

Statistical Thermodynamics of r -Mer Fluids and Their Mixtures

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ABSTRACT: A modified fluid-lattice theory of fluids considering a finite quasi-lattice coordination number and a constant lattice site volume for all r -mers is developed. The theory is tested against experimental information on specific volumes, vapor pressures, orthobaric densities and heats of vaporization of pure components. Some common polymers and some typical polymer solvents have been chosen for testing the theory. The theoretical treatment has been extended to mixtures and tested against experimental data on volumes of mixing, heats of mixing, and χ interaction parameters of polymer solutions. Results have been compared with those obtained with a two-parameter new Flory theory and with the three-parameter new Huggins theory. Both for pure components and for mixtures, the effect of introducing a non-random quasi-chemical correction is discussed.

KEY WORDS Statistical Thermodynamics / Hole Theory / Polymer Solutions / Quasi-Chemical Approximation / r -Mer Fluids / Mixtures /

Considerable effort has been made in recent years towards the development and refinement of statistico-mechanical theories of the liquid state. The radial distribution function approach¹ has provided with a successful treatment of liquids formed by small molecules of nearly spherical force fields. For polymeric molecules, however, its applicability is limited and exact theoretical treatments remain elusive.

In this work we study the applicability of an approximate model to some polymer fluids, to some common polymer solvents and to their mixtures. In this approximation, a molecule is assumed to be divided in r segments occupying r consecutive lattice sites. The unoccupied sites of the quasi-lattice are called holes. Each site of the quasi-lattice is assumed to have Z neighboring sites. In this work, for simplicity, the value of the coordination number of the quasi-lattice, Z , has been arbitrarily assumed to be equal to ten. Each mer (segment of a molecule or a hole) is assumed to have a constant volume, v_H .

In this model, the relative number of holes play the role of free volume. Thus, the model does not require explicit consideration of the motion of segments around their equilibrium lattice positions

as required by cell theories,^{2,3} nor does it require explicit assumptions regarding the flexibility of the polymer molecules.² Simha and co-workers,⁴ and more recently Nose,⁵ have included a separate free volume term in their hole theories, thus incorporating a parameter c , similar to that of Prigogine,² to account for the flexibility of the molecule. The disadvantage of this approach is the need to consider the volume dependence of c if the theory is to be applicable to both the liquid and the gaseous phases. A more detailed discussion of this subject is given elsewhere.⁶

In the following sections we discuss the applicability of the random and non-random versions of the theory to pure components and concentrated polymer solutions.

PURE COMPONENTS

The Partition Function

In our previous work,^{7,8} we have presented detailed equations for the case of non-random distribution of molecules and holes in a quasi-lattice of constant lattice site volume, v_H , and finite coordination number, Z . We have also discussed a par-

ticular application of the model for calculation of volumetric properties of polymeric fluids.⁹ In this work we retain the basic formalism of our previous work^{7,8} and develop in detail the equations for the case of random distribution of molecules and holes.

For N_1 molecules of pure component 1, the maximum term of the canonical partition function may be written as,^{7,8,10,11}

$$Q = \left(\frac{\delta_1}{\sigma_1}\right)^{N_1} g_c g_{NR} \exp \frac{-E}{RT} \quad (1)$$

Since we are concerned with fluid regions not affected by high fluctuations, the maximum term is overwhelmingly larger than any other term in the sum over all microstates and may be considered to represent the configurational integral of the system.

The first term of eq 1, (δ_1/σ_1) , taking into account the flexibility and symmetry of the molecules,¹¹ does not contribute to the thermodynamic properties of interest to this study.

For g_c , the random combinatorial term, we adopt the Guggenheim-Huggins-Miller¹⁰ approximation,

$$g_c = \frac{N_r!}{N_H! N_1!} \left(\frac{N_q!}{N_r!}\right)^{Z/2} \quad (2)$$

where N_r is the total number of lattice sites, namely,

$$N_r = N_H + r_1 N_1 \quad (3)$$

with N_H and N_1 being the number of holes and the number of molecules of component 1, respectively. Similarly, the total number of external contacts displayed by the system, ZN_q , is given by

$$ZN_q = Z(N_H + q_1 N_1) \quad (4)$$

where the number of external contacts for each r -mer, Zq_r , is assumed related to r_1 by

$$Zq_1 = (Z-2)r_1 + 2 \quad (5)$$

The non-random correction factor, g_{NR} , included in eq 1, has been discussed in detail in our previous work^{7,8} and more recently by Nose and Okada.¹¹

Finally, the lattice energy E of the system appearing in eq 1, may be considered to be determined by the nearest neighbor interactions only. If N_{11} denotes the number of nearest neighbor contact pairs of molecular segments interacting with a characteristic energy ε_{11} , E is given by

$$-E = N_{11} \varepsilon_{11} \quad (6)$$

Since ε_{11} represents an average value over all pos-

sible configurations of the system, it has been suggested¹⁰ to consider it as an interactional free energy composed by an "enthalpic" and an "entropic" contribution. Thus,

$$\varepsilon_{11} = \varepsilon_{11h} + T\varepsilon_{11s} \quad (7)$$

The evaluation of N_{11} depends on the assumption made regarding the randomness or non-randomness of pure component segments and holes in the system.

If a random distribution of the free volume (holes around segments of a molecule) is assumed, $g_{NR} = 1$, N_{11} is approximated by its random value N_{11}° ,

$$N_{11}^\circ = \frac{N_1 Z q_1}{2} \theta_1 \quad (8)$$

where θ_1 is the fraction of the total external contacts in the system that corresponds to mer-mer contacts in a random array

$$\theta_1 = \frac{Z q_1 N_1}{Z N_q} \quad (9)$$

On the other hand, if a non-random array of segments and holes is assumed, according to the quasi-chemical approximation, g_{NR} takes the form,^{7,8,10}

$$g_{NR} = \frac{N_{11}^\circ! N_{HH}^\circ! \left[\left(\frac{N_{1H}^\circ}{2}\right)!\right]^2}{N_{11}! N_{HH}! \left[\left(\frac{N_{1H}}{2}\right)!\right]^2} \quad (10)$$

