An Examination of Paul J. Flory's Equation of State Using Statisitical Thermodynamics

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Introduction

1.0 Objectives

This work is a detailed examination of the development of the partition function and the corresponding equation of state due to Paul J. Flory. After the partition function and equation of state are developed, the equation of state will then be tested for agreement with experimental data. To provide an easier deciphering, notation used in this paper shall imitate, as close as closely as possible, Flory's[1,2] notation. Comparisons to other developments of either partition functions or equations of state such as Prigogine or Simha's shall be to elucidate Flory's concepts or equations.

In accomplishing the above, this paper will also provide future students with a comprehensive overview of the theory and mathematics involved with modeling of chain molecule liquids.

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[1] P.J. Flory, R.A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3508 (1964).

[2] P.J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).

1.1 General Background

Correlating experimental chain molecule liquid data with theory has long been an objective of many scientists. Ilya Prigogine, the 1977 recipient of the Nobel Prize for Chemisty, modeled chain molecule liquids to occupy lattice sites.[3] Prigogine has adapted this "cell" model to chain molecule liquids and derived an equation of state, thus correlating theory with experimental results for normal paraffins and selected hydrocarbons. Robert Simha and others[4,5], using graphical-empirical methods by application of a law of corresponding states, have expanded on Prigogine's cell model to formulate an equation of state which also encompasses oligomers and high polymer liquids. In spite of the success of the cell model, there are still discrepancies between theory and experiment. It must be noted that Prigogine's later models did attain very good agreement, even at high pressure, and this has led to arguments over whether or not to use the cell model. This paper opts to support Flory's argument that there are some conceptual difficulties with the cell model, and therefore contributes to the above argument.

The above discrepancies ensue because the cell model ignores changes in volume and local disorder that are characterisitic of chain molecule liquids. That is, the cell model, which assigns "prisoner" molecules to cells, places the nearest neighboring molecules at their average positions. The cell model then takes on a regular array structure which contradicts the randomness of liquids. Since intermolecular energy is a function of the distance between molecules, the regular array structure presented by the cell model affords a misrepresentation of

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[3] Tyler Wasson, ed., *Nobel Prize Winners*, 837 (1987).

[4] R. Simha and A.J. Havlik, *J. Am. Chem. Soc.*, **86**, 197 (1964).

[5] R. Simha and S. T. Hadden, *J. Chem. Phys.*, **25**, 702 (1956); **26**, 425 (1957).

the intermolecular energy. Therefore, an inadequate representation of intermolecular energy is also intrinsic in the cell model.

Paul J. Flory, recipient of the 1974 Nobel Prize for Chemistry[6], addresses the above discrepancies by creating a model that uses a linear sequence of segments instead of cell theory. Using this linear sequence of segments, an analytical partition function is created and from this an equation of state is derived. It must be noted that Flory embraces the law of corresponding states in his development and assumes that intermolecular energy depends only on volume.

Flory's formulation, although analytical and applicable to mixtures, still needs refinement. This formulation however has fair correlation with experiment and therefore offers a much less complicated development than those created using graphical-empirical methods.

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[6] Tyler Wasson, ed., *Nobel Prize Winners*, 333 (1987).

The Partition Function

2.0 Introduction

In the past, partition functions formulated for chain molecule liquids have been based on the cell model or lattice model. Intrinsic in the cell model is the dependence of the intermolecular energy on the volume of the lattice cells and the arrangement of the "prisoners" within the cells. Flory, Orwoll, and Vrij reject this basis for expressing the intermolecular energy of a chain molecule liquid, and, if fact, reject the cell model alltogether. Instead they offer a linear sequence of segments endowed with hard-sphere repulsive potentials. Embracing the law of corresponding states, they have formulated an analytical expression for the partition function from which an equation of state may be derived.

This section will examine in detail and develop comprehensively the partition function of Flory, Orwoll, and Vrij.

2.1 Definition of a Segment and the variable s

In lieu of the refutation of the cell model[7], a linear sequence of segments is formulated. Before defining a segment, it is first necessary to characterize a linear chain molecule, for example polyethylene $-(CH_2\text{-}CH_2)_n-$. The chain molecule is composed of n repeating units or mers and is terminated by two end groups which differ from mid-chain groups in that they exert different intermolecular forces.[8] Of course, the chain is assumed to be flexible. Let the chain be subdivided into x segments. Flory's definition of a segment is left ambiguous by the fact that x is not equal to n; however, x is proportional to the "hard core" volume $v^* = xv^*$ where v^* is the net volume of a molecule inside a single segment. Note that v^* is also sometimes called the net volume of a molecule.[9]

It is worth mentioning that the definition of a segment is arbitrary. For instance, if a segment is confined to a cell as defined by the cell model, then it is necessary to define the length of the segment, assuming spherical symmetry, as equal to the diameter of the chain. Referring to solution theory for another example, monomeric solvents diffusing in chain molecule liquids might require setting the net volume v^* equal to the volume of the solvent.

Following Flory[10], define s as the mean number of external contact sites per segment of a molecule, thus let

$$xs = xs_m + s_e \tag{1}$$

where xs is thought of as molecular surface, s_m is the number of contacts for an internal segment,

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[7] P.J. Flory, R.A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3508 (1964).

[8] P.J. Flory, R.A. Orwoll, and A. Vrij, 3508.

[9] P.J. Flory, R.A. Orwoll, and A. Vrij, 3508.

[10] P.J. Flory, R.A. Orwoll, and A. Vrij, 3508.

and s_e is the number added for the chain ends. This equation parallels the equation used by Simha and Havlik[11], $qz = s(z - 2) + 2$. In their formulation, a chain molecule is divided into s units and z is the coordination number of the lattice defining the average positions of the chain units. Here, qz/s is the mean number of contacts per unit and the addition of two to the right-hand side of the equation represents the erroneous assumption that an end group contributes only one more contact site. This assumption can be corrected by either appropriately defining s or by adjusting z. Flory opts for a subjective definition of s or in our case x rather than using z, which is an outgrowth of the cell model.

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[11] R. Simha and A.J. Havlik, *J. Am. Chem. Soc.,* **86**, 197 (1964)

2.2 Molecular Degrees of Freedom

With the definition of a segment complete, we now examine the movement of the molecules, or in particular, the segments. Since intermolecular energy is a function of the movement or degrees of freedom of the molecules in a polymer liquid, it is necessary to distinguish the degrees of freedom. Prigogine[12] offers a sound twofold categorization: 1) those degrees of freedom which are due to the translational motion of the molecule's center of mass, and 2) all other degrees of freedom such as rotation and vibration. The former degrees of freedom are considered external or intermolecular degrees of freedom and the latter are considered internal or intramolecular degrees of freedom. The difference between external and internal degrees of freedom is that external degrees of freedom are independent of the valence forces between segments or molecules; instead, they depend only on the environment of the segment or molecule.[13] The intramolecular degrees of freedom oscillate at a higher frequency than the intermolecular degrees of freedom; however, the intramolecular degrees of freedom are assumed to be minimally affected by neighbors in the liquid, while the intermolecular degrees of freedom are appreciably affected by neighbors. This can be attributed to the fact that the external degrees of freedom are constrained by negligible intramolecular potentials; these external degrees of freedom are then considered translatory motions. If we incorporate these into the three degrees of freedom due to the molecular center of mass, we have then the total number of intermolecular degrees of freedom per segment

$$3c = 3(c_m + c_e)$$

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[12] I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc., New York, N.Y., 24 (1957).

[13] I. Prigogine, 328.

where c (<1) accounts for the restrictions on the movement of a segment. These restrictions have numerous causes: bond lengths and angles, lateral displacements, and/or structural connections.[14] The variable c is a parameter used in defining the reduced variables necessary in creating the equation of state. These reduced variables will be defined later. We can then extend 3c to the total number of intermolecular degrees of freedom per molecule

$$3xc = 3(xc_m + c_e)$$

where $xc > 1$.

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[14] P.J. Flory, R. A. Orwoll, an d A. Vrij, *J. Am. Chem. Soc.*, **86**, 3508 (1964).

