A Parameterization of the Configurational Energy for Short-Chain Molecules

Arun Thomas, John M. Walsh, and Marc D. Donohue
Dept. of Chemical Engineering, The Johns Hopkins University, Baltimore, MD 21218

Introduction

As a general rule, for an equation of state to be applied easily it must have a simple and direct dependence on the parameters (for example, molecular volume, surface area, dispersion energy, multipole moments, and so on). Most empirical equations (for example, Peng-Robinson, Redlich-Kwong) have a simple dependence, but accurate parameters are difficult to estimate because of the approximations made in the equations. Conversely, more rigorous equations (for example, perturbation theories) involve spatial correlation functions which must be evaluated by computer simulations or the numerical solution of integral equations such as Reference Interaction Site Model (RISM), and have an indirect and complicated dependence on the parameters. Although they are realistic, most parameter values cannot be measured or estimated by independent means (*ab initio* calculations, second virial coefficients, spectroscopy), and must be regressed to fit experimental data. For regression to be efficient, the equation must depend on the parameters in such a way that a change in parameters does not require an extensive reevaluation of complicated functions using data from computer simulations or the numerical solution of integral equations.

In this article, molecular dynamics simulations are used to calculate the configurational energy of short chain molecules, such as n-butane, in a parameterized form that is similar to the parameterization used in the perturbation chain theories, which are parameterized for efficient parameter regression. The perturbation chain theories and the Flory lattice theory are shown to be similar in two respects, they treat the interactions between molecules as the sum of interactions between sites, and they both use a so-called surface-area parameter. Both of these theories can be derived by starting with the site-interaction perturbation theory of Lombardero et al. (1981) and proceeding by a series of well-defined approximations. The concept of surface area is shown to be a configurational quantity with a statistical mechanical definition and has contributions from both the intermolecular site-site pair interaction potential and the site-site pair correlation function.

Theory

Various models for the properties of dense fluids make use of the concept of excluded volume, which is the volume that a molecule excludes from the presence of other molecules, and is defined by the repulsive part of the potential. For a spherical molecule, the excluded volume is given by its hard-sphere diameter ($v_e = 4\pi d^3/3$), and has a sharp boundary. For chain molecules, the excluded volume is calculated from the bond lengths, bond angles, and repulsive potentials of the sites in the molecule. Different methods to calculate the excluded volume are discussed by Walsh (1989), Denlinger and Hall (1990), and Dodd and Theodorou (1991).

Just outside the region of repulsive potential energy, is a region of attractive potential energy, referred to as the "interaction volume." The boundary of the interaction volume is diffuse because the attractive part of the potential decays slowly. For spherical molecules, the interaction volume surrounds the entire molecule, whereas for a site on a chain molecule, the interaction volume has to take into account the excluded volume of the neighboring sites. This difference is shown in Figure 1 where the excluded volume for a chain and a sphere, and the interaction volumes for an end site and an internal site of a chain, and that for a sphere, are shown.

In the perturbation theory of Barker and Henderson (1967), the first-order contribution to the Helmholtz free energy is given by

$$\frac{A_1}{N} = 2\pi\rho\epsilon\sigma^3 I \tag{1}$$

in which $I = \int_1^\infty \tilde{u}' g^0 \tilde{r}^2 \, d\tilde{r}$, where $\tilde{u}' = u'/\epsilon$ is the dimensionless perturbation potential which is spherically symmetric, and g^0 is the pair correlation function for the reference fluid. The integral I essentially is the average number of molecules that a certain molecule has in its interaction volume.

Current address of J. M. Walsh: Shell Development Co., P.O. Box 1380, Houston, TX 77251.

Correspondence concerning this article should be addressed to M. D. Donohue.

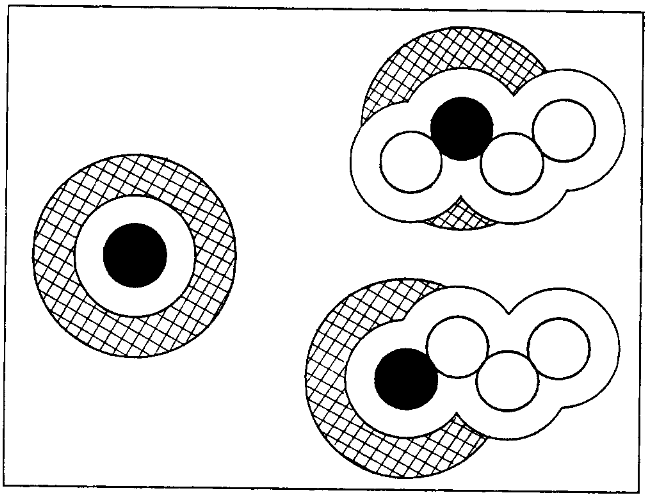

Figure 1. Schematic representation of the interaction volume for spherical and chain molecules.