with

$$N_{11} = N_{11}^\circ \Gamma_{11} \quad (11a)$$

$$N_{HH} = N_{HH}^\circ \Gamma_{HH} \quad (11b)$$

and

$$N_{1H} = N_{1H}^\circ \Gamma_{1H} \quad (11c)$$

In eq 11b, N_{HH}° is approximated in a similar way as N_{11}° in eq 8, i.e., $N_{HH}^\circ = (N_H Z/2)\theta_H$, with $\theta_H = 1 - \theta_1$. In eq 11c, N_{1H}° is given by $N_{1H}^\circ = (N_1 Z q_1)\theta_H = (N_H Z)\theta_1$. The non-random factors Γ_{11} , Γ_{HH} , and Γ_{1H} are related by

$$\theta_1 \Gamma_{1H} + \theta_H \Gamma_{HH} = \theta_H \Gamma_{1H} + \theta_1 \Gamma_{11} = 1 \quad (12)$$

and Γ_{1H} is given by the quasi-chemical expression,

$$\Gamma_{1H} = \frac{2}{1 + \sqrt{1 - 4\theta_1 \theta_H (1 - G)}} \quad (13)$$

with

$$G = \exp\left(\frac{\varepsilon_{11}}{RT}\right) \quad (14)$$

Equation of State and Second Order Thermodynamic Functions

The basic step to obtain the equation of state and related functions is to introduce the volume dependence explicitly in the terms of the partition function. Since each segment of the molecules and also the holes are assumed to have a constant volume v_H , the total volume of the system is given by

$$V = (N_H + N_1 r_1) v_H \quad (15)$$

$N_H v_H$ represents the free volume of the system and $N_1 r_1 v_H$ the "hard core" contribution that will be given the symbol V^*

$$V^* = N_1 r_1 v_H \quad (16)$$

V^* , or more properly, the related specific hard core volume v_{sp}^* , is considered to be a characteristic parameter of the pure component. Thus, if a value for v_H is assumed, eq 16 defines r_1 and eq 15 allows the calculation of N_H .

The equation of state for the system is now obtained by

$$P = RT \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N_1} \quad (17)$$

For simplicity, we introduce the following conventional reduced quantities

$$\tilde{v}_1 = \frac{V}{V_1^*} = \frac{v_{sp}}{v_{sp,1}^*} \quad \tilde{T}_1 = \frac{T}{T_1^*} \quad \tilde{P}_1 = \frac{P}{P_1^*}$$

where the reducing temperature, T_1^* , and the reducing pressure, P_1^* , are defined by the relation

$$\frac{Z}{2} \varepsilon_{11} = P_1^* v_H = RT_1^* \quad (18)$$

Since ε_{11} is assumed to be temperature dependent, eq 7, P_1^* and T_1^* are also temperature dependent.

With the above nomenclature, the following expressions are obtained for the equation of state.

Random approximation:

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln \frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{Z}{2} \ln \left(\frac{\tilde{v}_1 + q_1/r_1 - 1}{\tilde{v}_1} \right) - \frac{\theta_1^2}{\tilde{T}_1} \quad (19a)$$

Non-random approximation:

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln \frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{Z}{2} \ln \left(\frac{\tilde{v}_1 + q_1/r_1 - 1}{\tilde{v}_1} \right) - \frac{Z}{2} \ln \Gamma_{HH} \quad (19b)$$

Each fluid is fully characterized by its three equation of state parameters, namely, v_{sp}^* , ε_{11h} , and ε_{11s} . Of considerable value for the calculation of these parameters, particularly in the case of polymers, are data on second order thermodynamic functions such as thermal expansion coefficient α_1 , isothermal compressibility coefficient β_1 and thermal pressure coefficient γ_1 . In the random approximation for pure components the following expressions for these functions are obtained:

Thermal expansion coefficient, α_1 :

$$T\alpha_1 = \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{(\tilde{P}_1/\tilde{T}_1) + (\varepsilon_{11h}\theta_1^2/\varepsilon_{11}\tilde{T}_1)}{1/(\tilde{v}_1 - 1) + (1/r_1 - 1)\theta_1/(q_1/r_1) - (2\tilde{v}_1\theta_1^3)/(\tilde{T}_1 q_1/r_1)} \quad (20)$$

Isothermal compressibility coefficient, β_1 :

$$P\beta_1 = -\frac{P}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{(\tilde{P}_1/\tilde{T}_1)}{1/(\tilde{v}_1 - 1) + (1/r_1 - 1)\theta_1/(q_1/r_1) - (2\tilde{v}_1\theta_1^3)/(\tilde{T}_1 q_1/r_1)} \quad (21)$$

Thermal pressure coefficient, γ_1 :

$$\frac{T}{P} \gamma_1 = \frac{T}{P} \left(\frac{\partial P}{\partial T} \right)_V = 1 + (\varepsilon_{11h}\theta_1^2/\varepsilon_{11}\tilde{P}_1) \quad (22)$$

For polymers, the above expressions simplify somewhat since $r_1 \rightarrow \infty$ and $1/r_1 \rightarrow 0$. In addition, if the assumption $Z=10$ is made, $q_1/r_1=0.8$ according to eq 5. Second order thermodynamic functions for the non-random case are obtained in a similar way from the equation of state 19b.

Liquid-Vapor Transition

The chemical potential is obtained from the canonical partition function as

$$-\frac{\mu_1}{RT} = \left(\frac{\partial \ln Q}{\partial N_1} \right)_{T, V} \quad (23)$$

Thus, for the random approach,

$$-\frac{\mu_1}{RT} = \left\{ \ln \frac{\delta_1}{\sigma_1} + \ln q_1 \right\} + \left\{ \ln \frac{(1-\theta_1)^{r_1}}{\theta_1} + \frac{\theta_1}{\bar{T}_1} (q_1 + r_1 \tilde{v}_1 \theta_1) \right\} \quad (24a)$$

and for the non-random approach

$$-\frac{\mu_1}{RT} = \left\{ \ln \frac{\delta_1}{\sigma_1} + \ln r_1 + r_1 \frac{q_1/r_1 - \bar{P}_1}{\bar{T}_1} \right\} + \left\{ \ln \tilde{v}_1 + \frac{Zq_1}{2} \ln \left(\frac{\tilde{v}_1 + q_1/r_1 - 1}{\tilde{v}_1 \Gamma_{11}} \right) \right\} \quad (24b)$$