2.3 Configuration Space

Having distinguished the total number of intermolecular degrees of freedom, we must now, assuming hard-sphere repulsion, develop the configuration space associated with the system. The configuration space may be defined as the spatial configuration present within the system. If we first consider a fictitious one-dimensional system composed of N particles, each having a length of *l** allocated within a space of length *L*, according to Tonks[15] the total configuration space available, sometimes called the free volume or free length, is

$$\Omega = (L - Nl^*)^N/N! \qquad (3)$$

$$\cong [(l - l^*)e]^N \qquad (3')$$

where $l = L/N$, the space available per particle. Converting to a three-dimensional system requires the conversions $(\gamma v^*)^{1/3} = l^*$ and $(\gamma v)^{1/3} = l$ where γ is defined as a geometric factor, $v = V/xN$ the volume per segment, and v^* as defined above. Here N is the number of molecules in the system and V is the volume of the system. Equation 3' then becomes

$$\Omega = [\gamma e^3(v^{1/3} - v^{*1/3})^3]^N \qquad (4)$$

The communal entropy e^{3N} which according to Flory[16] is fully realized in all liquids(because of their chaotic nature when heated), particularly the ones examined within the scope of this paper, can then be factored out giving

$$\Omega = [\gamma(v^{1/3} - v^{*1/3})^3]^N \qquad (4')$$

Since the total number of intermolecular degrees of freedom is 3xc, we have then the total configurational space available to the system

$$\Omega = [\gamma(v^{1/3} - v^{*1/3})^3]^{xNc} \qquad (4'')$$

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[15] L. Tonks, *Phys. Rev.*, **50**, 955 (1936)

[16] P.J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3508-9 (1964).

2.4 Derivation of the Partition Function

We are now ready to derive the partition function. The partition function, at some arbitrary volume, temperature, and composition, is defined as

$$Z = \sum^{n} g_n \exp(-E_n/kT) \tag{5}$$

where E_n represents the energy of some state n, g_n the degeneracy of E_n, and $\exp(-E_n/kT)$ the statistical weight. The partition function is the essentially the product of the degrees of freedom adding to the energy of some state n. Since the various degrees of freedom are separated into two categories as shown above, the partition function becomes

$$Z = Z_{internal} Z_{external} \tag{6}$$

Concerning ourselves with $Z_{external}$, we then introduce the Hamiltonian,

$$H = (1/2m)\sum_{i=1}^{n}(p_i)^2 + U(r_1 . . . r_N) \tag{7}$$

where p_i is the momentum for the ith molecule's center of mass at position r_i and U is the system's potential energy for N molecules.[17] The Hamiltonian is an accurate estimate of the system's energy due to the motion of the molecule's mass centers and their potential energy. Following conventional procedure, we approximate 3xNc intermolecular degrees of freedom which gives

$$Z_{external} = (1/N!\ h^{3N}) \exp(-H/kT)\ d\underset{\sim}{p}_1 . . . d\underset{\sim}{p}_N\ d\underset{\sim}{r}_1 . . . d\underset{\sim}{r}_N \tag{8}$$

We now integrate $Z_{external}$ over the momenta from -infinity to infinity, this gives

$$Z_{external} = \left\{(2\pi mkT)^{3xNc/2}/h^{3xNc}\right\} \left\{1/N! \int . . . \int \exp(-U/kT) d\underset{\sim}{r}_1 . . . d\underset{\sim}{r}_N\right\}^{18} \tag{8'}$$

Since the first term on the right hand side is the kinetic energy, which is a function of only temperature, it is absorbed into $Z_{internal}$. The second term on the right hand side of the equation is

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[17] K.E. Van Ness, Ph.D. Thesis, 4, (1985)

[18] K.E. Van Ness, Ph. D. Thesis, 4, (1985)

defined as the configurational partition function $Z_{config.}$,

$$Z_{config.} = 1/N! \int . . . \int \exp(-U/kT) d\underset{\sim}{r}_1 . . . d\underset{\sim}{r}_N \tag{9}$$

Note that this is in one-dimensional space, therefore we convert to three-dimensional space and following conventional procedure, $Z_{config.}$ becomes

$$Z_{config.} = \Omega \exp(-E_o/kT) \tag{9'}$$

where E_o is the intermolecular energy. Note that E_o evolves out of U from the separation of internal and external degrees of freedom.

Combining the above concepts, the partition function Z then becomes

$$Z = Z_{internal} Z_{config.} \tag{10}$$

$$Z = Z_{internal}\, \Omega \exp(-E_o/kT) \tag{10'}$$

On comparison with the Prigogine's partition function, we also add a combinatorial factor C which accounts for the number of ways of distributing xN segments over a xN sites. The communal entropy factor e^{3N} is sometimes assumed to be absorbed into C. Therefore the partition function is

$$Z = Z_{internal}\, C\, \Omega \exp(-E_o/kT) \tag{10''}$$

$$Z = Z_{internal}\, C\, [\gamma(v^{1/3} - v^{*1/3})^3]^{xNc} \exp(-E_o/kT) \tag{10'''}$$

The configurational partition function is then defined as

$$Z_{config.} = C\, [\gamma(v^{1/3} - v^{*1/3})^3]^{xNc} \exp(-E_o/kT) \tag{11}$$

which resembles the configurational partition function formulated by Flory, Orwoll, and Vrij.

2.5 Development of Energy term E_o

Equation 11 also resembles the configurational partition function constructed by Prigogine, Trappeniers, and Mathot[19,20], $Z = Z_0 g \Psi^N \exp(-E_c/kT)$, where Z_o is the internal partition function, g is the combinatory factor, Ψ is the cell partition function of a molecule moving in a mean field of all its neighbors, and E_c is the configurational energy of the system when the molecules are at rest confined to the center of their cells. However since Flory rejected the use of the cell model as an adequate representation of the intermolecular energy, a new energy term E_o is contrived.

Flory finds error in the cell model based on the fact that the energy of interaction between two molecules is a function of intermolecular distance. The cell model assumes the energy of a "prisoner," defined as a molecule confined in its cell, at its cell center to be greatly affected by its nearest neighbors, all equidistant from the prisoner. Considering the "chaotic" nature of liquids, this assumption, that the nearest neighbors are equidistant from the prisoner, introduces a substantial error in the energy and its dependence on the volume. In fact, one or more neighboring molecules has a high probability of being in closest proximity to the prisoner(nearly in contact).

Flory opts for the radial distribution function to account for the above energy corrections. Turning to Prigogine[21] for a definition, we first define the distribution function $n^{(2)}(r_1,r_2)\, dr_1\, dr_2$ as the probability that a molecule is in the volume element dr_1 about coordinate r_1 and at the same time there is another molecule in dr_2 about coordinate r_2. The radial distribution function $g(r_1,r_2)$

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[19] I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc. New York, N.Y., 1957.

[20] I. Prigogine, N. Trappeniers, and V. Mathot, *Discussions Faraday Soc.*, **15**, 93 (1953).

[21] I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc., New York, N.Y., 89 (1957).

is defined by

$$n^{(2)}(r_1,r_2) = n^{(1)}(r_1)\, n^{(1)}(r_2)\, g(r_1,r_2)$$

where $n^{(1)}(r)$ is a number density. Assuming the intermolecular energy is additive between intermolecular segments, we take $g(r_1,r_2)$ to be independent of volume thus making the intermolecular energy proportional to the density ρ. This was first formulated by Hildebrand and Scott.[22]

Taking this into account, we then let the mean intermolecular energy per pair of segments be

$$\varepsilon = -\eta / v^{23} \tag{12}$$

where η defines the mean interaction between each segment pair in the chain molecule liquid. Obviously, η would be constant for chain homologs, but once again the assumption that end groups offer different intermolecular forces than mid-chain groups must be taken into account. Thus, we take the intermolecular energy of the system, E_o, to be the product of x segments, s external contact sites per segment, the average intermolecular energy per segment pair ε, and N molecules,

$$E_o = -N\,\eta\,x\,s / 2\,v \tag{13}$$

The term xs must be divided by two to account for the pairs of segments present in a molecule, therefore justifying ε. Acknowledging that end groups exert different interactions than mid-chain groups, E_o can be written,

$$E_o = -(1/v)(N_m\eta_m + N_{em}\eta_{em} + N_e\eta_e) \tag{14}$$

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[22] J.H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corporation, New York, N.Y., 92 (1950).

[23] P.J. Flory, R.A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3509 (1964).