For a spherical molecule the interaction volume surrounds the entire molecule. In contrast, the interaction volumes for an end site and an internal site for a 4-mer are shown (cross-hatched).

Lombardero et al. (1981) presented an interaction site model for nonspherical molecules based on the Barker-Henderson theory. The first-order contribution to the Helmholtz free energy for Lennard-Jones interactions is given by:

$$\frac{A_1^{LJ}}{N}=2\pi\rho\sum_{\alpha}\sum_{\beta}\epsilon_{\alpha\beta}\sigma_{\alpha\beta}^3 I_{\alpha\beta} \tag{2}$$

in which $I_{\alpha\beta}=\int_1^\infty \tilde{u}'_{\alpha\beta}g^0_{\alpha\beta}\tilde{r}^2\,d\tilde{r}$, where $\tilde{u}'_{\alpha\beta}$ is the dimensionless perturbation potential for sites α and β, $g^0_{\alpha\beta}$ is the site-site pair correlation function for sites α and β in the reference fluid, and $\tilde{r}$ refers to the dimensionless distance ($\tilde{r}_{\alpha\beta}=r_{\alpha\beta}/\sigma_{\alpha\beta}$) between sites α and β. The integral $I_{\alpha\beta}$ is the average number of α and β sites in each others interaction volume. Lombardero et al. (1981) applied the theory to a homonuclear diatomic molecule, using Boublik's hard convex body equation (1975) to calculate the properties of the reference hard-dimer fluid, and using RISM (Chandler, 1973; Lowden and Chandler, 1973) to calculate the site-site pair correlation functions. Encisco and Lombardero (1981) and Abascal et al. (1985) used this theory to calculate the thermodynamic properties of chain molecules and smaller n-alkanes.

Although the polymer equation of state of Flory (1953) was derived using lattice concepts, the attractive contribution to the Helmholtz free energy can alternatively be derived from first-order site-interaction perturbation theory, and is written as:

$$\frac{A^{att}}{N}=-2\pi\rho\sum_{\alpha}\sum_{\beta}\epsilon_{\alpha\beta}S_{\alpha\beta}\sigma_{\alpha\beta}^3 \tag{3}$$

in which $S_{\alpha\beta}$ is "the number of contacts" (Flory, 1953), and is assumed to be independent of temperature and density. It can be seen that Eq. 3 is the same as Eq. 2 if the following approximation is used.

$$S_{\alpha\beta}\approx\int_1^\infty \tilde{u}_{\alpha\beta}g^0_{\alpha\beta}\tilde{r}^2 d\tilde{r} \tag{4}$$

Beret and Prausnitz (1975) and Donohue and Prausnitz (1978) extended the Barker-Henderson perturbation theory to chain molecules using the polymer lattice concepts of Flory and Prigogine. They modeled each segment to be surrounded by segments of other molecules, with the distributions of these segments assumed to be similar to that for a spherical reference fluid. Therefore, the model requires only the pair correlation function for the spherical reference fluid. In the perturbation chain theories, the first-order contribution to the Helmholtz free energy is given by:

$$\frac{A_1}{N}=2\pi\rho\epsilon q\sigma^3 I \tag{5}$$

in which $I=\int_1^\infty \tilde{u}' g^0\tilde{r}^2\,d\tilde{r}$, as in the Barker-Henderson theory. The parameter q was interpreted as a surface area parameter. Walsh et al. (1991) obtained the above equation from the site interaction perturbation theory of Lombardero et al. (1981) by using the approximation:

$$I_{\alpha\beta}=q_{\alpha\beta}I \tag{6}$$

and by defining molecular parameters as the sum of site parameters,

$$\sigma^3=\sum_{\alpha}\sum_{\beta}\sigma_{\alpha\beta}^3$$

$$\epsilon q=\sum_{\alpha}\sum_{\beta}\epsilon_{\alpha\beta}q_{\alpha\beta} \tag{7}$$

Walsh et al. (1991) have shown that the thermodynamic behavior of complex molecules can be accurately correlated, when this approach is used to calculate the parameters, which are obtained as a summation over the individual site parameters, rather than using molecular parameters. In the following sections, we calculate the different $I_{\alpha\beta}$ and show that Eq. 6 is a good approximation for short-chain molecules.

Molecular Dynamics Simulations

Molecular dynamics simulations were performed for a butane-like molecule, that is composed of four overlapping Lennard-Jones spheres. The two end sites (—CH_3) were treated as indistinguishable as were the two internal sites (—CH_2—), such that the molecule has only two types of sites (end and internal). All sites have the same Lennard-Jones parameters (ϵ, σ), and their values were given in Table 1. The bond-vibration and bond-bending potentials are harmonic with respect to the bond length and cosine of the bond angle respectively, and the force constants and equilibrium values are given in Table 1. All the above parameters were obtained from literature (Bondi, 1968; Ryckaert and Bellemans, 1978; Swindoll, 1981). The bond-rotation or dihedral potential is the same as that used by Ryckaert and Bellemans (1978).