For the calculation of the heats of vaporization, it is usually assumed that the rotational and vibrational modes of motion in the gas and the liquid states are the same. Thus, the configurational energy of the liquid state may be considered equal to the internal energy of vaporization into vacuum with a likely small error. The configurational energy of each phase is obtained as

$$U = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{v, N_1} \quad (25)$$

The heat of vaporization ΔH^{vap} is then obtained from the enthalpy $H = U + PV$, of each phase as

$$\Delta H^{\text{vap}} = H_v - H_L \quad (26)$$

For the random approach,

$$H = PV - \frac{N_1 Z q_1}{2} \theta_1 \varepsilon_{11h} \quad (27a)$$

and for the non-random approach

$$H = PV - \frac{N_1 Z q_1}{2} \theta_1 \Gamma_{11} \varepsilon_{11h} \quad (27b)$$

The condition for vapor-liquid equilibrium of a pure component is

$$\left(\frac{\mu_1}{RT} \right)_L = \left(\frac{\mu_1}{RT} \right)_v \quad (28)$$

The terms in the first brackets in eq 24a and 24b will cancel out in eq 28. Thus, eq 28 may be written as

$$F_L = F_v \quad (28a)$$

where the auxiliary function F represents only the terms of the second bracket in eq 24a and 24b.

For the vapor pressure, the model does not provide with a direct analytical expression.

However, the numerical calculation of the vapor-pressure at a given temperature is straightforward. In this work we have used the following computational scheme: a value of the vapor pressure is assumed and from the equation of state the liquid volume is obtained. Using eq 24a or eq 24b, the left-hand side of eq 28a is evaluated and the vapor volume is obtained from the right-hand side. With this vapor volume, the pressure is evaluated from the equation of state and the procedure is repeated until the assumed and calculated values of the

Table I. Comparison of random and non-random approach with data on acetone

Molecular parameters			
	ε_{11h}	ε_{11s}	v_{sp}^*
	cal mol ⁻¹	cal mol ⁻¹ K ⁻¹	cm ³ g ⁻¹
Random	255.59	-0.0306	1.1785
Non-random	262.15	-0.0479	1.1671
Specific volume			
cm ³ g ⁻¹			
Temperature	Experimental	Random approach	Non-random approach
°C			
0.0	1.2308	1.2502	1.2444
15.0	1.2566	1.2640	1.2604
20.0	1.2649	1.2690	1.2662
25.0	1.2739	1.2742	1.2722
30.0	1.2832	1.2795	1.2785
40.0	1.3021	1.2909	1.2919
50.0	1.3228	1.3031	1.3065
Vapor pressures			
atm			
35.11	0.47	0.47	0.47
45.76	0.69	0.70	0.69
56.13	1.00	1.00	1.00
66.62	1.41	1.41	1.41
71.92	1.67	1.67	1.67
Heat of vaporization			
cal mol ⁻¹			
56.2	7277	7170	7207

Table II. Equation of state parameters for some common polymers

Polymer	Reference	ϵ_{11h}	ϵ_{11s}	v_{sp}^*	Temperature range	Pressure range	Maximum deviation	Average % error in density	
		cal mol ⁻¹	cal mol ⁻¹ K ⁻¹	cm ³ g ⁻¹	°C	bars	× 100	Present theory	S-L theory
Polystyrene (atactic)	15	167.54	+0.222	0.8801	115—195	1—2000	0.5	0.15	0.30
Poly(<i>o</i> -methyl styrene)	15	182.60	+0.203	0.9000	139—198	1—1600	0.3	0.09	0.16
Poly(methyl methacrylate)	16	221.46	+0.131	0.7900	124—159	1—2000	0.9	0.15	0.22
Poly(<i>n</i> -butyl methacrylate)	16	197.97	+0.103	0.8810	34—200	1—2000	0.5	0.19	0.38
Poly(cylo-hexyl methacrylate)	16	197.38	+0.157	0.8400	123—199	1—2000	0.8	0.21	0.30
Poly(vinyl acetate)	17	239.01	-0.007	0.7850	35—100	1—800	0.3	0.10	0.10
Polyethylene (branched)	16	184.46	+0.141	1.0954	135—198	1—1000	0.3	0.10	0.12
Polyisobutylene	18	190.49	+0.124	1.0080	53—110	1—1000	0.4	0.13	0.18
Poly(propylene oxide)	19	203.54	+0.011	0.9162	—	—	—	—	—
Polyethylene (ultra HMW, linear)	16	244.80	+0.011	1.1077	147—200	1—1000	0.3	0.11	—
Poly(dimethyl siloxane)	18	133.13	+0.145	0.8911	25—70	1—1000	0.7	0.18	0.20
Polyethylene (linear)	16	226.41	+0.053	1.0951	153—200	1—1000	0.3	0.12	0.09
Overall average %								0.14	0.20

pressure agree within a tolerance error.

*Comparison of the Theory with Experimental Data for Pure *r*-Mers*

In the original fluid-lattice theory,^{12,13} the volume of a lattice site was assumed to be different for different fluids. When extending their theory to mixtures, Sanchez and Lacombe¹⁴ were forced to consider a composition dependent volume of a lattice site. Consequently, the number of segments of a given molecule resulted as a function of the composition of the mixture. Sometimes, the number of segments of a given molecule duplicated or triplicated and this was interpreted as a "surface effect." However, in order to "facilitate the analysis" of phase stability, the author¹⁴ assumed a constant lattice-site volume. In our previous work,⁹ we have discussed the advantages of assuming a constant lattice-site volume for all fluids and their mixtures. In this work, we continue this practice and assume $v_H = 9.75$ ($\text{cm}^3 \text{mol}^{-1}$) as suggested previously.⁹

Preliminary calculations showed that there is little practical advantage in considering the more complex non-random approach for pure components. As an example, Table I presents a comparison of results for acetone at different temperature.