Here, η_m depicts the interactions of the external contact sites of two adjacent mid-chain segments, η_{em} depicts the interactions of the external contact sites between an end segment and a mid-chain segment, and η_e depicts the interactions of the external contact sites between two adjacent end segments. N_m, N_{em}, and N_e are the number of adjacent pairs in their particular categories; these numbers are a function of random mixing of segments. Flory now offers a simplification by letting the number of end segments equal the definite number s_e as defined in equation 1.[24] Justification for this simplification proceeds from appropriately adjusting η without substantially altering the structure of the solution. In accordance with this reasoning, we now compare equations 13 and 14 and note that

$$(N_m\eta_m + N_{em}\eta_{em} + N_e\eta_e) = N\,\eta\,x\,s/2 \tag{15}$$

where $Nxs/2$ is the number of contact pairs for Nx segments and $xs = xs_m + s_e$. Since the N's on the left hand side of this equation are based on random mixing, there is a probability involved with each of these terms. For random mixing the generalized probability that a segment of type q, for example, will interact with another segment of the same type is the probability of a q-segment present multiplied by the probability of another q-segment being in the vicinity. Thus,

$$N_m \sim (xs_m/xs)(xs_m/xs) = s_m^2/s^2 \tag{16}$$

$$N_{em} \sim (s_e/xs)(xs_m/xs) = s_e s_m/xs^2 \tag{16''}$$

$$N_{me} \sim (xs_m/xs)(s_e/xs) = s_m s_e/xs^2 \tag{16'''}$$

$$N_e \sim (s_e/xs)(s_e/xs) = s_e^2/x^2s^2 \tag{16''''}$$

Respective of equation 15, η is then defined as a weighted sum of the η's as defined in equation

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[24] P.J. Flory, R.A. Orwoll, and A. Vrij, 3509.

14,

$$\eta = \bar{\eta} = (s_m{}^2/s^2)\eta_m + (2s_m s_e/xs^2)\eta_{em} + (s_e{}^2/x^2s^2)\eta_e \tag{17}$$

Note that the probabilities of N_{em} and N_{me} of equations 16" and 16"' are algebraically equal, but account for two different probabilities: the probability of a end segment being in the vicinity of a mid-chain segment and vice versa.

We then substitute η into equation 13 to get the final E_o,

$$E_o = (-Nx\,s/2\,v)\eta \tag{18}$$

$$E_o = (-Nx\,s/2\,v)[(s_m{}^2/s^2)\eta_m + (2s_m s_e/xs^2)\eta_{em} + (s_e{}^2/x^2s^2)\eta_e] \tag{18'}$$

Or putting E_o in a form resembling Flory's[25] E_o,

$$E_o = (-Nx\;/2\,s\,v)[s_m{}^2\eta_m + (2s_m s_e/x)\eta_{em} + (s_e{}^2/x^2)\eta_e] \tag{18''}$$

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[25] P.J. Flory, R.A. Orwoll, and A. Vrij, 3509.

2.6 Introduction of Reduced Variables

The configurational partition function is now ready to be arranged in form in which an equation of state may be derived. We shall leave E_o in the form of equation 13 for simplicity. From the law of corresponding states, we define the reduced variables as follows,

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

$$\tilde{T} = T / T^* = 2\, v^*\, ckT / s\eta \tag{20}$$

Now substituting equation 13 into equation 11 gives,

$$Z_{config.} = C\ [\gamma(v^{1/3} - v^{*1/3})^3]^{xNc}\ \exp(xNs\eta/2vkT) \tag{21}$$

From this point on, $Z_{config.}$ shall be denoted as Z. Solving equation 20 for T gives

$$T = \tilde{T}\, s\eta / 2v^*ck \tag{22}$$

Substituting equation 22 into equation 21 gives,

$$Z = C\ [\gamma(v^{1/3} - v^{*1/3})^3]^{xNc}\ \exp(xNv^*c/v\tilde{T}) \tag{23}$$

Recognizing that $v^*/v = 1/\tilde{v}$ and rearranging equation 23 we then have,

$$Z = C\ \gamma^{xNc}\, (v^{1/3} - v^{*1/3})^{3xNc}\ \exp(xNc/\tilde{v}\tilde{T}) \tag{24}$$

Noting that $v = \tilde{v}\, v^*$, we insert this into equation 24 to get,

$$Z = C\ \gamma^{xNc}\, ((\tilde{v}\, v^*)^{1/3} - v^{*1/3})^{3xNc}\ \exp(xNc/\tilde{v}\tilde{T}) \tag{25}$$

Now concerning ourselves with the $[((\tilde{v}\, v^*)^{1/3} - v^{*1/3})^3]^{xNc}$ term, we expand the cubic inside the brackets, which is equal to,

$$[(\tilde{v}\, v^*)^{2/3} - 2\tilde{v}^{1/3}v^{2/3} + v^{*2/3}][(\tilde{v}\, v^*)^{1/3} - v^{*1/3}]$$

$$= (\tilde{v}\, v^* - 2\tilde{v}^{2/3}v^* + \tilde{v}^{1/3}v^* - \tilde{v}^{2/3}v^* + 2\tilde{v}^{1/3}v^* - v^*)$$

$$= (\tilde{v}\, v^* - 3\tilde{v}^{2/3}v^* + 3\tilde{v}^{1/3}v^* - v^*)$$

Factoring out v^* gives,

$$= v^*(\tilde{v} - 3\tilde{v}^{2/3} + 3\tilde{v}^{1/3} - 1)$$

$$= v^*(\tilde{v}^{1/3} - 1)^3$$

Plugging this back into equation 25 and rearranging produces,

$$Z = C\ (\gamma v^*)^{xNc}\ (\tilde{v}^{1/3} - 1)^{3xNc}\ \exp(xNc/\tilde{v}\tilde{T}) \tag{26}$$

The configurational partition function is then complete and an equation of state may now be derived from it. This is the configuration partition function formulated by Flory, Orwoll, and Vrij[26].

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[26] P.J. Flory, R.A. Orwoll, and A. Vrij, 3509.

2.7 Conclusion

In conclusion, it must be stated that the equation of state derived from this partition function is strikingly successful in correlating data for n-paraffin hydrocarbons from n = 6 to 40 and beyond. However, there is still room for improving the partition function. The intermolecular energy E_o and its dependence on volume could be modified by expressing the volume as an exponential function. The number of external degrees of freedom, c, could be made a variable of perhaps temperature or volume. Doing so would involve a more complicated working of the partition function and more available experimental data. Acting on the above suggested revisions would only diverge from the original intent of this section, to formulate an analytical expression for a partition function from which an equation of state can be derived. In comparison with the graphical-empirical methods of application of the law of corresponding states such as that of Simha and Havlik, the former formulation warrants an easier application to nonpolar liquids and mixtures, not to mention a more straightforward development.

The Equation of State

3.0 Thermodynamic Rationale for an Equation of State

The rationale for an analytical equation of state comes from classical thermodynamics: if one of the thermodynamic potentials is known as a function of its "natural" variables, then all other thermodynamic variables can be found as a function of this potential and its derivatives. The Helmholtz free energy F has been found to be related to the partition function through the relationship[19]

$$F = -k\,T \ln Z \tag{27}$$

where k is Boltzmann's constant. Since $Z = Z_{internal}Z_{config.}$, equation 27 then becomes

$$F = -k\,T \ln Z_{internal}Z_{config.} \tag{27'}$$

In accordance with the assumption that the internal degrees of freedom are independent of the position of a molecule's center of mass, the equation of state is then derived from the classical thermodynamic relation[20]

$$p = -(\partial F/\partial V)_T = k\,T\,(\partial \ln Z_{config.}/\partial V)_T \tag{28}$$

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[19] H. C. Callen, " Thermodynamics And An Introduction toThermostatistics," 2nd ed. John Wiley & Sons, Inc., New York, N.Y., 351 (1985)

[20] I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc., New York, N.Y., 89 (1957)

3.1 Derivation of the Equation of State

We are now ready to derive an reduced equation of state in the form $\tilde{p} = \tilde{p}(\tilde{v}, T)$. Therefore, taking the natural logarithim of the partition function Z (refer to equation 26), we have

$$\ln Z = \ln \Big[C\,(\gamma v^*)^{xNc}\,(\tilde{v}^{1/3} - 1)^{3xNc}\,\exp(xNc/\tilde{v}\widetilde{T}) \Big]$$

Substituting in $\tilde{v} = v / v^*$ and rearranging

$$\ln Z = \Big[\ln C + xNc \ln(\gamma v^*) + 3xNc \ln((v/v^*)^{1/3} - 1) + (xNc/(v/v^*)\widetilde{T}) \Big]$$

Now, taking the partial derivative of ln Z with respect to V at constant T gives

$$\partial \ln Z/\partial V\big)_T = \partial \ln Z/\partial v\big)_{T,N=1,x} = \Big(3c\big[(v/v^*)^{1/3} - 1\big]^{-1}\, 1/3(v/v^*)^{-2/3}\, 1/v^* \Big) - cv^*/v^2\widetilde{T}$$

