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Hole Theories for Liquids and Compressed Gases: A Theoretical Comparison of Equations of State

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ABSTRACT: The theoretical expressions for the equation of state of a pure component, derived from the hole theory of Simha and Somcynsky and the lattice gas model of Kleintjens and Koningsveld, are examined in detail. Similarities and differences are discussed. From this, the comparable quality of description for experimental data offered by both theories can be appreciated. For the Kleintjens–Koningsveld theory, a scaled equation of state is derived. However, no principle of corresponding states is obtained.

I. Introduction

A few years ago, an effort was made to compare the hole theory[1] of Simha and Somcynsky (S–S) with the lattice gas model[2] of Koningsveld and Kleintjens (K–K). At that time a numerical comparison was offered, based on experimental data for ethylene.[3] The experimental data consisted of the critical conditions and a series of isotherms for both gaseous and liquid states. It was observed that both theories have a similar overall quality of agreement with experimental data. However, a detailed comparison of the theoretical expressions was not made.

II. The Configurational Partition Function

Both theories model a pure component in its liquid state as a quasi-lattice structure with sites either vacant or occupied by a segment of a linear s-mer. The quasi-lattice allows the evaluation of the configurational partition function Z which is factored into three contributions:

$$Z = [g][v_f]^N[\exp(-E_0/kT)] \tag{1}$$

where g is a factor due to the configurational entropy, E_0 the internal energy, v_f the cell partition function of a molecule in a given configuration on the lattice, k Boltzmann's constant, T the temperature, and N the number of s-mers.

a. Combinatorial Entropy. Both theories make use of the Flory approximation[4] for the combinatorial entropy, brought about by mixing of vacant and occupied sites, and this gives

$$g(N,y) = [(z-1)/e]^{(s-1)N}(y/s)^{-N}(1-y)^{-Ns(1-y)/y} \tag{2}$$

where y is the fraction of occupied sites and z the lattice coordination number.

b. Internal Energy. The internal energy is equated to the lattice energy which, evaluated in a mean field approximation, can be written as an energy per contact ϵ_c times the number of contacts N_c in the system:

$$E_0 = N_c\epsilon_c \tag{3}$$

For the contact energy, as well as the number of contacts, different expressions are used in the two theories. Nanda et al. use the expression for the lattice energy from de Boer and Prigogine:[5]

$$N_c = yNqz/2 \tag{4.a}$$

$$\epsilon_c = \epsilon^*(A(v^*/w)^4 - B(v^*/w)^2) \tag{4.b}$$

where qz $(=s(z-2)+2)$ is the number of intermolecular contact sites of the s-mer, ϵ^* and v^* are the characteristic energy and volume per segment, w $(=yV/Ns)$ is the cell volume, and A (=1.011) and B (=2.409) are constants.

In the K–K theory, an approximation for the lattice energy, derived by Staverman,[6] is adopted:

$$N_c = \frac{yNs\sigma_1(1-\gamma)}{2(1-\gamma y)} \tag{5.a}$$

$$\gamma = 1 - \sigma_1/\sigma_0 \tag{5.b}$$

$$\epsilon_c = w_{\mathrm{ull}} \tag{5.c}$$

where $\sigma_0(\sigma_1)$ is the surface area of a vacant (occupied) site and w_{ull} is the (constant) interaction energy per unit surface area.

This approximation exhibits an extra concentration dependence, i.e., $(1-\gamma y)^{-1}$. Kleintjens and Koningsveld also introduced some extra parameters[7] which, formally, can be added to the expression for E_0. In this way, following Guggenheim, the concept of a cooperative free energy is introduced.[8] This makes the interaction energy temperature dependent. Furthermore, an extra entropy correction is made.[7] The following equation for the lattice energy results:

$$E_0 = \frac{yNs}{2}\left(-2RTa_s + \frac{(1-\gamma)\sigma_1}{(1-\gamma y)}(-2RTw_{\mathrm{s11}} + w_{\mathrm{ull}})\right) \tag{6}$$

where w_{sll} (w_{ull}) is the entropy (energy) contribution to the cooperative free energy per unit surface area and a_s is an empirical entropy correction.

c. Cell Partition Function of the s-Mer. The introduction of vacant sites, i.e., free volume, allows the theories to handle volume-dependent thermodynamic properties. For the lattice gas model, it is the only way. In the hole theory, however, an extra free volume, derived from the motion of the molecules in their respective cells, is introduced. This cell free volume is approximated by[9]

$$v_f = [v^{*1/3}(y(\tilde{w}^{1/3} - \alpha) + (1-y)\tilde{w}^{1/3})]^{3c} \tag{7}$$

where $3c$ is the effective, i.e., volume-dependent, number of external degrees of freedom of the s-mer and α $(=2^{-1/6})$ is a geometrical constant.