In view of the above results, the random model of molecules and holes was adopted for pure components. The main advantage of the random approach for pure components becomes evident in the treatment of mixtures. If non-randomness is considered for pure components, binary molecular systems have to be treated as ternary systems and so on. With the random approach for pure components, correction for non-randomness may still

Table III. Equation of state parameters for some common solvents

Solvent	ϵ_{11h}	ϵ_{11s}	v_{sp}^*
	cal mol^{-1}	$\text{cal mol}^{-1} \text{K}^{-1}$	$\text{cm}^3 \text{g}^{-1}$
Acetone	255.59	-0.0306	1.1785
Benzene	234.78	0.0121	1.0576
Carbon tetrachloride	221.23	0.0202	0.5781
Chloroform	242.94	-0.0132	0.6200
<i>n</i> -Heptane	177.92	0.0615	1.2826
<i>n</i> -Pentane	182.27	0.0185	1.3695

be applied to binary molecular systems formally treating them as binaries, as is explained in the section on mixtures.

Table II presents a comparison of the performance of the theory with volumetric data of some common polymers over an extended range of temperature and pressure. For comparison, we have included in Table II the results obtained with the fluid-lattice theory of Lacombe and Sanchez.¹³ For the determination of the parameters for poly(propylene oxide), second order thermody-

Table IV. Densities, vapor pressures, and heats of vaporization for *n*-heptane

Temperature °C	Experimental ²⁰	Calculated
	Specific volumes	
$\text{cm}^3 \text{g}^{-1}$		
0.0	1.4278	1.4261
10.0	1.4449	1.4409
15.0	1.4539	1.4486
20.0	1.4622	1.4566
25.0	1.4716	1.4649
30.0	1.4810	1.4733
40.0	1.4997	1.4911
50.0	1.5197	1.5100
Vapor pressures		
atm		
0.0	0.275	0.279
80.0	0.561	0.572
100.0	1.046	1.075
120.0	1.799	1.873
140.0	2.933	3.072
160.0	4.539	4.782
180.0	6.699	7.124
200.0	9.554	10.203
220.0	13.296	14.175
230.0	15.539	16.536
Heats of vaporization		
cal mol^{-1}		
25.00	8735	8726
58.06	8244	8393
77.33	7938	8171
90.48	7715	8006

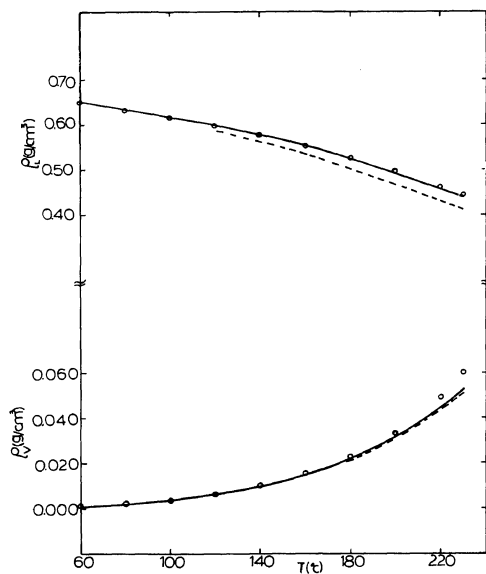


Figure 1. Orthobaric densities of *n*-heptane: ○, experimental data²⁰; —, present theory; ---, fluid-lattice theory.¹²

dynamic functions were used. As shown in Table II, the maximum percent deviation in the computation of the specific volume obtained with the present treatment is 0.9. For the same polymers, Lacombe and Sanchez¹³ have reported a maximum percent deviation of 1.2.

For small molecules, such as common polymer solvents, a more stringent test of the theory is possible due to the plethora of data including heats of vaporization and vapor pressures.²⁰⁻²³ The data have been chosen at conditions far from the critical point since the model is not expected to be valid in the proximity of the critical region.

Table III presents the equation of state parameters for some common polymer solvents obtained with the random approach. It is not our purpose to endeavor on the physical significance of the parameter ϵ_{11s} . It is, however, worthy of mention that the parameter ϵ_{11s} is at least sensitive to the nature of interactions involved in the fluid. As it is shown in Table III, the two fluids acetone and chloroform, where strong interactions are involved, show a negative ϵ_{11s} in contrast to all other studied fluids. Similar behavior is ob-

served for poly(vinyl acetate) in Table II.

In addition to the detailed comparison for acetone previously presented in Table I, Table IV presents a detailed comparison for data of *n*-heptane. Figure 1 compares the predicted orthobaric densities of *n*-heptane with experimental data²⁰ and with the predictions obtained with the fluid lattice theory of Lacombe and Sanchez.¹²

As it may be seen from Figure 1, the present model presents a definite improvement in the prediction of orthobaric densities.

MIXTURES

The Partition Function

The basic formalism of the quasi-chemical correction for non-randomness, in terms of non-random factors, has been discussed in detail previously.^{7,8,24} In a rigorous application of the Hole theory,⁷ a binary system is formally a ternary one (the third component being the holes) and implicit expressions for the non-random factors are obtained. In this work we follow an approximation that has been previously used to correct for non-randomness the new Flory theory,^{24,25} *i.e.*, to consider that the molecular segments are non-randomly distributed while the free volume (holes) is evenly distributed throughout the system. For a binary system, this approximation²⁴ produces explicit expressions of the form of eq 44 for the non-random factors.

The canonical partition function for a system containing N_H holes, N_1 molecules of r_1 -mer and N_2 molecules of r_2 -mer, may be written as

$$Q = \left(\frac{\delta_1}{\sigma_1}\right)^{N_1} \left(\frac{\delta_2}{\sigma_2}\right)^{N_2} g_c g_{NR} \exp\left(-\frac{E}{RT}\right) \quad (29)$$

As for pure components, the first two factors include the geometric characteristics of the molecules and do not contribute to mixing properties of interest in this work.