Inserting this into equation 28, we then have

$$p = kTc\big[(v/v^*)^{1/3} - 1\big]^{-1}\,(v/v^*)^{-2/3}\,1/v^* - kTcv^*/v^2\widetilde{T} \tag{29}$$

$$p = kTc\Big[[(v/v^*)^{1/3} - 1]^{-1}\,(v/v^*)^{-2/3}\,1/v^* - v^*/v^2\widetilde{T}\Big] \tag{29'}$$

Multiplying equation 29' by v and rearranging gives

$$pv/kTc = \Big((v/v^*)^{1/3}/\,[(v/v^*)^{1/3} - 1]\Big) - v^*/v\widetilde{T} \tag{29'''}$$

Respective of the law of corresponding states, we define the reduced p as

$$\tilde{p} = p/p^* = 2pv^{*2}/s\eta \tag{30}$$

$$\tilde{p} = pv^*/ckT^* \tag{30'}$$

Solving equation 30' for p and then substituting it and the relation $v = \tilde{v}\ v^*$ into equation 29''' produces

$$pv/\widetilde{T} = \tilde{v}^{1/3} / (\tilde{v}^{1/3} - 1) - 1/\tilde{v}\widetilde{T} \tag{31}$$

This then is the reduced equation of state obtained by Flory, Orwoll, and Vrij;[21] It might be noted that this equation of state also resembles the reduced equation of state formulated earlier by Hirschfelder and Eyring.[22] The reduced equation of state may also be put in a reduced density form by defining the reduced density as

$$\rho = 1/\tilde{v} \tag{32}$$

The reduced equation of state in density form then becomes

$$\tilde{p} / \rho^2 = \tilde{T}/\rho(1 - \rho^{1/3}) - 1 \tag{33}$$

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[21] P.J. Flory, R.A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3509 (1964)

[22] H. Eyring and J.O. Hirschfelder, *j. Phys. Chem.*, **41**, 249 (1937)

3.2 Derivation of Thermodynamic Derivatives

The reduced variables in this formulation are defined by three primary parameters: c; v^*, the net volume; and sη, the interaction per segment. These parameters are evaluated using three thermodynamic derivatives: the coefficient of thermal expansion α, the coefficient of compressibility κ_T, and the thermal pressure coefficient γ. These derivatives are defined respectively as

$$\alpha = 1/v\ (\partial v/\partial T)_p$$

$$\kappa_T = -1/v\ (\partial v/\partial p)_T$$

$$\gamma = (\partial p/\partial T)_v = \alpha/\kappa_T$$

Expressing these in terms of the reduced variables, we have

$$\alpha = (\tilde{T}/T\tilde{v})\ (\partial\tilde{v}/\partial\tilde{T})_{\tilde{p}}$$

$$\kappa_T = -(\tilde{p}/p\tilde{v})\ (\partial\tilde{v}/\partial\tilde{p})_{\tilde{T}}$$

$$\gamma = (\tilde{T}p/T\tilde{p})\ (\partial\tilde{p}/\partial\tilde{T})_{\tilde{v}}$$

To evaluate the three primary parameters c, sη, and v^*, we must first solve the reduced equation of state(equation 31) for T and then for $\tilde{p}$. We shall solve for T and $\tilde{p}$ at zero pressure which corresponds to the experimental data available. Next, we differentiate both of these equations and then eliminate T. This process is outlined below.

First, solving the equation of state(equation 31) at zero pressure gives

$$1/\tilde{v}\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) \qquad (34)$$

Solving for T, we have

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (35)$$

Now taking the partial derivative with respect to T at constant $\tilde{p}$ of both sides gives

$$1 = [\tilde{v}^{4/3} - 1/3(\tilde{v}^{-2/3}\partial\tilde{v}/\partial T) - (\tilde{v}^{1/3} - 1)(4/3)\tilde{v}^{1/3}(\partial\tilde{v}/\partial T)]/\tilde{v}^{8/3} \tag{36}$$

Dividing both sides of the expression by $(\partial\tilde{v}/\partial T)$ and factoring out 1/3, we then have

$$(\partial\tilde{v}/\partial T)^{-1} = 1/3[\tilde{v}^{2/3} - (\tilde{v}^{1/3} - 1)4\tilde{v}^{1/3}]/\tilde{v}^{8/3} \tag{36'}$$

Multiplying both sides of the equation by $\tilde{v}$ gives

$$\tilde{v}(\partial\tilde{v}/\partial T)^{-1} = 1/3[\tilde{v}^{5/3} - (\tilde{v}^{1/3} - 1)4\tilde{v}^{4/3}]/\tilde{v}^{8/3} \tag{36''}$$

Since the left hand side of equation 36" equals $1/\alpha$ where $\alpha = \alpha / T^* = \alpha T / T$, equation 36" becomes

$$1/\alpha(T/T) = 1/3[\tilde{v}^{1/3} - (\tilde{v}^{1/3} - 1)4]/\tilde{v}^{4/3} \tag{37}$$

Moving T, which is defined by equation 35, to the right hand side of the equation gives

$$1/\alpha T = [1/3[\tilde{v}^{1/3} - (\tilde{v}^{1/3} - 1)4]/\tilde{v}^{4/3}](\tilde{v}^{4/3}/(\tilde{v}^{1/3} - 1)) \tag{37'}$$

$$1/\alpha T = 1/3[\tilde{v}^{1/3} - (\tilde{v}^{1/3} - 1)4]/(\tilde{v}^{1/3} - 1) \tag{37''}$$

Expanding the equation, we have

$$1/\alpha T = 1/3[\tilde{v}^{1/3} - 4\tilde{v}^{1/3} - 4]/(\tilde{v}^{1/3} - 1) \tag{37'''}$$

$$1/\alpha T = 1/3[\tilde{v}^{1/3} - 4\tilde{v}^{1/3} - 4]/(\tilde{v}^{1/3} - 1) \tag{37^{iv}}$$

or

$$1/\alpha T = 1/3[(-3(\tilde{v}^{1/3} - 1) + 1)/(\tilde{v}^{1/3} - 1) \tag{37^{v}}$$

Finally, solving for αT gives Flory's[23] equation for αT

$$\alpha T = 3(\tilde{v}^{1/3} - 1)/(1 - 3(\tilde{v}^{1/3} - 1)) \tag{38}$$

A similar formulation follows for the evaluation of κ. Solving equation 34 for $\tilde{p}$ we then have

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[23] P.J. Flory, R.A. Orwall, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3511 (1964)

$$\tilde{p} = (\widetilde{T}/\tilde{v}^{2/3}(\tilde{v}^{1/3} - 1)) - 1/\tilde{v}^{2} \tag{39}$$

Taking the partial derivative with respect to $\tilde{p}$ at constant T of both sides of the equation gives

$$1 = \widetilde{T}\{-[\tilde{v}^{2/3}(1/3\tilde{v}^{-2/3})\partial\tilde{v}/\partial\tilde{p} + (\tilde{v}^{1/3} - 1)2/3\tilde{v}^{-1/3}\partial\tilde{v}/\partial\tilde{p}]/\tilde{v}^{4/3}(\tilde{v}^{1/3} - 1)^{2}\} -(-2\,(1/\tilde{v}^{3})\,\partial\tilde{v}/\partial\tilde{p}) \tag{40}$$

or

$$1 = \widetilde{T}\,[-1/3(\partial\tilde{v}/\partial\tilde{p}) \;-2/3((\tilde{v}^{1/3} - 1)/\tilde{v}^{1/3})\,\partial\tilde{v}/\partial\tilde{p}\,][\tilde{v}^{-4/3}(\tilde{v}^{1/3} - 1)^{-2}]+2/\tilde{v}^{3}(\partial\tilde{v}/\partial\tilde{p}) \tag{40'}$$

Plugging T, as defined in equation 35, into equation 40' and rearranging, we have

$$-(\partial\tilde{v}/\partial\tilde{p})^{-1} = [1/3((\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3})+2/3((\tilde{v}^{1/3} - 1)^{2}/\tilde{v}^{5/3})][1/\tilde{v}^{4/3}(\tilde{v}^{1/3} - 1)^{2}] - 2/\tilde{v}^{3} \tag{40''}$$