The molecular dynamics simulation method as described by Swindoll (1981), Haile and Mansoori (1983), and Lee (1988) was used. The simulations were done with 64 molecules. The intermolecular site-site pair potential was truncated at 2.5σ, and the truncated potential was shifted so that the force on the interacting sites goes smoothly to zero at the point of truncation. A neighbor list was maintained using the algorithm

Table 1. Molecular Dynamics Parameters

Parameter	Value	Description
ϵ/k	74.0 K	Lennard-Jones energy
σ	4.009 Å	Lennard-Jones diameter
l/σ	0.3826	Equilibrium bond-length
θ	109° 28′	Equilibrium bond-angle
$k_V\sigma^2/\epsilon$	2.402×10^4	Bond-vibration constant
k_B/ϵ	210.04	Bond-bending constant

of Verlet (1968). A fifth-order Gear predictor-corrector algorithm was used to calculate the particle trajectories at each time-step. A time-step of 0.002 pico-second was used, and each simulation was run for a total of 20 pico-seconds. An equilibration stage was done until the mean-square-displacement exceeded a value of 1, and normally has a duration of 1.5 to 2 pico-seconds. The total force on each site was calculated as a sum of the contributions from the intermolecular interactions, and from the bond-vibration, bond-bending, and bond-rotation potentials. The potential energy between molecules A and B was calculated as the sum of site-site interactions:

$$u(AB)=\sum_{\alpha}^{m}\sum_{\beta}^{m}u_{\alpha\beta}(r_{\alpha\beta}^{AB}) \tag{8}$$

where molecules A and B are indistinguishable (pure fluid), each has m sites, $u_{\alpha\beta}$ is the site-site pair interaction potential, and $r_{\alpha\beta}^{AB}$ is the scalar distance between site α on molecule A and site β on molecule B. $u_{\alpha\beta}$ was calculated using the Lennard-Jones potential:

$$u_{\alpha\beta}(r_{\alpha\beta}^{AB})=4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}^{AB}}\right)^{12}-\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}^{AB}}\right)^{6}\right] \tag{9}$$

The configurational energy ($E^c=E-E^0$) was then calculated by summing the potential between all pairs of molecules:

$$E^c=\frac{1}{2}\sum_{A}\sum_{B}u(AB) \tag{10}$$

Alternatively, since the site-site pair correlation functions also were calculated during the simulations, the configurational energy can be calculated by integrating the product of the pair potential and the pair correlation function:

$$\frac{E^c}{N}=2\pi\rho\sum_{\alpha}^{m}\sum_{\beta}^{m}\epsilon_{\alpha\beta}\sigma_{\alpha\beta}^{3}\int\tilde{u}_{\alpha\beta}g_{\alpha\beta}\tilde{r}^2d\tilde{r} \tag{11}$$

where $g_{\alpha\beta}$ is the site-site pair correlation function for sites α and β, and dimensionless variables are used, $\tilde{u}=u/\epsilon$, and $\tilde{r}=r/\sigma$. The site-site pair correlation functions were calculated in terms of the ensemble average:

$$g_{\alpha\beta}(r)=\frac{1}{n_\alpha n_\beta N(N-1)}\left\langle\sum_{A}^{N}\sum_{B\neq A}^{N}\sum_{\alpha}^{n_\alpha}\sum_{\beta}^{n_\beta}\delta(r_{\alpha\beta}^{AB}-r)\right\rangle \tag{12}$$

where δ is the Dirac delta function, n_α and n_β are the number of α and β sites on each molecule, and $\langle\,\rangle$ denotes the average over the whole simulation run.

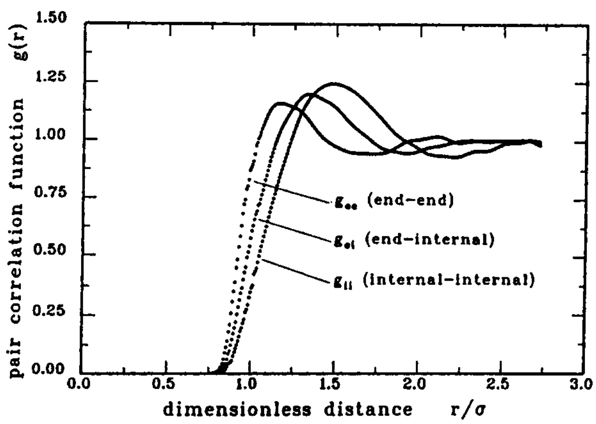

Figure 2. Intermolecular site-site pair correlation functions for the butane-like molecule at $kT/4\epsilon=1.725$ and $\tilde{\rho}=0.324$.

