq 49 at $\bar{P} = 0$, $z = 12$, and $r = 6$ ($n\text{-C}_6$); (f) eq 49 at $\bar{P} = 0$, $z = 12$, $r = 16$ ($n\text{-C}_{16}$); (g) Flory-Orwoll-Vrij theory; (h) Simha and Somcynsky hole theory.

placed to the right of the plot only for clarity. As can be seen on Figure 1, eq 2 and 4 give the correct trend (negative slope). We believe that SL theory and our extension are, in this respect, comparable with the other theories.

A more severe test is provided by the quantity $\alpha^{-2}(\partial \alpha / \partial T)$ as a function of αT . Both these quantities are dimensionless and hence reduced. Experimentally, all liquids lie in a single curve⁸ showing how the principle of corresponding states is largely obeyed in this test. Although eq 4 does not follow a corresponding states principle, it is possible to compare it with data for specific alkanes. Figure 2 shows the experimental curves for $n\text{-C}_6$ and $n\text{-C}_{16}$ taken from Patterson and Bardin work. In SL theory, the quantity $\alpha^{-2}(\partial \alpha / \partial T)$ at $\bar{P} = 0$ is given by

$$\frac{1}{\alpha^2} \frac{\partial \alpha}{\partial T} = -2(\alpha T)^{-1} - 3 + (\alpha T) \left(\frac{\bar{T}\bar{v}^2}{(\bar{v} - 1)^2} - 2 \right) \quad (48)$$

whereas in the present model

$$\frac{1}{\alpha^2} \frac{\partial \alpha}{\partial T} = -2(\alpha T)^{-1} - \frac{3\bar{v}}{\bar{v} - \phi} + (\alpha T) \left[\frac{\bar{T}\bar{v}(\bar{v} - \phi)}{(1 - \phi)(\bar{v} - 1)^2} + \frac{2\bar{v}}{\bar{v} - \phi} \left(1 - \frac{2\bar{v}}{\bar{v} - \phi} \right) \right] \quad (49)$$

When eq 48 was used, lines c and d on Figure 2 were obtained for $n\text{-C}_6$ ($r = 8.37$) and $n\text{-C}_{17}$ ($r = 15.83$), respectively. By means of eq 49 with $z = 12$ lines e and f were calculated for $n\text{-C}_6$ ($r = 6$) and $n\text{-C}_{16}$ ($r = 16$). Line g is given by the Flory theory whereas line h corresponds to the Simha-Somcynsky hole theory.⁸ The similarity between line h and the lines given by SL theory and our extension is striking. Why the hole theories display such a behavior is still an open question.

In Figure 3 is shown the quantity $\log(\alpha \gamma v T)$ against αT , where v is the specific volume. Curves a and b are experimental data¹¹ for $n\text{-C}_6$ and $n\text{-C}_{16}$. In SL theory at $\bar{P} = 0$

$$\bar{\alpha} \bar{\gamma} \bar{v} \bar{T} = \frac{\alpha \gamma v T}{rR} = \frac{\bar{\alpha} \bar{T}}{\bar{v} \bar{T}} \quad (50)$$

and in the present model

$$\bar{\alpha} \bar{\gamma} \bar{v} \bar{T} = \frac{\alpha \gamma v T}{rR} = \frac{\bar{v}(1 - \phi)^2}{\bar{T}(\bar{v} - \phi)^2} (\bar{\alpha} \bar{T}) \quad (51)$$

(9) R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **8**, 6814, 6822 (1967).

(10) R. Simha and T. Somcynsky, *Macromolecules* **2**, 342 (1969).

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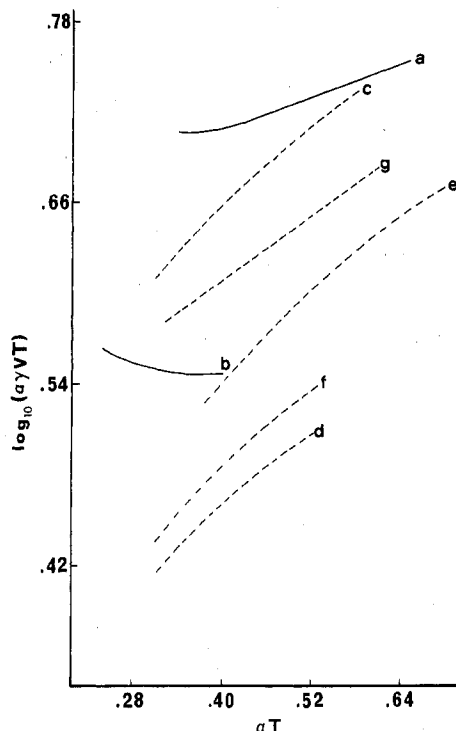