In this approximation an averaging over free lengths is assumed. The first term of the right-hand side of eq 7 represents a "solid-like" and the second one a "gas-like" contribution to the free volume. In the K–K treatment, no cell free volume is present. To have similar expressions for the configurational partition function Z, we can write

$$v_f = 1 \tag{8}$$

d. The Configurational Partition Function. The configurational partition functions for both theories are

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obtained when the appropriate equations for the different terms are substituted in eq 1. In comparing the expressions for the different factors in the partition function that have been summarized, it is clear that the main distinction is found in the expressions for the cell free volume. The differences in the internal energy, although significant, are not of fundamental importance to the comparison we wish to present: in the S–S theory an equivalent concentration dependence for the internal energy can be obtained if the calculations of the number of contacts are based on the strictly regular lattice model.[10] In this case the parameter γ of eq 5.b receives a different physical meaning, i.e.,

$$\gamma = (2/z)(1 - 1/s) \tag{9}$$

III. Application of Theories to Thermodynamic Properties

We now turn to thermodynamic properties that can be determined experimentally. In the comparison of theoretical predictions with experimental data, one needs to know the fraction y of occupied sites. In the K–K theory, y is directly proportional[11] to the density ρ:

$$y = \rho v^* s/M \tag{10}$$

where M is the molar mass of the s-mer.

In principle, this proportionality can be substituted directly into the partition function. The situation for the hole theory is somewhat more complex. The hole fraction $(1 - y)$ is determined by minimization of the Helmholtz configurational free energy or, equivalently[5]

$$(\partial Z/\partial y)_{V,T} = 0 \tag{11}$$

This results in an extra implicit equation that has to be satisfied simultaneously with the theoretical expression for the thermodynamic properties to be studied. To make this issue more explicit, we focus on the equation of state (EOS) for a single-component fluid, given by the thermodynamic relation

$$p = -(\partial A/\partial V)_T \tag{12}$$

where A is the Helmholtz free energy.

For the K–K theory, the equation of state reads

$$PV/(NkT) = (1 - s) - sy^{-1} \ln (1 - y) - ys[a_s + \sigma_1(1 - \gamma)(1 - \gamma y)^{-2}(w_{\mathrm{sll}} + w_{\mathrm{ull}}/2kT)] \tag{13}$$

where $y = \rho v^* s/M$. For the S–S theory,

$$PV/(NkT) = (1 - s) + sy^{-1} \ln (1 - y) + 3cy\alpha(\tilde{w}^{1/3} - \alpha y)^{-1} + (yqz\epsilon^*/2kT)[A(v^*/w)^4 - B(v^*/w)^2] \tag{14}$$

As already mentioned, also the minimization condition has to be taken into account:

$$(s/3c)[(s - 1)/s + y^{-1} \ln (1 - y)] + (\tilde{w}^{1/3}/3 - \alpha y)/(\tilde{w}^{1/3} - \alpha y) + (yqz\epsilon^*)/(6kTc)(3A(v^*/w)^4 - B(v^*/w)^2) = 0 \tag{15}$$

For the S–S theory, it is general practice to present the equation of state in reduced form. A characteristic scaling pressure P^*, volume V^*, and temperature T^* are defined:

$$P^* = qz\epsilon^*/(sv^*) \tag{16.a}$$

$$V^* = Nsv^* \tag{16.b}$$

$$T^* = qz\epsilon^*/(kc) \tag{16.c}$$

After these scaling parameters are introduced and combined with eq 14 and 15, the reduced EOS and minimization condition can be written[9] as

$$\tilde{P}\tilde{V}/\tilde{T} = (2y/\tilde{T})\tilde{w}^{-2}(A\tilde{w}^{-2} - B/2) + (1 - Q)^{-1} \tag{17}$$

$$(s/3c)[(s - 1)/s + y^{-1} \ln (1 - y)] = (y/6\tilde{T})\tilde{w}^{-2}[B - 3A\tilde{w}^{-2}] + (Q - 1/3)(1 - Q)^{-1} \tag{18}$$

where $Q = \alpha y\tilde{w}^{-1/3}$. It turns out that the equation of state does not obey the principle of corresponding states because s and s/c appear in these equations explicitly. However, for polymers the equation of state is not very sensitive to the exact values of s and s/c. Thus, a *practical* principle of corresponding states emerges.[5,9]