ϵ and σ are the Lennard-Jones parameters for the site-site interactions and are given in Table 1.

Computer Simulation Results and Discussion

For the butane-like molecule there are three types of site-site interactions among the two types of sites: end-end (*ee*), end-internal (*ei*), and internal-internal (*ii*). For each type of interaction, we calculate the configurational integral:

$$I_{\alpha\beta}=\int_{1}^{\infty}\tilde{u}g_{\alpha\beta}\tilde{r}^2d\tilde{r} \tag{13}$$

where α and β are either end or internal. Figure 2 shows the intermolecular site-site pair correlation functions at $kT/4\epsilon=1.725$ and $\tilde{\rho}=0.324$. The results confirm the physically intuitive expectation that on an average, end sites are closer together than internal sites, which is caused by the presence of the covalently bonded neighbors.

The integrand ($\tilde{u}g\tilde{r}^2$) is an interaction intensity which depends on distance (as well as density and temperature), and extends only a relatively short distance in the fluid as shown in Figure 3. The integrands are much smoother and they have less detail than the site-site pair correlation functions. In effect, multiplying the pair correlation function by the potential func-

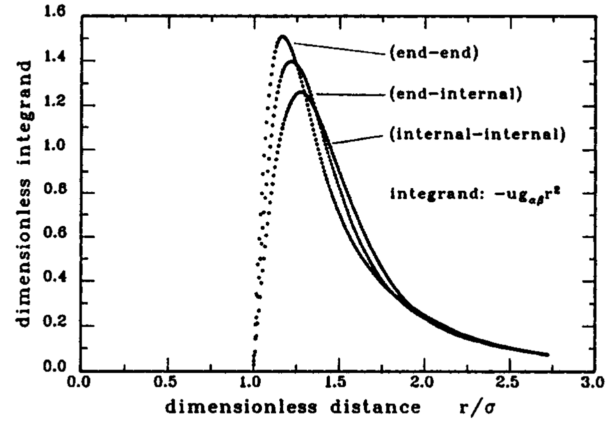

Figure 3. The integrand $\tilde{u}g_{\alpha\beta}\tilde{r}^2$ for the butane-like molecule at $kT/4\epsilon=1.725$ and $\tilde{\rho}=0.324$.

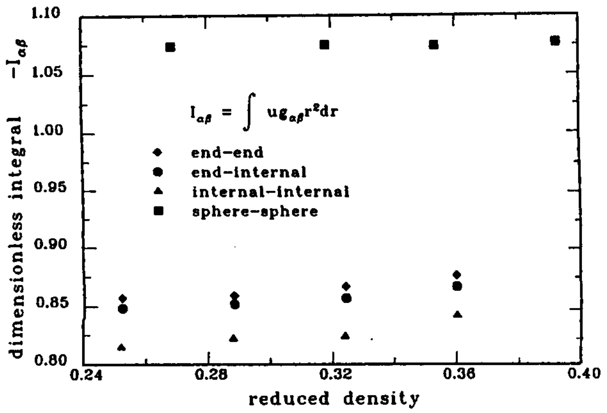

Figure 4. The site-site integrals for the butane-like molecule calculated using Molecular Dynamics simulations at $kT/4\epsilon = 1.725$.

For comparison the integral for the methane-like molecule at $kT/\epsilon = 1.725$ is also shown.

tion kills off the structural detail of the pair correlation function except at close distances. Figure 4 shows results for these integrals, which are obtained by numerical integration, as a function of density for the butane-like (4-site) and the methane-like (spherical) molecules. The integral for methane is numerically greater than that for the site-site interactions in butane. Note also that at liquid-like densities, each of the integrals has roughly the same density dependence, which suggests that a parameter $q_{\alpha\beta}$ can be used to collapse the curves into a single curve as suggested by Eq. 6.

Summary and Conclusions

The approximation evaluated here has certain appealing features. More work needs to be done in evaluating its generality and in evaluating the extent to which $q_{\alpha\beta}$ can be calculated from simple geometrical considerations, to obtain the simplification that the integral need be evaluated only once for some reference pair. At this point the choice of the universal integral I is arbitrary. Walsh et al. (1991) have used the parameter q as the ratio of the configurational integral for a site-site interaction to that for the reference hard-sphere fluid, and have used this approximation to accurately correlate the thermodynamic behavior of complex molecules. By evaluating q from simulations or geometric considerations, the model of Walsh et al. (1991) can be used to *predict* thermodynamic properties.

Acknowledgment

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