The total number of sites of the fluid lattice, N_t , is given by

$$N_t = N_H + r_1 N_1 + r_2 N_2 = N_H + rN \quad (30)$$

where

$$N = N_1 + N_2 \quad (31)$$

and

$$r = x_1 r_1 + x_2 N_2 \quad (32)$$

x_i being the mole fraction of component i . In addition, the total number of external contracts between the molecules is

$$ZN_q = Z(N_H + q_1 N_1 + q_2 N_2) = Z(N_H + qN) \quad (33)$$

where

$$q = x_1 q_1 + x_2 q_2 \quad (34)$$

Thus, for a binary mixture, the combinatorial factor has the form

$$g_c = \frac{N_r!}{N_H! N_1! N_2!} \left(\frac{N_q!}{N_r!} \right)^{Z/2} \quad (35)$$

The factor g_{NR} in eq 29 is unity for the random case. In order to treat the non-random case, we define the molecular surface fraction $\bar{\theta}_i$ by

$$\bar{\theta}_i = \frac{Zq_i N_i}{ZqN} \quad (i=1, 2) \quad (36)$$

In addition, to simplify the nomenclature, we define the overall surface fraction θ_i as it was done in eq 9 for pure components, namely

$$\theta_i = \frac{Zq_i N_i}{ZN_q} \quad (37)$$

While the summation of the values of $\bar{\theta}_i$ over all the components adds to unity, the summation of θ_i adds to $(1 - \theta_H)$. Thus, for convenience, we also define

$$\theta = \theta_1 + \theta_2 = 1 - \theta_H \quad (38)$$

Combination of eq 36 to 38 gives

$$\theta_i = \bar{\theta}_i \theta \quad (39)$$

Furthermore, we define \bar{N}_{ij} by

$$\bar{N}_{11} = \frac{N_{11}}{\theta} = \frac{N_1 Zq_1}{2} \bar{\theta}_1 \dot{r}_{11} \quad (40a)$$

$$\bar{N}_{22} = \frac{N_{22}}{\theta} = \frac{N_2 Zq_2}{2} \bar{\theta}_2 \dot{r}_{22} \quad (40b)$$

and

$$\bar{N}_{12} = \frac{N_{12}}{\theta} = N_1 Zq_1 \bar{\theta}_2 \dot{r}_{12} = N_2 Zq_2 \bar{\theta}_1 \dot{r}_{12} \quad (40c)$$

where N_{ij} are the number of external (energetic) contacts between segments of molecules i and j . The dot over the non-random factors \dot{r}_{ij} denotes the assumption of random distribution of holes.

Because of this even distribution of holes, for the non-random case, we may assume that g_{NR} is given by

$$g_{NR} = \frac{\bar{N}_{11}! \bar{N}_{22}! \left[\frac{\bar{N}_{12}!}{2} \right]^2}{\bar{N}_{11}! \bar{N}_{22}! \left[\frac{\bar{N}_{12}!}{2} \right]^2} \quad (41)$$

The potential energy of the system, in turn, is obtained as

$$-E = N_{11} \epsilon_{11} + N_{12} \epsilon_{12} + N_{22} \epsilon_{22} \\ = \theta (\bar{N}_{11} \epsilon_{11} + \bar{N}_{12} \epsilon_{12} + \bar{N}_{22} \epsilon_{22}) \quad (42)$$

where ϵ_{ij} is a characteristic energy for the contacts of segments of molecules i and j .

The non-random factors \dot{r}_{ij} are related by

$$\bar{\theta}_1 \dot{r}_{11} + \bar{\theta}_2 \dot{r}_{12} = \bar{\theta}_2 \dot{r}_{22} + \bar{\theta}_1 \dot{r}_{12} = 1 \quad (43)$$

and \dot{r}_{12} is given by the quasi-chemical expression,²⁴

$$\dot{r}_{12} = \frac{2}{1 + \sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}} \quad (44)$$

with

$$\dot{G} = \exp \left[\frac{\theta(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})}{RT} \right] = \exp \left[\theta \frac{\Delta\epsilon}{RT} \right] \quad (45)$$

From the above equations, it may be observed that for the random case, $\Delta\epsilon = 0$, $\dot{r}_{11} = \dot{r}_{22} = \dot{r}_{12} = 1$. In addition, even if $\Delta\epsilon \neq 0$, when the volume of the system increases, $\theta \rightarrow 0$ and the random array is approached. This limiting qualitative behavior of the above expressions is in agreement with physical expectation.

Equation of State

The total volume of the system V , the hard core volume V^* and the reduced volume \tilde{v} , are expressed in terms of the previously defined variables by

$$V = N_r v_H \quad (46)$$

$$V^* = r N v_H \quad (47)$$

and

$$\tilde{v} = V/V^* = N_r/rN \quad (48)$$

We define a characteristic energy of the system ϵ^* by

$$\epsilon^* = (\bar{\theta}_1 \epsilon_{11} + \bar{\theta}_2 \epsilon_{22} - \bar{\theta}_1 \bar{\theta}_2 \dot{r}_{12} \Delta\epsilon) \quad (49)$$

For a given composition and temperature of the system, the characteristic temperature T^* and the characteristic pressure P^* are then obtained from

$$\frac{Z}{2} \varepsilon^* = P^* v_H = RT^* \quad (50)$$

The reduced temperature and the reduced pressure are then

$$\tilde{T} = T/T^* \quad \text{and} \quad \tilde{P} = P/P^*$$

With the above nomenclature, the equation of state obtained from eq 17 is formally identical to the equation of state for pure components, *i.e.*, eq 19a. Thus, for both the random and non-random cases, we write

$$\frac{\tilde{P}}{\tilde{T}} = \ln \left(\frac{\tilde{v}}{\tilde{v}-1} \right) + \frac{Z}{2} \ln \left(\frac{\tilde{v} + q/r - 1}{\tilde{v}} \right) - \frac{\theta^2}{\tilde{T}} \quad (51)$$

Chemical Potential

For a binary mixture, ε_{11} , ε_{22} , and ε_{12} are considered to be functions of temperature of the form given by eq 7. While we consider ε_{12h} to be an adjustable parameter, for simplicity, the small "entropic" contribution ε_{12s} is approximated by the arithmetic mean of ε_{11s} and ε_{22s} .