IV. Comparison of the Theoretical EOS Expressions

In the S–S theory, we have a set of two nonlinear equations (eq 14 and 15) that have to be solved in order to calculate the desired property. In the K–K treatment, there is only one equation. In general, for every thermodynamic property, the hole theory will have a more complex set of equations to be studied. Comparing eq 13, 14, and 15, it becomes clear that it is impossible to compare the theoretical expressions as they stand. If we want to study the relationship between theories on the level of the theoretical expressions, it is necessary to simplify the minimization procedure. As noted by Simha and Wilson,[12] the cell volume changes only slightly for an extensive range in reduced volume and temperature. A strict constancy of the cell volume would imply a van der Waals type of interaction energy, which is not confirmed by all experimental evidence, e.g., internal pressures.[13] The observed changes in cell volume thus appear to be necessary for the quantitative success of the S–S theory. This is especially true regarding the prediction of phase transitions which can involve large volume changes, assuming a constant cell volume emasculates the S–S theory and consequently reduces the range of phenomena over which it can be compared to any other theory. However, for the sake of comparison of dilatometric data over a limited range of temperatures and pressures, it would be worthwhile to study the equations of the S–S theory with a constant cell volume. As it turns out, a considerable simplification is found because the minimization condition 15 is then replaced by

$$\tilde{w} = \tilde{w}_0 = w_0/v^* \tag{19}$$

where w_0 is a constant. This new condition results in a simple expression for the EOS:

$$PV/(NkT) = (1 - s) - (s/y) \ln (1 - y) + 3cy\alpha/(\tilde{w}_0{}^{1/3} - \alpha y) + k_1yqz\epsilon^*/(2kT) \tag{20}$$

where k_1 is a constant depending on the exact value of w_0 and equals −1 approximately.

We are now left with only one equation, and it is possible to make a direct comparison with the lattice gas model. For a first comparison, we also simplify the lattice gas model to some extent. The extra concentration and temperature dependence of the lattice energy and the empirical entropy correction are abandoned. In this way the familiar Flory–Huggins approximation for the interaction energy, i.e., a van der Waals type interaction energy, is obtained. The lattice gas EOS becomes

$$pV/(NkT) = (1 - s) - s/y \ln (1 - y) + ys\sigma_1 w_{\mathrm{ull}}/(2kT) \tag{21}$$

Now, the similarities and differences between the two (simplified) theories become obvious. The first two terms in eq 20 and 21 are derived from the combinatorial entropy. Since both models make use of the Flory approximation, the same expressions are obtained. The last term in both equations is derived from the internal energy. Also in this case, identical expressions are obtained because in both theories the same approximation for counting the number of contacts is applied. Identical relations are obtained if the definitions for the molecular interaction energy in both models are considered; i.e.,

$$k_1\epsilon^* qz = w_{\text{ull}}\sigma_1 s \tag{22}$$

At the proposed level of approximation, the only difference between the theories is in the second term of the right-hand side of eq 20. This term is derived from the cell free volume and has no counterpart in the simplified K-K theory. The contribution of the cell free volume to the EOS can be rewritten as

$$3c\alpha y/(\tilde{\omega}_0{}^{1/3} - \alpha y) = 3c\tilde{\tau}y/(1 - \tilde{\tau}y) \tag{23}$$

where $\tilde{\tau}$ ($=\alpha/\tilde{\omega}_0{}^{1/3}$) is proportional to the reciprocal reduced cell radius.