Figure 3. The quantity $\log(\alpha\gamma\delta T)$ against αT . $\alpha\gamma\delta T$ units are $\text{bar cm}^3 \text{K}^{-1} \text{g}^{-1}$. Full lines, experimental data: (a) $n\text{-C}_6$, (b) $n\text{-C}_{16}$. Dotted lines: (c) SL eq 50 for $n\text{-C}_6$ ($r = 8.37$); (d) SL eq 50 for $n\text{-C}_{17}$ ($r = 15.83$); (e) eq 51 at $\bar{P} = 0$, $z = 12$, $r = 6$ ($n\text{-C}_6$); (f) eq 51 at $\bar{P} = 0$, $z = 12$, $r = 16$ ($n\text{-C}_{16}$); (g) Flory-Orwoll-Vrij theory.

where R is the gas constant.

Equation 50 gives line c ($n\text{-C}_6$) and line d ($n\text{-C}_{17}$) while lines e ($n\text{-C}_6$) and f ($n\text{-C}_{16}$) were obtained by means of equation 51 with $z = 12$. Line g is given by the Flory theory and in the case of Figure 1 it can be shifted. The quantity $\alpha\gamma\delta T$ is closely related to the heat capacity¹² since $C_p = C_v + \alpha\gamma\delta T$. The discrepancy shown in Figure 3 is possible due to the fact that it was assumed that the flexibility parameter δ is independent of temperature and pressure. This being so, a property like the heat capacity that depends in part on internal degrees of freedom will not correlate well. Nevertheless, both eq 50 and 51 give higher values for $\alpha\gamma\delta T$ for the shorter alkane than for the longer chain alkane as it is the case experimentally. It is important to point out that it is the high value of $r = 8.37$ assigned to $n\text{-C}_6$ by SL model that moves the $\alpha\gamma\delta T$ curve upward with respect to the one calculated with our model ($r = 6$) by means of eq 51, i.e., it is not the finite z value used to calculate curve e that makes this curve lie below curve c. In fact, if one uses the SL model (eq 50) with $r = 6$ the resulting curve lies below curve e, i.e., the curve for z finite is closest to the experimental one than the one for $z \rightarrow \infty$ at the same value of r . For the case of $n\text{-C}_{16}$, in the SL model $r = 15.83$ while in our model $r = 16$. Since the values of r are very close, it is the value of z that makes the difference. It can be seen that for finite z (curve f) the resulting curve is above that of $z \rightarrow \infty$ (curve d).

It is interesting to contrast the Flory theory $\bar{\alpha}\bar{\gamma}\bar{\delta}\bar{T} = \alpha\gamma\delta T/cR$ (where c is taken in Prigogine's sense, i.e., the number of external degrees of freedom = $3c$) with the present model $\bar{\alpha}\bar{\gamma}\bar{\delta}\bar{T} = \alpha\gamma\delta T/rR$. This indicates that the lowering of the external degrees of freedom of a mer are not characterized in the present model by a parameter like c but achieved by other means which we now discuss.

IV. Comparison between "c" Parameter and Rigid Lattice Theories

The "c" parameter theories are based on Prigogine's¹ fundamental idea that it is possible to separate the total degrees of freedom of an r -mer into two groups: the internal degrees of freedom which depend only in the valency forces and the external degrees of freedom which depend only on intermolecular forces. The internal degrees of freedom are vibrations of high frequency and low amplitude and hence have almost no effect on neighboring molecules. Only the external degrees of freedom of movement as a whole are considered to be important. The external degrees of freedom attributable to a mer in a polymer chain are less than those for a similar but smaller molecule. Prigogine introduced a parameter, c , to characterize this decrease. The assumption was made that the configurational partition function can be split into a product where one factor depends on internal degrees of freedom and the other on the external degrees of freedom,¹³ viz.