The chemical potential of component i in the mixture is obtained using eq 23 with N_2 constant. The difference of the chemical potential of component 1 in the mixture and the chemical potential of pure component 1 at the same temperature and pressure, $\Delta\mu_1$, for the non-random case takes the form

$$\begin{aligned} \frac{\Delta\mu_1}{RT} = & \ln \phi_1 + \ln \frac{\tilde{v}_1}{\tilde{v}} + q_1 \ln \left(\frac{\tilde{v}}{\tilde{v}-1} \frac{\tilde{v}_1-1}{\tilde{v}_1} \right) \\ & + q_1 \left(\frac{2\theta_{1,p} - \theta}{\tilde{T}_1} - \frac{\theta}{\tilde{T}} \right) + \frac{Zq_1}{2} \ln \dot{r}_{11} \end{aligned} \quad (52)$$

and for the random case,

$$\begin{aligned} \frac{\Delta\mu_1}{RT} = & \ln \phi_1 + \ln \frac{\tilde{v}_1}{\tilde{v}} + q_1 \ln \left(\frac{\tilde{v}}{\tilde{v}-1} \frac{\tilde{v}_1-1}{\tilde{v}_1} \right) \\ & + 2q_1 \left(\frac{\theta_{1,p} - \theta_1}{\tilde{T}_1} - \frac{\theta_2}{\tilde{T}_{12}} \right) \end{aligned} \quad (52a)$$

where $\theta_{1,p}$ refers to pure component 1 at the same temperature and pressure and \tilde{T}_{12} has been defined as

$$\tilde{T}_{12} = \frac{2RT}{Z\varepsilon_{12}} \quad (53)$$

ϕ is the segment fraction of component i ,

$$\phi_i = \frac{r_i N_i}{rN} = \theta_i \frac{(\tilde{v} + q/r - 1)}{(q_i/r_i)} \quad (54)$$

The Flory-Huggins χ_{12} interaction parameter may be directly obtained from eq 52 or 52a and its defining equation:

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{r_1}{r_2} \right) \phi_2 + \chi_{12} \phi_2^2 \quad (55)$$

For the non-random approach

$$\begin{aligned} \chi_{12} = & \frac{r_1 - r_2}{r_2 \phi_2} + \frac{1}{\phi_2^2} \left\{ \ln \frac{\tilde{v}_1}{\tilde{v}} + q_1 \ln \left(\frac{\tilde{v}}{\tilde{v}-1} \frac{\tilde{v}_1-1}{\tilde{v}_1} \right) \right. \\ & \left. + q_1 \left(\frac{2\theta_{1,p} - \theta}{\tilde{T}_1} - \frac{\theta}{\tilde{T}} \right) + \frac{Zq_1}{2} \ln \dot{r}_{11} \right\} \end{aligned} \quad (56)$$

For the random approach

$$\begin{aligned} \chi_{12} = & \frac{r_1 - r_2}{r_2 \phi_2} + \frac{1}{\phi_2^2} \left\{ \ln \frac{\tilde{v}_1}{\tilde{v}} + q_1 \ln \left(\frac{\tilde{v}}{\tilde{v}-1} \frac{\tilde{v}_1-1}{\tilde{v}_1} \right) \right. \\ & \left. + 2q_1 \left(\frac{\theta_{1,p}}{\tilde{T}_1} - \frac{\theta_2}{\tilde{T}_{12}} \right) \right\} \end{aligned} \quad (56a)$$

Expressions for the activity coefficient of component 1 in the mixture, γ_1' , are readily obtained combining eq 56 or 56a with

$$\frac{\Delta\mu_1}{RT} = \ln (x_1 \gamma_1') \quad (57)$$

Volume Change and Heats of Mixing

The volume change of mixing is given by

$$\frac{\Delta V}{N} = v_H (\tilde{v} - \phi_1 \tilde{v}_1 - \phi_2 \tilde{v}_2) \quad (58)$$

for both random and non-random approaches.

For low to moderate pressures, the identification of enthalpies with configurational energies is a satisfactory approximation. Thus, for the non-random case, the heats of mixing are given by

$$\begin{aligned} \frac{\Delta H}{N} = & \frac{Zq}{2} [\bar{\theta}_1 (\theta_{1,p} - \theta) \varepsilon_{11h} + \bar{\theta}_2 (\theta_{2,p} - \theta) \varepsilon_{22h} \\ & + \bar{\theta}_1 \bar{\theta}_2 \dot{r}_{12} \theta \Delta \varepsilon] \end{aligned} \quad (59)$$

while, for the random case,

$$\begin{aligned} \frac{\Delta H}{N} = & \frac{Zq}{2} [\bar{\theta}_1 (\theta_{1,p} - \theta_1) \varepsilon_{11h} + \bar{\theta}_2 (\theta_{2,p} - \theta_2) \varepsilon_{22h} \\ & - 2\bar{\theta}_1 \bar{\theta}_2 \theta \varepsilon_{12h}] \end{aligned} \quad (59a)$$

For polymer solutions, it is usual to find information of the heat of mixing at infinite dilution, ΔH^∞ , or of the equivalent quantity B , given by

$$B = \frac{r_1}{r_2} \Delta H^\infty \quad (60)$$

With the present model, in both random and non-random approximations, gives

$$B = \frac{Zr_1}{2} \left\{ \left[\theta_{1,p} \frac{q_1}{r_1} \left(\frac{r_1}{q_1} \frac{q_2}{r_2} \theta_{1,p} + 1 - \theta_{1,p} \right) \varepsilon_{11h} + \theta_{2,p} \frac{q_2}{r_2} \varepsilon_{22h} - 2\theta_{1,p} \frac{q_2}{r_2} \varepsilon_{12h} \right] + 2 \frac{q_2}{r_2} \frac{r_1}{q_1} \frac{\theta_{1,p}^4 \bar{v}_1 \beta_1 RT}{\bar{T}_1 v_H} \left[\left(\frac{r_2}{q_2} \frac{r_1}{q_1} - 1 \right) (1 - \theta_{1,p}) - \frac{\varepsilon_{12}}{\varepsilon_{11}} + 1 \right] \varepsilon_{11h} \right\} \quad (61)$$

Application of the Theory to Polymer Solutions

Complete and accurate data on heats of mixing, volumes of mixing and vapor pressure lowering have been reported by Kershaw and Malcolm¹⁹ for the systems chloroform–poly(propylene oxide) and carbon tetrachloride–poly(propylene oxide). Data on the latter system were used by Huggins²⁶ to test his three parameter theory and data of both systems were used by the authors to test the two parameter new Flory non-random theory.²⁴ From our previous experience with the new Flory theory,²⁴ one single parameter (X_{12}) is insufficient to reproduce both sets of data, especially the data of the first system.