Multiplying equation 40" by $\tilde{v}$ gives

$$-\tilde{v}\,(\partial\tilde{v}/\partial\tilde{p})^{-1} = [1/3((\tilde{v}^{1/3} - 1)/\tilde{v}^{1/3})+2/3((\tilde{v}^{1/3} - 1)^{2}/\tilde{v}^{2/3})][1/\tilde{v}^{4/3}(\tilde{v}^{1/3} - 1)^{2}] - 2/\tilde{v}^{2} \tag{40'''}$$

Since the left hand side of the above equation is equal to κ^{-1}, we rearrange equation (40''') to get

$$\kappa^{-1} = 1/3(1/\tilde{v}^{5/3}(\tilde{v}^{1/3} - 1)) + 2/3(1/\tilde{v}^{2}) -2/\tilde{v}^{2} \tag{40^{IV}}$$

or

$$\kappa^{-1} = [\tilde{v}^{1/3} + 2(\tilde{v}^{1/3} - 1) - 6(\tilde{v}^{1/3} - 1)]/3\tilde{v}^{2}(\tilde{v}^{1/3} - 1) \tag{40^{V}}$$

Therefore κ equals

$$\kappa = 3\tilde{v}^{2}(\tilde{v}^{1/3} - 1)/[\tilde{v}^{1/3} + 2(\tilde{v}^{1/3} - 1) - 6(\tilde{v}^{1/3} - 1)] \tag{41}$$

$$\kappa = 3\tilde{v}^{2}(\tilde{v}^{1/3} - 1)/-3\tilde{v}^{1/3} + 4 \tag{41'}$$

Multiplying both sides of the equation by $\tilde{p}$ and rearranging gives

$$\tilde{p}\kappa = p\kappa = 3\tilde{v}^{2}(\tilde{v}^{1/3} - 1)\tilde{p}/\ 1 - 3(\tilde{v}^{1/3} - 1) \tag{41''}$$

Putting this equation in a form resembling Flory's[24] κ, we finally have

$$\kappa = 3\tilde{v}^{2}(\tilde{v}^{1/3} - 1)/\ 1 - 3(\tilde{v}^{1/3} - 1)p^{*} \tag{42}$$

The term αT is noted to be embedded in κ, therefore κ may also be written as

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[24] P.J. Flory, R.A. Orwoll, and A. Vrij, 3511.

$$\kappa = \alpha T\tilde{v}^2/p^* \tag{43}$$

The term γ is just the quotient of α/κ, thus we have

$$\gamma = \alpha/\kappa = \alpha/\alpha T\tilde{v}^2/p^* = p^*/T\tilde{v}^{\ 2} \tag{44}$$

A straightforward evaluation of the primary parameters c, sη, and v^* then follows.

3.3 Evaluation of Primary Parameters

The primary paramters v^*, $s\eta$, and c are evaluated as follows. Given equation 38,

$$\alpha T = 3(\tilde{v}^{1/3} - 1)/(1 - 3(\tilde{v}^{1/3} - 1))$$

we bring the term $(1 - 3(\tilde{v}^{1/3} - 1))$ to the left-hand side of the equation

$$(1 - 3(\tilde{v}^{1/3} - 1))\alpha T = 3(\tilde{v}^{1/3} - 1)$$

Dividing by 3 and then expanding gives

$$(\alpha T/3) - 3(\tilde{v}^{1/3} - 1)(\alpha T/3) = (\tilde{v}^{1/3} - 1)$$

Collecting the $(\tilde{v}^{1/3} - 1)$ terms

$$(\alpha T/3) = (\tilde{v}^{1/3} - 1)(1 + \alpha T)$$

Then solving for $\tilde{v}^{1/3}$ we have

$$\tilde{v}^{1/3} = \alpha T/3(1 + \alpha T)$$

or

$$\tilde{v} = [\alpha T/3(1 + \alpha T)]^3 \qquad (45)$$

Equation 45 gives $\tilde{v}$ and along with the experimental volume v, we can solve for the net volume v^* using equation 19

$$v^* = v / \tilde{v}$$

Next, substituting $\tilde{v}$ into equation 35 yields $\tilde{T}$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}$$

Substituting $\tilde{T}$ into equation 20 along with the experimental T gives T*

$$T^* = T / \tilde{T} \qquad (46)$$

The term p* may now be evaluated using either equation 42 or 43

$$\kappa = 3\tilde{v}^2(\tilde{v}^{1/3} - 1)/\ 1 - 3(\tilde{v}^{1/3} - 1)p^*$$

or

$$\kappa = \alpha T\tilde{v}^2/p^*$$

Finally, the parameters sη and c may be evaluated using equations 30 and 30' respectively

$$p/p^* = 2pv^{*2}/s\eta$$

and

$$\tilde{p} = pv^*/ckT^*$$

Or solving for sη and c explicitly

$$s\eta = 2p^*v^{*2}$$

and

$$c = pv^*/\tilde{p}kT^* = p^*v^*/kT^*$$

This equation of state can now be tested against experimental data.

Fitting the Equation of State

4.0 Introduction

In testing the above equation of state for accuracy, we will apply it to normal paraffin hydrocarbons as Flory[25] does. This section will then provide a detailed description of the process involved in fitting the equation of state using such available variables as α, β, and κ. In doing so, this section can then be used by future students as an aide to applying Flory's equation of state to experimental data.

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[25] P.J. Flory, R.A. Orwoll, and A. Vrij, 3511.

4.1 The Experimental Data

The experimental data for this section is tabulated in Table I and Table II. This is the same data Flory[26] used and any slight discrepancies are inherent in the software used, Quattro Pro for Windows(Version 5). The normal paraffin hydrocarbon data at ordinary pressure($p = 0$) is representative of four temperatures: 20, 50, 100, and 150^{O} Celcius or 293, 323, 373, and 423^{O} Kelvin respectively. Please refer to Flory's paper[27] for sources of the data.

Densities, ρ, and thermal expansion coefficients, α, located in columns 3 and 5 respectively, are fairly accurate as evidenced by the smooth plots of ρ and α against 1/n in Figure 1. The only deviations from these smooth curves are observed with increasing temperature, notably 373 and 423 K. Thermal pressure coefficients, γ, are listed in columns 11 and 12 of Table I and II. These values have either come directly from experiment or have been found by empirical equations from the isotherm, such as Tait's or Huddleston's equations.

The reduced volumes $\tilde{v}$ are listed in column 6 of Tables I and II. These were previously calculated from the coefficient of thermal expansion, α, using equation 45. The net volumes per mole v* listed in column 6 are then calculated using the equation

$$\mathrm{v}^* = \mathrm{M} / \tilde{v}\,\rho \tag{47}$$

Here, M is the molecular weight of the n-mer. This above equation was previously shown as

$$\mathrm{v}^* = v^*\mathrm{x} \tag{48}$$

Since $\mathrm{x} = n + n_e$ and n_e is close to unity (= 1), $\mathrm{x} = n + 1$. Thus the values of v^* listed in column 7 of Tables I and II are calculated using

$$v^* = \mathrm{v}^* / (n + 1) \tag{49}$$

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[26] P.J. Flory, R.A. Orwoll, and A. Vrij, 3511.

[27] P.J. Flory, R.A. Orwoll, and A. Vrij, 3511. (At the top of the page)

The value v^* is remarkably linear with n(see figure 2.), which thus substantiates Prigogine's principle of corresponding states; the volumes are also linear with n at reduced temperature. The only discrepancies in this linearity again commences in the higher temperature regions. This linear dependence also pervades v^*, but there is a slight dependence on temperature as indicated in Table 2:

Table 2

Reference Volumes per Segment at Specified Temperatures[28]

T, (C^{O})	v^* (cc. mole^{-1})
20	14.15 - 0.02
50	14.14 - 0.03
100	14.25 - 0.05
150	14.42 - 0.07

An error is therefore introduced into this formulation with v^* varying with temperature. Flory[29] goes on to investigate this dependency of v^* on T through the second derivatives of v by combining equations 35 and 38 to get the equation

$$d\alpha / dT = (7 + 4\alpha T)\alpha^2/3 \tag{50}$$

This equation suffices to predict the increase in the thermal expansion coefficient with temperature. Since we are more interested in fitting the equation of state, we shall assume the above dependency of v^* on temperature to be a minor error in the formulation, which it is.

The values of T* listed in column 9 of Tables I and II have been previously calculated using equation 46. According to equation 20, T* depends on two the primary parameters, c and $s\eta$; these two parameters can then be evaluated based on their dependence on x. Following the

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[28] P.J. Flory, R.A. Orwoll, and A. Vrij, 3512.