We now consider the lattice gas model and reintroduce the Staverman approximation for the internal energy; i.e.,

$$E_0 = yNs\sigma_1(1 - \gamma)w_{\text{ull}}/(2(1 - \gamma y)) \tag{24}$$

The Staverman expression for the interaction energy does not have the simple van der Waals form. However, eq 24 does not describe the dependence of internal pressure on volume as documented by Olabisi and Simha.[13] The expression for the EOS can be read from eq 13 if the entropy corrections a_s and w_{sll} are neglected:

$$PV/(NkT) = (1 - s) - s/y \ln (1 - y) + ys\sigma_1 w_{\text{ull}}(1 - \gamma)/(2kT(1 - \gamma y)^2) \tag{25}$$

The contribution to the EOS of the lattice energy term in the K-K model shows a functional concentration dependence similar to that of the cell free volume in the hole theory. The terms containing $(1 - \gamma y)$ and $(1 - \tilde{\tau}y)$ differ only in the exact value of the exponent and in the physical interpretation of the parameters γ and $\tilde{\tau}$. The functional similarity of the two concentration dependencies explains the comparable quality of predictions offered by both theories. Koningsveld and co-workers found that the expression for the lattice energy, as proposed in eq 24, is essential if a quantitative description of experimental data with the lattice gas model is desired.[2] However, here it is demonstrated that a similar concentration dependence is derived from the cell free volume. This explains also the comparable descriptive quality of both theories, noted in the numerical comparison presented earlier.

V. Scaled Equation of State

For the EOS derived from the hole theory, it is general practice to present it in reduced form (eq 17). The lattice gas EOS, normally applied in its unreduced form, can be arranged in reduced representation also. In analogy with eq 16, the scaling parameters can be defined as

$$P^* = s\sigma_1 w_{\text{ull}}/(sv^*) \tag{26.a}$$

$$V^* = Nsv^* \tag{26.b}$$

$$T^* = s\sigma_1 w_{\text{ull}}/(ks) \tag{26.c}$$

And the scaled EOS reads

$$\tilde{P}\tilde{V}/\tilde{T} = (1/s - 1) - 1/y \ln (1 - y) - y(-(1 - \gamma)/2\tilde{T}(1 - \gamma y)^2 + w_{\text{sll}}\sigma_1(1 - \gamma)/(1 - \gamma y)^2 + a_s) \tag{27}$$

A similar equation has been derived by Beckman et al.,[14] starting with the free energy of mixing and using different definitions for the scaling parameters. The introduction of the scaling parameters reveals a correlation between parameters that was unnoticed in the unreduced EOS. Simha et al. realized that the scaling parameters are not independent but that an extra relation exists among them,[15] i.e.,

$$P^*\nu^*/T^* = (c/s)R/M_s \tag{28}$$

where M_s is the molar mass of a segment of the s-mer and ν^* ($=V^*/(nsM_s)$) is the reducing specific volume.

The correlation between the parameters for the lattice gas model reads

$$P^*\nu^*/T^* = R/M_s \tag{29}$$

Thus, in the analysis of experimental data with the reduced K-K EOS, eq 29 has to be taken into consideration. The K-K scaled equation of state does not obey a principle of corresponding states because s appears explicitly in this equation and because of the introduction of the extra parameters a_s, w_{sll}, and γ. For polymers, the first condition is of no importance.[9] One possibility for the lattice gas model to conform to the principle of corresponding states would be that the parameters a_s, w_{sll}, and γ are universal constants. Upon inspection of literature data for these parameters, it becomes clear that this is certainly not the case.[11] Alternatively, it is possible that the descriptive quality of the EOS is independent of the exact values of these parameters. That is, a change in the values of these parameters would only alter the values of the scaling parameters but conserve the quality of the description. This is similar to the situation encountered in the S-S theory where c/s is explicitly present in the EOS. Simha and Somcynsky showed that the value of this ratio, which can vary between 0 and 1, did not influence the description.[9] For the parameters a_s, w_{sll}, and γ, no limiting values can be derived. Thus, it is difficult to test for a practical principle of corresponding states.

VI. Conclusions

The K-K theory and S-S theory offer a comparable descriptive quality for experimental data. These similarities can be understood from the theoretical equations for both theories. If for the S-S theory a constant cell volume is assumed, the contribution of the cell free volume to the partition function gives a concentration dependence in the equation of state similar to the one found in the K-K theory where it is derived from the interaction energy. However, one can expect that different molecular origins will result in marked differences for certain physical properties. This will be addressed in future research. For both theories, the equation of state can be presented in a scaled form. However, these reduced equations of state do not obey a principle of corresponding states. Also, for the K-K theory it is not straightforward to test for a practical principle of corresponding states.