In the new Flory theory,²⁷ a second adjustable parameter has been introduced in order to account for an extra entropic contribution in the interaction energies, absent in the parameter X_{12} . Thus, X_{12} has essentially been replaced by \bar{X}_{12} , using

$$\bar{X}_{12} = X_{12} - \bar{v} T Q_{12} \quad (62)$$

With the above substitution, the equation of state and the expressions for volumes and heats of mixing of the new Flory theory remain unchanged, while the expression for χ_{12} is modified. In the present theory, the same effect is obtained replacing the adjustable parameter ε_{12h} by

$$\bar{\varepsilon}_{12h} = \varepsilon_{12h} - \left(\frac{1}{\theta} \right) T Q_{12} \quad (62a)$$

since $(1/\theta)$ is the formal equivalent to \bar{v} in the new Flory theory.

However, Simha,²⁸ studying the applicability of his hole theory to polymer mixtures, has found the 1–2 interaction energy parameter to be composition dependent. Preliminary calculations with the present theory have shown the same effect. After some trials the following empirical composition dependence of the parameter Q_{12} has been found to give a better representation of the data

$$Q_{12} = (1 + \kappa_{12} \bar{\theta}_1) R Q'_{12} \quad (63)$$

The gas constant R has been included in eq 63 in order to have Q'_{12} dimensionless. As with the new Flory theory, this correction affects the expressions for χ_{12} . For the non-random approach, the following term should be added to eq 56:

$$Z q_1 \bar{\theta}_1 Q_{12} \bar{r}_{12} \left(\frac{\bar{\theta}_2}{\phi_2} \right)^2$$

while, for the random approach the additional term is:

$$Z q_1 (1 + 2\kappa_{12} \bar{\theta}_1) Q'_{12} \left(\frac{\bar{\theta}_2}{\phi_2} \right)^2$$

In the random approach the parameter ε_{12h} may be derived from data on heats of mixing and/or volumes of mixing while the other two parameters κ_{12} and Q'_{12} may be obtained from fitting the data on χ_{12} interaction parameters.

In Table V we present experimental and calculated volumes and heats of mixing for the system chloroform (1)–poly(propylene oxide) (2) at 5.53°C.

Two sets of parameters have been used in the random approach as indicated in Table V. Set #1 reproduces satisfactorily heats of mixing and χ_{12} interaction parameters as shown in Figure 2, but overestimates somehow the volumes of mixing. The second set reproduces in an identical manner the χ_{12} interaction parameters and quite satisfactorily the volumes of mixing but underestimates the heats of mixing. The non-random approach makes an intermediate representation of heats and volumes of mixing and good representation of the χ_{12} interaction parameters. The overall performance of the model is rather satisfactory if one takes into account the nature of the intermolecular interactions involved in this system. On the other hand, there is a considerable improvement over the two-parameter new Flory theory.²⁴

Table V. Experimental and calculated mixing functions for the system: chloroform (1)–poly(propylene oxide) (2) at 5.53°C

Binary parameters				
		ϵ_{12h} cal mol ⁻¹	κ_{12}	Q'_{12}
Random approach	Set #1	258.4	0.705	0.026
	Set #2	246.2	3.320	0.006
Non-random approach		251.9	0.943	0.035

Volume fraction, ϕ_2	Experimental ¹⁹	Calculated		
		Set #1	Set #2	Non-random approach
Volumes of mixing cm ³ cm ⁻³				
0.1396	-0.00426	-0.00704	-0.00473	-0.00585
0.2887	-0.00793	-0.01198	-0.00818	-0.01006
0.4127	-0.00988	-0.01430	-0.00981	-0.01207
0.5213	-0.01037	-0.01504	-0.01032	-0.01270
0.5928	-0.01006	-0.01483	-0.01014	-0.01252
0.6800	-0.00883	-0.01376	-0.00933	-0.01156
0.7620	-0.00697	-0.01182	-0.00793	-0.00988
0.8551	-0.00458	-0.00831	-0.00541	-0.00683

Heats of mixing cal cm ⁻³				
0.1512	-3.12	-3.96	-2.58	-3.24
0.2725	-5.23	-6.11	-3.98	-5.01
0.3744	-6.97	-7.22	-4.70	-5.94
0.4690	-7.64	-7.68	-5.00	-6.32
0.5223	-7.84	-7.69	-5.01	-6.34
0.6126	-7.70	-7.32	-4.76	-6.03
0.6923	-6.87	-6.57	-4.27	-5.41
0.7985	-5.24	-4.96	-3.21	-4.07
0.9054	-2.62	-2.62	-1.68	-2.13

In the second system, carbon tetrachloride (1)–poly(propylene oxide) (2), no hydrogen bonding is involved and a better agreement is expected. In Table VI we present experimental and calculated data for the volumes and heats of mixing for this system. The agreement is quite satisfactory. Only the random approach has been used. The non-random approach is not expected to make any perceptible improvement for this system. In Figure 3 the present model is compared with the three

parameter new Huggins theory²⁶ and the two-parameter new Flory theory²⁴ against experimental data on χ_{12} interaction parameters for the same system. The maximum in χ_{12} calculated by the present model is a handicap obviously stemming from the simple linear composition dependence of the corrective term to ϵ_{12h} .

As a further test of the theory the data reported by Bawn and Wajid²⁹ for the system acetone (1)–polystyrene (2) at 25°C have been chosen. For this

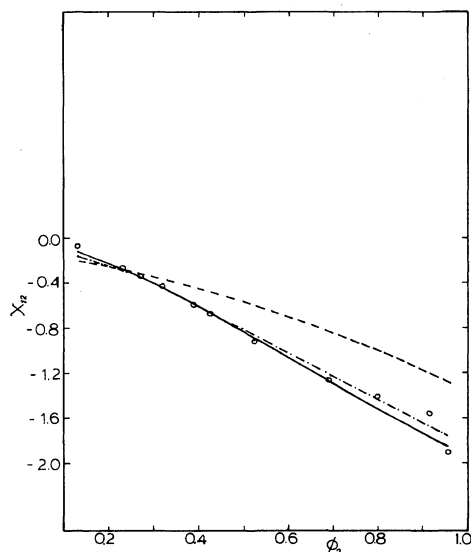


Figure 2. χ_{12} interaction parameters for the system: chloroform (1)-poly(propylene oxide) (2) at 5.53°C: \circ , experimental data¹⁹; —, present theory (random approach); - - -, present theory (non-random approach); - · -, new Flory theory.²⁴