[29] P.J. Flory, R.A. Orwoll, and A. Vrij, 3512.

procedure of Flory[30], we rearrange equation 17 and multiply it by s to get

$$s\eta = s_m\eta_m(s/s^m)^{-1}[1 + (2s_e\eta_{em}/s_m\eta_m)x^{-1} + (s_e^2\eta_e/s_m^2/\eta_m)x^{-2}] \quad (51)$$

Solving equation 1 for s / s_m, which equals 1 + $(s_e/s_m)x^{-1}$, and substituting it into equation 51 gives

$$s\eta = s_m\eta_m(1 + (s_e/s_m)x^{-1})^{-1}[1 + (2s_e\eta_{em}/s_m\eta_m)x^{-1} + (s_e^2\eta_e/s_m^2/\eta_m)x^{-2}] \quad (51')$$

Next, using a Taylor's series, we take the reciprocal of $(1 + (s_e/s_m)x^{-1})$ and expand it to the second power in 1/x; the Taylor's series is as follows

$$1 / 1 + s_e/s_m(1/x) = 1 - s_e/s_m(1/x) + \ldots$$

Plugging this into equation 51' and multiplying gives

$$s\eta \cong s_m\eta_m[1 + ax^{-1} + bx^{-2}] \quad (52)$$

where

$$a = (2\eta_{em}/\eta_m - 1)(s_e/s_m)$$

and

$$b = (\eta_e/\eta_m - 2\eta_{em}/\eta_m + 1)(s_e/s_m)^2$$

or combining a and b

$$b = (\eta_e/\eta_m)(s_e/s_m)^2 - a(s_e/s_m)$$

We now procede to solve for c from the previously stated equation

$$3xc = 3(xc_m + c_e)$$

and substitute it along with equation 52 for sη into equation 20 to give

$$1/ T^* \cong (1/T_\infty^*)[1 + (c_e/c_m - a)x^{-1} + (a^2 - b - ac_e/c_m)x^{-2}] \quad (53)$$

Here

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[30] P.J. Flory, R.A. Orwoll, and A. Vrij, 3513.

$$T_\infty^* = s_m\eta_m/2kv^*c_m \quad (54)$$

Again the problem arises where the data is temperature dependent. This can be seen in the relationships between $1/T^*$ and $1/x$ shown in Figure 3. Since these relationships are sufficiently linear, the coefficient in front of the x^{-2} term is assumed to be small and can be neglected. This dependence on temperature is a result of equation 50 and Flory[31] again conceives the relationship between v^* and T as a result of equations 35 and 38

$$d \ln T^*/ dT = (\alpha T)^{-1}\, d \ln v^*/ dT \quad (55)$$

Finally, concerning ourselves with the variable p^*, listed in Tables I and II in column 13, we note that these values are calculated from thermal pressure coefficients, γ, and $\tilde{v}$ using equation 44. There are some experimental uncertainties, which are accounted for in the tables(i.e. Temperature 293K, $n = 7$, $\gamma = 212 - 3$). The variable p^* is then found by substituting equation 52 into the previously mentioned equation

$$s\eta = 2p^*v^{*2} \quad (56)$$

$$p^* \cong p_\infty^*(1 + a/x + b/x^2) \quad (57)$$

Here

$$p_\infty^* = s_m\eta_m/2v^{*2} = c_m kT_\infty^*/v^* \quad (58)$$

Flory, in another paper[32], finds b to be relatively small compared to a and thus equation 56 can be written as

$$p^* \cong p_\infty^*(1 + a/x) \quad (59)$$

A plot of these values against $1/x$ only reveals an obvious relationship that p^* decreases sufficiently with x and again a dependence on temperature. Since the above plot is quantitatively

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[31] P.J. Flory, R.A. Orwoll, and A. Vrij, 3513.

[32] P.J. Flory, R.A. Orwoll, and A. Vrij, *J. Am Chem. Soc.*, **86**, 3517 (1964).

useless, Flory again extracts a relation, in this case p*, from a later paper[33] .

$$p^* = 120(1 - 1.5/x), \text{ cal. cc.}^{-1} \qquad (60)$$

Thus on comparison with equation 59, $p_\infty^* = 120$ cal. cc.$^{-1}$ and $a = -1.5$. A working of all necessary parameters for the fitting of the equation of state is now possible.

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[33] P.J. Flory, R.A. Orwoll, and A. Vrij, 3517.

4.2 Parameters

As an example, all necessary parameters, relating to 293 K, will be shown. From Table 2 comes $v^* = 14.15$ cc. mole^{-1}. Next using equations 53, 59, and 60 comes

$$T_\infty^* = 7080 \text{ K}$$

$$p_\infty^* = 120 \pm 5 \text{ cal. cc.}^{-1} \text{(uncertainty comes from Flory's subsequent paper)}$$

$$a = -1.5$$

$$c_e/c_m - a = 4.17$$

These combined with following and equations 53, 54, and 58 gives

$$s_m\eta_m = 2v^{*2}p_\infty^* = 4.8 \times 10^4 \text{ cc. cal. mole}^{-2}$$

$$c_m = v^*p_\infty^*/RT_\infty^* = 0.121$$

$$c_e/c_m = 4.17 + a = 2.7$$

$$c_e = 0.32$$

These values, as Flory suggests, could be improved with better experimental data, but they suffice for the given data.

5.0 Conclusion

In conclusion, a few of Flory's[34] points should be reiterated. First, the above formulation correlates experimental data for n-paraffin hydrocarbons fairly well from n = 6 to n = 40, and perhaps even up to n = ∞. However, the equation of state does not reflect consistency over wide ranges of temperature and pressure.

This theory can be improved in two areas: a better representation of the Energy term E_o by letting $E_o = -xNs\eta/2v^m$ and m = 1or by not treating the number of external degrees of freedom c as a constant. Although both of these suggestions sound logical, the first is virtually impossible due to restrictions from isotherms and isobars and the second would make the partition function unworkable. This in turn would contradict Flory's purpose in this formulation, to make a workable scheme adaptable to mixtures. This formulation, in representing n-paraffin hydrocarbons fairly well, entices its application to nonpolar liquid mixtures and other chain molecule mixtures.

In giving a detailed account of the development of Flory's partition function, equation of state, and later reiteration of their application to experimental data, this paper should aid future students of Polymer liquid theory.

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[34] P.J. Flory, R.A. Orwoll, and A. Vrij, 3514.

Table 1: Data for Normal Paraffin Hydrocarbons

		Hydroge	1.0079
Temperature	293 degrees K	Carbon	12.011

n	1/n	p g. cm^-3	1/x ,= 1/n + 1	10^3 Alpha deg. ^-1		vtilda	v* cc . mole^-1		v* = v*/(n+1)	T* K	1/T* 1/K	Gamma x 10^3 cal. cc. ^-1 deg ^-1			p* cal. cc. ^-1	
5	0.2000	0.6262	1.200	1.565		1.3485	85.44		14.24	4165	0.000240					
6	0.1667	0.6594	1.167	1.360		1.3129	99.55		14.22	4435	0.000225	211	200		107	101
7	0.1429	0.6838	1.143	1.230		1.2890	113.69		14.21	4655	0.000215	212	+or-3		103	+or-1
8	0.1250	0.7025	1.125	1.140		1.2719	127.84		14.20	4838	0.000207	217	240		103	114
9	0.1111	0.7176	1.111	1.070		1.2582	142.05		14.20	5002	0.000200	226	234		105	109
10	0.1000	0.7301	1.100	1.020		1.2482	156.14		14.19	5134	0.000195					
11	0.0909	0.7402	1.091	0.980		1.2401	170.30		14.19	5250	0.000190					
12	0.0833	0.7487	1.083	0.950		1.2339	184.38		14.18	5343	0.000187	239			107	
13	0.0769	0.7564	1.077	0.925		1.2287	198.36		14.17	5425	0.000184	235			104	
14	0.0714	0.7628	1.071	0.890		1.2214	212.93		14.20	5549	0.000180					
15	0.0667	0.7685	1.067	0.870		1.2172	227.08		14.19	5624	0.000178					
16	0.0625	0.7734	1.063	0.855		1.2140	241.17		14.19	5682	0.000176	248			107	
17	0.0588	0.7780	1.059	0.835		1.2097	255.50		14.19	5764	0.000173					
18	0.0556	0.7819	1.056	0.820		1.2065	269.78		14.20	5828	0.000172					