$$Z = Z_0 \Omega_1 \psi(V)^{3Nc} \exp(-E_0/kT) \quad (52)$$

Here Z_0 includes the internal degrees of freedom, Ω is the Guggenheim combinatorial assumed to be independent of V , $\psi(V)$ is the cell partition function where, through the c parameter, the external degrees of freedom are taken into account, and E_0 is the potential energy when all the mers are at cell centers. In the lattice model, we have for Z

$$Z = Z_0 \Omega(E, V, N) \exp(-E_0/kT) \quad (53)$$

where $\Omega(E, V, N)$ is the Guggenheim "combinatorial" assumed to be dependent on V and Z_0 and E_0 have the same meaning as above. In essence, the lattice model introduces the volume dependence via $\Omega(E, V, N)$ while in the cell model it is introduced through the cell partition function $\psi(V)$. The two different mechanisms of introducing the free volume are clear. While in the cell model the free volume is reached by letting the cell expand or contract due to a potential, in the rigid lattice model it is reached by imagining there are empty cells (holes).

In the cell model, expansion and free volume are characterized by a dimensionless ratio \bar{T} (not to be confused with our definition (eq 27)) of the thermal energy to the cohesive energy¹

$$\bar{T} = \frac{c}{r} \frac{kT}{\epsilon^*} \quad (54)$$

where here ϵ^* is the depth of the interaction potential between neighboring nonbonded segments and c/r is one-third the number of external degrees of freedom per segment. For spherical molecules (monomers), \bar{T} depends only on the cohesive energy parameter ϵ^* since $c/r = 1$. For chain-molecule liquid, however, \bar{T} and free volume also depend on how the segments are connected into chains, i.e., on the length and flexibility, through the c/r parameter, called a structural parameter. For long molecules c/r drops asymptotically to a value characteristic of chain flexibility and side group motion.

In the lattice model, these structural considerations are taken into account through the fraction of nonbonded pairs f_{NB} (see eq 23). Since the system as a whole is isotropic, f_{NB} is not only the fraction of nonbonded pairs in the system but also the fraction of nonbonded pairs per r -mer.

(13) I. Prigogine, N. Trappeniens, and V. Mathot, *Discuss. Faraday Soc.*, **15**, 93 (1953).

(14) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).

(12) S. N. Bhattacharya and D. Patterson, *J. Phys. Chem.*, **83**, 2979 (1979).

In the gas phase $\bar{p} \rightarrow 0$ and the $f_{\text{NB}} \rightarrow 1$. This means an r -mer in the gas phase is placed on the lattice completely surrounded by empty sites. The number of possible configurations it can take is unrestricted; in other words, its number of external degrees of freedom are that of a free molecule. In going from the gas phase to the liquid phase $\bar{p} \rightarrow 1$ and f_{NB} decreases. This decrease depends on the coordination number z and the length of the molecule r . In the liquid phase an r -mer is surrounded by holes and other r -mers. This environment restricts the number of configurations the r -mer can take compared to those in the gas phase, i.e., the number of external degrees of freedom of the r -mer are decreased. It is clear that in the lattice model f_{NB} characterize the decrease of the external degrees of freedom in going from the gas to the liquid phase. This being so, we can express the number of external degrees of freedom $3c$ of the molecule as

$$3c = (\text{number of external degrees of freedom in the gas phase})f_{\text{NB}} \quad (55)$$

In the SL model with $z \rightarrow \infty$, $f_{\text{NB}} = 1$ for gas and liquid phases. The fact $z \rightarrow \infty$ implies in the liquid that although an r -mer can be surrounded by many other r -mers it still can take as many configurations as it can in the gas phase. This is to say that the number of external degrees of freedom in the infinite z theories do not decrease in going from the gas to the liquid.

If we assume, for a chain molecule, that each segment is a "hard ball" containing no low frequency vibrations then a dimer ($r = 2$) has five external degrees of freedom corresponding to three translations plus two rotations in the gas phase. Provided there is free rotation about bonds between segments, the addition of successive segments to make the trimer, tetramer, etc, each add one external degree per segment. If the rotation is restricted, more than one segment must be added to give an additional external degree of freedom. For the free rotation case we have, using eq 55

$$3c = (r + 3)f_{\text{NB}} \quad (r \geq 2)$$

$$\frac{c}{r} = \left(\frac{1}{3} + \frac{1}{r}\right) \left(1 - \frac{2}{z} \left(1 - \frac{1}{r}\right) \bar{p}\right) \quad (56)$$

As we pointed out above, when $r \rightarrow \infty$ and $\bar{p} \rightarrow 0$ (gas phase), c/r tends to a characteristic value that in this case is $1/3$.