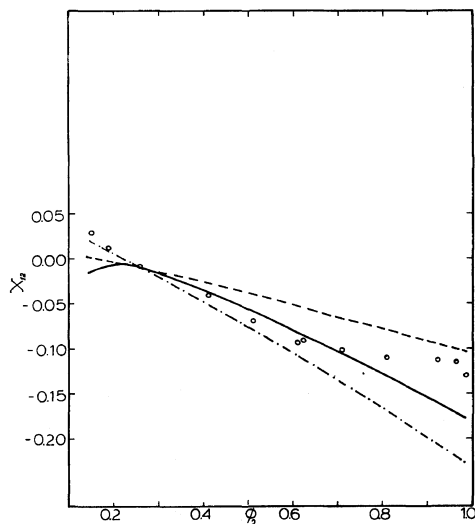


Figure 3. χ_{12} interaction parameters for the system: carbon tetrachloride (1)-poly(propylene oxide) (2) at 5.53°C: \circ , experimental data¹⁹; —, present theory (three parameters); - - -, new Flory theory (two parameters); - · -, new Huggins theory (three parameters).

Table VI. Experimental and calculated mixing functions for the system: carbon tetrachloride (1)-poly(propylene oxide) (2) at 5.53°C

Binary parameters		
$\epsilon_{12h} = 218.5 \text{ cal mol}^{-1}$, $\kappa_{12} = 0.246$, $Q'_{12} = 0.007$		
Volume fraction, ϕ_2	Experimental ¹⁹	Calculated
Volumes of mixing		
$\text{cm}^3 \text{ cm}^{-3}$		
0.1918	-0.00166	-0.00177
0.3240	-0.00245	-0.00250
0.4437	-0.00277	-0.00279
0.5099	-0.00281	-0.00281
0.5986	-0.00263	-0.00264
0.7313	-0.00211	-0.00201
0.8381	-0.00154	-0.00113
Heats of mixing		
cal cm^{-3}		
0.2040	-0.74	-0.85
0.3511	-1.12	-1.19
0.5010	-1.30	-1.31
0.6630	-1.12	-1.15
0.7923	-0.83	-0.83
0.8985	-0.53	-0.43

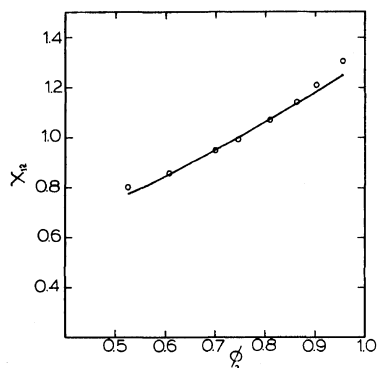


Figure 4. χ_{12} interaction parameters for the system: acetone (1)-polystyrene (2) at 25°C: \circ , experimental data²⁹; —, calculated.

system the quantity B , eq 67, is $B = 87 \pm 5 \text{ cal mol}^{-1}$. The following set of parameters in the random approach:

$$\varepsilon_{12h} = 213.4 \text{ cal mol}^{-1}, \quad \kappa_{12} = -0.363,$$

$$Q'_{12} = 0.025$$

estimates $B = 89 \text{ cal mol}^{-1}$ and reproduces the χ_{12} interaction parameters as shown in Figure 4. Again, no perceptible improvement is expected with the non-random approach.

CONCLUSIONS

A molecular theory of fluids and their mixtures has been developed and tested against experimental data of pure components and polymer solutions. The results are rather satisfactory. In the pure component case the third parameter (variable cell size) of the well known fluid-lattice theory^{12,14} has been replaced by an "entropic" contribution to the interaction energy parameter. This leads to a simpler formulation of the mixture treatment and gives an equally good, if not better, representation of the pure component data. For mixtures, the formalism has been developed in close parallel to the new Flory theory.³ Three parameters have been used for an adequate representation of experimental data on concentrated polymer solutions. The necessity of the empirical correction for the entropic contribution to the residual chemical potentials obviously points to inherent shortcomings of this rather elementary model. The non-random approximation has been found to be unnecessary for pure components. For mixtures, the non-random approximation improves the results for the system chloroform-poly(propylene oxide).

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NOTATION

B	heat of mixing constant given by eq 60
E	potential energy of the system
F	auxiliary function
G	quasi-chemical constant defined by eq 14 and 45
g_c	random combinatorial term
g_{NR}	non-random combinatorial correction factor
H	enthalpy
N	number of moles
N_{ij}	total number of external contacts i - j
\bar{N}_{ij}	quantities defined by eq 42a, b, c

N_r	total number of lattice sites
P	pressure
Q	partition function
Q_{12}	binary parameter
Q'_{12}	binary parameter defined by eq 63
R	gas constant
r	number of mers in a fluid
T	temperature (K)
U	configurational energy
V	total volume of the system
v	volume per segment
X_{12}	binary parameter in new Flory theory
Z	lattice coordination number
ZN_q	total number of external contacts
Zq	number of external contacts per r -mer

Greek Letters

α	thermal expansion coefficient
β	isothermal compressibility coefficient
Γ_{ij}	non-random factors
γ	thermal pressure coefficient
Δ	property difference
δ	flexibility factor
ε_{ij}	interaction energy for contact of type i - j ($=\varepsilon_{ijh} + T\varepsilon_{ijs}$)
θ	overall surface fraction
$\bar{\theta}_i$	molecular surface fraction of component i
κ_{12}	binary parameter
μ	chemical potential
ρ	density (g cm^{-3})
σ	symmetry factor
ϕ_i	segment fraction of component i
χ_{12}	Flory-Huggins interaction parameter

Superscripts

\circ	values pertaining to the random case
$*$	reducing quantities
\sim	reduced quantities
\cdot	non-random quantities with even distribution of holes
∞	quantity at infinite dilution

Subscripts

i	quantity pertaining to component i
ij	quantity pertaining to contact of type i - j
i,p	quantity pertaining to pure component i
H	quantity pertaining to holes
L	liquid state
sp	specific
V	gas state

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