Temperature 323 degrees K

n	1/n	p g. cm^-3	1/x ,= 1/n + 1	10^3 Alpha deg. ^-1		vtilda	v* cc . mole^-1		v* = v*/(n+1)	T* K	1/T* 1/K	Gamma x 10^3 cal. cc. ^-1 deg ^-1			p* cal. cc. ^-1	
6	0.1667	0.63160	1.167	1.510		1.3650	99.96		14.28	4475	0.000223	164			99	
7	0.1429	0.65830	1.143	1.330		1.3316	114.31		14.29	4724	0.000212	181	+or-2	169	104	+or-1, 97
8	0.1250	0.67840	1.125	1.225		1.3111	128.42		14.27	4905	0.000204	180	191		100	106
9	0.1111	0.69440	1.111	1.150		1.2960	142.51		14.25	5055	0.000198	187	+or-3		101	+or-2
10	0.1000	0.70730	1.100	1.095		1.2847	156.59		14.24	5180	0.000193					
11	0.0909	0.71800	1.091	1.045		1.2742	170.86		14.24	5304	0.000189	196			103	
12	0.0833	0.72710	1.083	1.020		1.2688	184.63		14.20	5371	0.000186	204			106	
13	0.0769	0.73490	1.077	0.980		1.2602	199.07		14.22	5486	0.000182	206			106	
14	0.0714	0.74170	1.071	0.960		1.2559	212.99		14.20	5547	0.000180					
15	0.0667	0.74760	1.067	0.940		1.2515	227.04		14.19	5611	0.000178					
16	0.0625	0.75280	1.063	0.920		1.2470	241.22		14.19	5678	0.000176	225			113	
17	0.0588	0.75750	1.059	0.900		1.2426	255.48		14.19	5747	0.000174	221			110	
18	0.0556	0.76160	1.056	0.885		1.2392	269.66		14.19	5802	0.000172					
19	0.0526	0.76540	1.053	0.870		1.2358	283.89		14.19	5858	0.000171					
20	0.0500	0.76880	1.050	0.86		1.2335	297.95		14.19	5897	0.000170	226			111	

Table 2: Data for Normal Paraffin Hydrocarbons

Temperature 373 degrees K

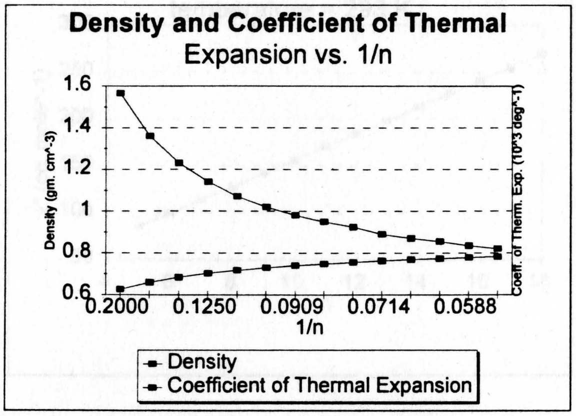
n	1/n	p g. cm^-3	1/x ,= 1/n + 1	10^3 Alpha deg. ^-1		vtilda	v* cc . mole^-1		v* = v*/(n+1)	T* K	1/T* 1/K	Gamma x 10^3 cal. cc. ^-1 deg ^-1			p* cal. cc. ^-1		
7	0.1429	0.61100	1.143	1.580		1.4185	115.61		14.45	4810	0.000208	116	130	154	87	98	116
8	0.1250	0.63520	1.125	1.420		1.3878	129.59		14.40	5002	0.000200	132	142		95	102	
9	0.1111	0.65360	1.111	1.305		1.3644	143.82		14.38	5172	0.000193	136	+or-7		94	+or-5	
10	0.1000	0.66810	1.100	1.210		1.3443	158.42		14.40	5339	0.000187						
11	0.0909	0.68000	1.091	1.145		1.3301	172.82		14.40	5470	0.000183	142			94		
12	0.0833	0.69000	1.083	1.100		1.3201	187.01		14.39	5570	0.000180	158			103		
13	0.0769	0.69850	1.077	1.060		1.3110	201.34		14.38	5666	0.000176	155			99		
14	0.0714	0.70590	1.071	1.035		1.3052	215.33		14.36	5730	0.000175						
15	0.0667	0.71230	1.067	1.010		1.2994	229.51		14.34	5798	0.000172						
16	0.0625	0.71800	1.063	0.985		1.2935	243.83		14.34	5869	0.000170	167			104		
17	0.0588	0.72300	1.059	0.965		1.2887	258.09		14.34	5929	0.000169	167			103		
18	0.0556	0.72760	1.056	0.950		1.2851	272.18		14.33	5976	0.000167						
19	0.0526	0.73170	1.053	0.935		1.2815	286.37		14.32	6024	0.000166						
20	0.0500	0.73540	1.050	0.920		1.2779	300.67		14.32	6074	0.000165	173			105		
28	0.0357	0.75550	1.036	0.840		1.2580	415.35		14.32	6370	0.000157						
30	0.0333	0.75900	1.033	0.825		1.2543	444.15		14.33	6432	0.000155	179			105		
36	0.0278	0.76670	1.028	0.795		1.2466	530.45		14.34	6564	0.000152						

Temperature 423 degrees K

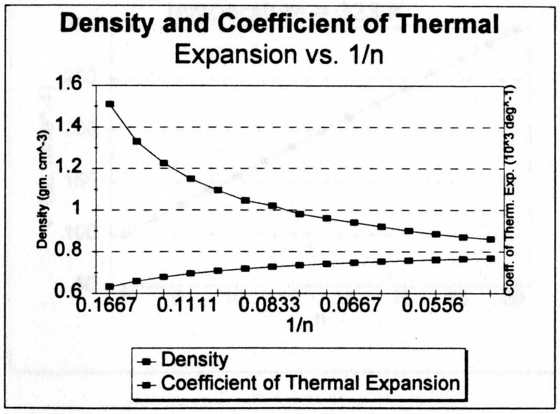
n	1/n	p g. cm^-3	1/x ,= 1/n + 1	10^3 Alpha deg. ^-1		vtilda	v* cc . mole^-1		v* = v*/(n+1)	T* K	1/T* 1/K	Gamma x 10^3 cal. cc. ^-1 deg ^-1			p* cal. cc. ^-1	
10	0.1000	0.62600	1.100	1.420		1.4242	159.60		14.51	5418	0.000185					
11	0.0909	0.63960	1.091	1.320		1.4028	174.21		14.52	5562	0.000180	102			85	
12	0.0833	0.65090	1.083	1.250		1.3873	188.64		14.51	5677	0.000176					
13	0.0769	0.66040	1.077	1.185		1.3724	203.41		14.53	5797	0.000173	109			87	
14	0.0714	0.66850	1.071	1.150		1.3643	217.53		14.50	5867	0.000170					
15	0.0667	0.67560	1.067	1.100		1.3523	232.50		14.53	5976	0.000167					
16	0.0625	0.68190	1.063	1.075		1.3463	246.66		14.51	6035	0.000166					
17	0.0588	0.68740	1.059	1.050		1.3402	261.03		14.50	6097	0.000164	124			94	
18	0.0556	0.69240	1.056	1.030		1.3352	275.28		14.49	6148	0.000163					
19	0.0526	0.69680	1.053	1.015		1.3315	289.43		14.47	6188	0.000162					
20	0.0500	0.70090	1.050	0.999		1.3274	303.69		14.46	6232	0.000160	130			97	
28	0.0357	0.72350	1.036	0.890		1.2992	419.98		14.48	6578	0.000152					
30	0.0333	0.72700	1.033	0.880		1.2965	448.58		14.47	6614	0.000151	142			101	
36	0.0278	0.73570	1.028	0.830		1.2830	537.10		14.52	6808	0.000147					
40	0.0250	0.74050	1.025	0.825		1.2816	593.31		14.47	6829	0.000146	147			102	
64	0.0156	0.75790	1.016	0.770		1.2664	937.44		14.42	7077	0.000141					
inf		0.77900		0.685		1.2419										

Figure 1: Densities and Coefficients of Thermal Expansion vs. 1/n For Termperature 273 K, 323 K, 373 K, and 423 K.