We also may consider an r -mer which has only $r - 1$ stretching frequencies. There are then $2r + 1$ external degrees of freedom leading to

$$3c = (2r + 1)f_{\text{NB}}$$

$$\frac{c}{r} = \left(\frac{2}{3} + \frac{1}{3r}\right) \left(1 - \frac{2}{z} \left(1 - \frac{1}{r}\right) \bar{p}\right) \quad (57)$$

This type of r -mer was called by Prigogine¹ a "flexible r -mer". In this case, when $r \rightarrow \infty$ and $\bar{p} \rightarrow 0$, $c/r \rightarrow 2/3$.

Figure 4a illustrates for the case of $z = 12$ how the external degrees of freedom are lowered from the gas phase (upper curve) to the liquid state (lower curve). These curves were calculated by using eq 56 for $\bar{p} = 0$ and $\bar{p} = 1$, respectively. In the SL model c/r would be given only by the upper curve for all \bar{p} . Figure 4b shows a comparison between c/r calculated from eq 56 for $z = 12$ and $\bar{p} = 0.9$ (a "typical" liquid density in our model) and that calculated from enthalpic data (broken line) by means of the cell model (see ref 1) by Prigogine. We have plotted Prigogine's values, transforming his r values to the definition of r we have been using in this work. Then, for example, for $\text{C}_{19}\text{H}_{40}$ we use $r = 19$, while in Prigogine's

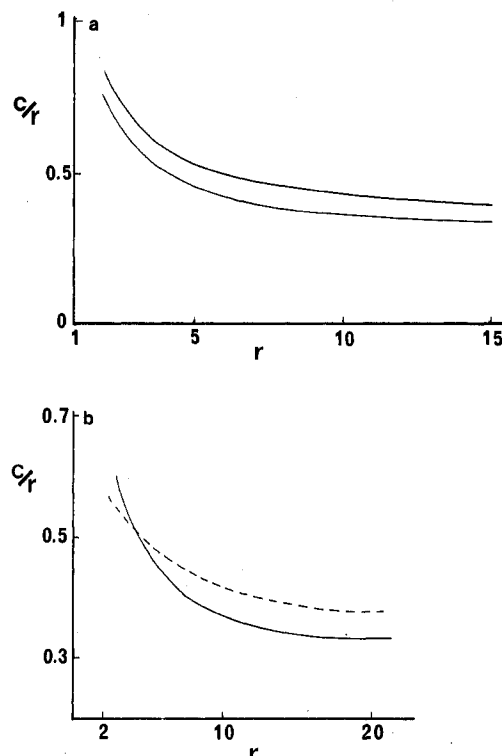


Figure 4. c/r against r . (a) Upper line for gas phase ($\bar{p} \rightarrow 0$) and lower line for liquid phase ($\bar{p} \rightarrow 1$). (b) Full line calculated from eq 56 for $z = 12$ and $\bar{p} = 0.9$; broken line deduced from enthalpic data, using the cell model (taken from ref 1).

work this molecule is represented by $r = 10$. The fact that c/r for the very simple picture of free rotation in the gas phase behaves qualitatively like c/r deduced from the experimental enthalpic data by using the cell model support the idea that f_{NB} from the lattice model characterizes effectively the decrease of the external degrees of freedom an r -mer undergoes on going from the gas to the liquid phase.

We can summarize some of the most important conclusions of this section as follows:

(a) The external degrees of freedom of an r -mer, $3c$, depends on how the r -mer is arranged in the lattice. The external degrees of freedom used in the cell model finds its equivalence on the lattice model in (i) lattice composition, through f and f_0 , and (ii) lattice structure through f_{NB} . The external degrees of freedom of an r -mer on the rigid lattice model are a function of its environment.

(b) It is necessary to preserve z finite in the Guggenheim formula in order to obtain the lattice composition dependence of c (via f_{NB}). We believe this is a powerful reason for treating z as finite.

(c) A system at T and P (\bar{T} and \bar{P}) has an $f = \bar{p}$ which gives a value for $3c$ that is different from that at different T and P . In other words, the average number of external degrees of freedom per molecule of the liquid is a function of T and P (or \bar{T} and \bar{V}) through the equation of state. That is, c is not a constant.