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Hydrogen Bonding in Polymer Blends. 5. Blends Involving Polymers Containing Methacrylic Acid and Oxazoline Groups

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ABSTRACT: The results of a Fourier transform infrared study of poly(ethylene-*co*-methacrylic acid) (EMAA) copolymer blends with polyethyloxazoline (PEOX) are presented. EMAA copolymers are strongly self-associated at ambient temperatures through the formation of intermolecular carboxylic acid dimers. PEOX, a polymer that is inherently weakly self-associated, forms a strong association with EMAA by forming intermolecular hydrogen bonds between the carboxylic acid and oxazoline groups. These polymer blends are highly mixed at the molecular level and quantitative measurements of both the fraction of methacrylic acid and oxazoline groups that are and are not hydrogen bonded have been obtained. The results are discussed in terms of competing equilibria.

Introduction

In two previous papers of this series we have described FTIR studies of poly(ethylene-*co*-methacrylic acid) (EMAA) blends with the polyethers,[1] poly(vinyl methyl ether) (PVME), and poly(ethylene oxide-*co*-propylene oxide) (EPO), and the pyridine-containing polymers,[2] poly(2-vinylpyridine) (P2VP) and poly(styrene-*co*-vinylpyridine) (SP2VP). The presence of intermolecular carboxylic acid dimers in pure EMAA copolymers at ambient temperatures leads to strong self-association. As we have stressed previously, molecular mixing of EMAA is feasible with chemically dissimilar polymers that are inherently weakly self-associated but which contain specific sites that can potentially form favorable intermolecular interactions (notably hydrogen bonds) with EMAA. This we have described quantitatively in terms of competing equilibria.[1,2] Equilibrium constants, K_A and K_B, were employed to express the self-association of EMAA and the association of EMAA with the ether- or pyridine-containing polymer, respectively.

Miscible systems are possible even if the magnitude of K_B is much smaller than K_A. This is the case for both the EMAA–polyether and EMAA–pyridine containing polymer blends studied. K_A was determined to be approximately 2 orders of magnitude greater than K_B in the former blend system and about 40 times greater in the latter.[1,2] The relative *strengths* (ΔH) of the specific hydrogen-bonded interactions associated with the carboxylic acid dimer (AA) and the carboxylic acid–ether pair (AB), however, are of similar magnitudes and that of the analogous carboxylic acid–pyridine interaction is significantly stronger than the carboxylic acid dimer. Again, without wishing to belabor the obvious, a knowledge of the relative strengths of the specific interactions alone is not sufficient and we must recognize that there is an entropic contribution (ΔS) to hydrogen bond dissociation and formation which is an integral part of the definition of the equilibrium constant.

In this paper we present FTIR studies of EMAA–polyethyloxazoline (PEOX) blends. The unique feature of this study concerns the amount of information that can be extracted from the infrared spectra as compared to the analogous studies of the EMAA–polyether[1] or EMAA–polypyridine[2] blends. In the former system it was only possible to quantitatively measure the fraction of EMAA carbonyl groups involved in hydrogen-bonded interactions with ether groups. Normal modes containing significant contributions to their potential energy distribution from displacements involving ether oxygen atoms tend to be highly mixed and are thus conformationally sensitive. Accordingly, changes in frequency, breadth, and intensity of these modes that we might observe in the spectra of our polymer blend systems do not lend themselves to straightforward analysis and are not amenable for the quantitative analysis of specific interactions. On the other hand, in the EMAA–polypyridine system it was only possible to directly measure the fraction of pyridine groups that were or were not hydrogen-bonded. In this case specific localized modes of the pyridine ring are sensitive to hydrogen bonding. Conversely, there were unexpected complications in the carbonyl stretching region of the infrared spectra especially in polypyridine-rich blends. Separate contributions attributed to carboxylic acid dimers and carboxylic acid–pyridine interactions were not found over the whole composition range, and it was not possible to use this region of the spectrum for quantitative analysis. The particular chemical structure of the EMAA–PEOX system, however, permits us to measure both the fraction of EMAA and PEOX groups that are and are not hydro-

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