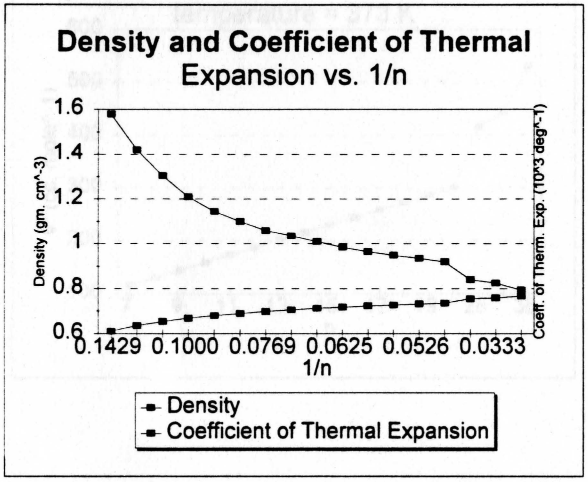
Temperature: 293 K



Temperature: 323 K



Temperature: 373 K



Temperature: 423 K

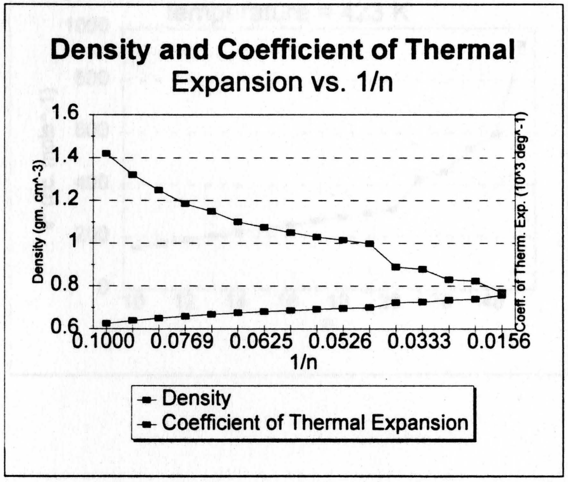


Figure 2: Plots of v* vs. n for temperatures 293, 323, 373, and 423 degrees K

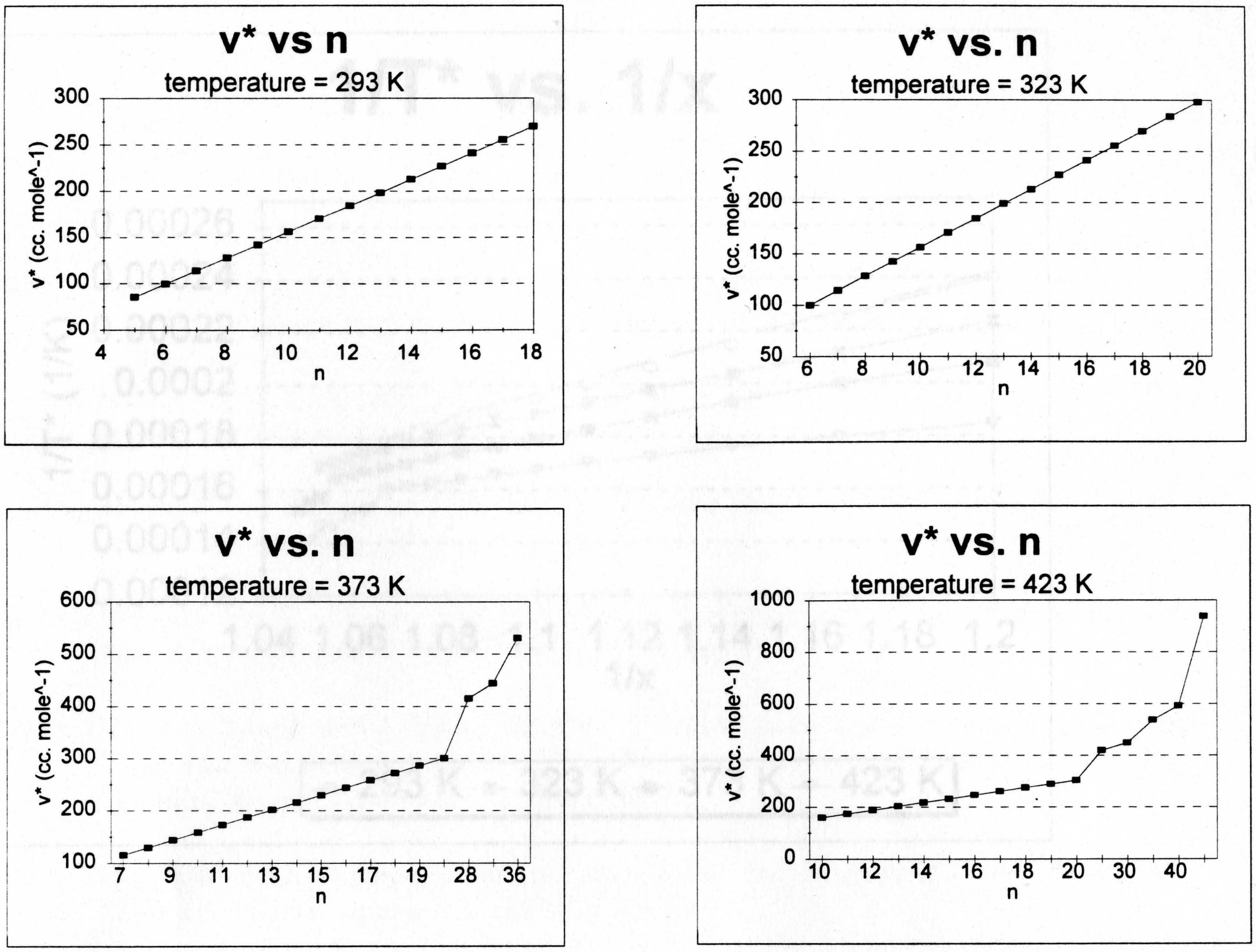
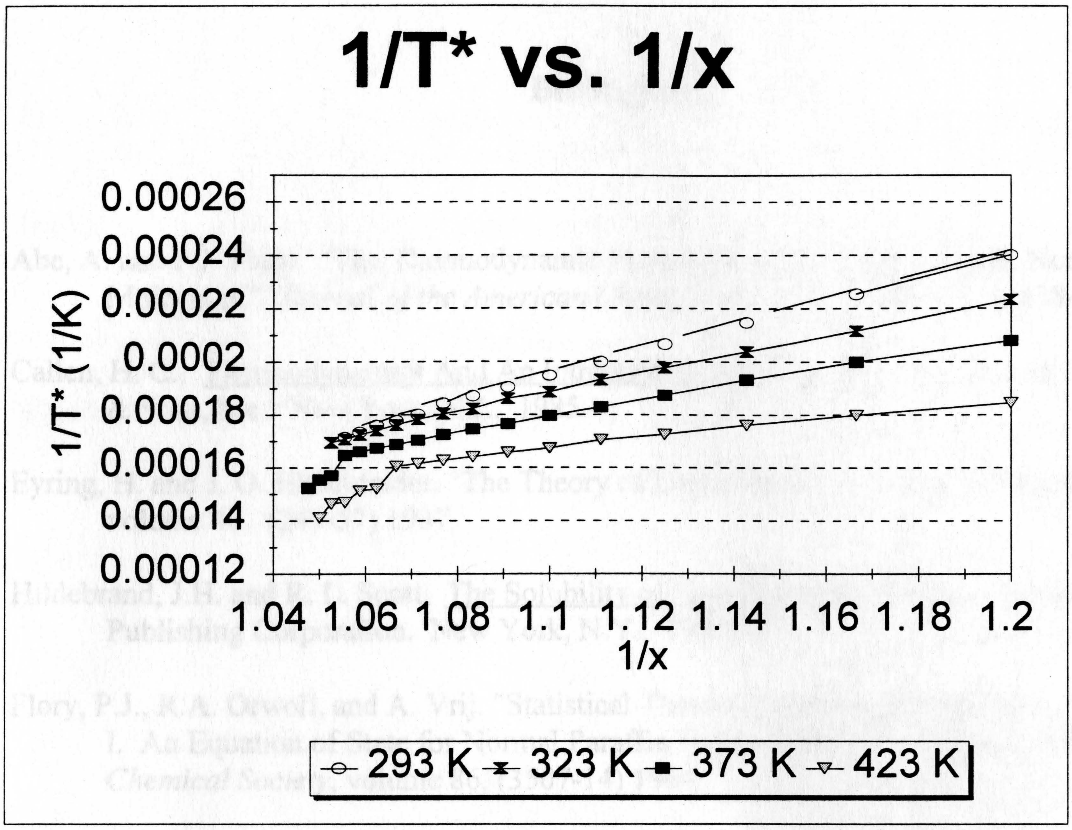


Figure 3: 1/T* vs. 1/x



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