V. Summary

In this paper a new equation of state for pure r -mers is presented, eq 4, which is derived from the complete combinatorics of Guggenheim, eq 18, without invoking the large z limit. A new parameter, in addition to ϵ^* and ν^* is introduced, namely, ϕ , which replaces r in the infinite z limit theory of Sanchez-Lacombe.

The parameter ϕ depends upon z and fixed r and vanishes for infinite z . In this limit the equation of state would

have only two adjustable parameters (ϵ^* and ν^*) unless r is allowed to vary.

The physical meaning of ϕ lies in eq 22 and is for a given coordination number z , the ratio of the fraction of bonded r -mer pairs to the fraction of sites occupied by r -mers. The value of ϕ depends critically on z . Varying z changes the structure of the liquid and can be visualized as follows. The number of bonded pairs must remain constant. However, as z increases, the total number of possible lattice pairs increases. This increases the number of nonbonded interactions until, in the limit of infinite z , the constant number of bonded pairs is negligible in comparison to nonbonded pairs. Analysis shows that the increase of f_{NB} with z at constant \bar{T} results primarily from an increase of nonbonded mer-mer interactions. It is because of these structural features that a comparison between our theory and the cell model of Prigogine is possible.

The use of ϕ over r has, to the authors, a fundamental and natural appeal. However, the test of the theory lies in its ability to reproduce and predict thermodynamic data. In this paper we have restricted our comparison to those data which qualitatively test the functional form of the

various measurable quantities. We find that the theory is comparable to others in that it shows similar, correct, trends. Like the SL theory, a liquid-vapor transition occurs, and comparable features for the compressibility coefficients are obtained. Both our theory and the SL theory are poor in the critical region. The ratio of the Boyle temperature to T_c is much improved in our approach. In the virial expansion, we find all the virial coefficients are temperature dependent, which is an extension of van der Waals' theories where B_n , $n > 2$, are constants. Finally, through the finite z approach, we find a correspondence between the lattice and cell models.

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Electric Birefringence Measurements on Micellar Solutions of Ionic Surfactants

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Electric birefringence measurements were carried out on surfactant solutions of $C_8F_{17}SO_3N(CH_3)_4$ and $C_8F_{17}SO_3N(C_2H_5)_4$, which were known to form anisotropic aggregates. Both amplitudes and relaxation time constants of the dynamic Kerr effect were studied as a function of total surfactant concentration, electric field strength, temperature, and counterion concentration. In the case of the pure surfactant solutions, the amplitudes of birefringence obeyed the Kerr law up to the highest values of field strength that were used (11.4 kV cm^{-1}). The decay of birefringence could be characterized by a single relaxation time constant. The birefringence of the solutions with excess counterion showed saturation behavior for the same electric fields, and the decay of birefringence was no longer single exponential. The size of the anisotropic aggregates was evaluated from the relaxation times of the electric birefringence. The results indicate the existence of rodlike micelles whose lengths and number density increase with $(c_0 - \text{cmc})^{1/2}$. Finally, the anisotropy of the electric polarizability of the counterion atmosphere was investigated, and the results were compared with theory.

Introduction

A review of the properties of micelles has recently been given by Wennerström and Lindman.¹ Further information on these systems can also be found in the somewhat older books by Tanford² and Shinoda et al.³ Micelles of ionic surfactants are usually visualized as aggregates of surfactant molecules with their ionic head groups located at the interface between the bulk water and the micelles.

Numerous investigations that were carried out by many authors using different techniques have shown that the micelles that are formed in most of the ionic detergent solutions for concentrations not too far above the critical micelle concentration (cmc) have a globular shape. There is also experimental evidence that in some solutions anisotropic aggregates are formed. These aggregates have

usually been observed for concentrations high above the cmc or when excess electrolyte was added to the surfactant solutions.⁴ While it is relatively easy to detect the presence of anisotropic aggregates by rheological, classical light scattering, kinetic, or streaming birefringence measurements, it is much more difficult to determine the exact shape and size of these nonspherical micelles. With most of these methods, it is necessary to extrapolate an experimental quantity to zero concentration in order to eliminate the micelle-micelle interaction and to obtain the size. However, this procedure can lead to erroneous results because the size of the aggregates changes with concentration, as was shown by NMR and quasi-elastic light scattering measurements.^{5,6} Because of these difficulties, there are very few reliable data available on the change

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