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MOLECULAR THERMODYNAMICS OF FLEXIBLE-MOLECULE FLUIDS *

EMMERICH WILHELM
Institut für Physikalische Chemie, Universität Wien,
Währingerstraße 42, A-1090 Wien, Austria

ABSTRACT

Some of the most important problems encountered in the statistical-mechanical treatment of dense, complex molecular fluids are indicated. Particular attention is given to the application of the generalized van der Waals concept to flexible-molecule fluids. Perturbed-hard-chain theory and chain-of-rotators theory are reviewed. This is followed by a brief summary of recent experimental work on thermodynamic excess properties of liquid mixtures of type (Y + an n-alkane). Several novel effects connected with local correlation of molecular orientation in the n-alkanes, with medium-induced conformational changes and with preferential orientation of strongly polar molecules are discussed (order/disorder phenomena).

1. INTRODUCTION

During the past decade, considerable progress has been made in the theory of dense pure fluids and fluid mixtures of nonelectrolytes[1-15], with a concomitant shift of emphasis from simple to more complex, molecular fluids. Prediction of thermodynamic equilibrium quantities from molecular properties of the constituent molecules, through application of appropriate statistical-mechanical model theories, is certainly a fascinating topic from the purely scientific point of view. It has, however, also many important practical applications. For instance, in the design of efficient and economical separation operations and manufacture of chemical products quantitative thermodynamic information on reactants and products is an indispensable requirement. Since life cannot exist without water, studies of aqueous solutions of simple molecules, such as the rare gases and hydrocarbons, hold a prominent position in biophysics. Such model studies provide information on hydrophobic effects, which are thought to be of importance in complex biological processes[16-18].

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If one had to name the single, most important physical concept associated with the evolution of ideas, most likely it would be the *generalized* van der Waals (GVDW) point of view of simple, dense fluids. For such fluids, that is to say for fluids composed of molecules interacting through spherically symmetric potentials, this concept presumes that the *repulsive* (hard) interactions by far dominate the *structure*, while contributions due to attractive interactions are nearly negligible[19]. In other words, the structure of a simple liquid should resemble by and large that of the corresponding hard-sphere fluid. The majority of the modern statistical-mechanical theories of the liquid state have assimilated this idea and have used the hard-sphere (HS) model fluid as a stepping stone towards the treatment of liquids with more realistic interparticle potentials. For a mixture, of course one has to start with the appropriate mixture of hard spheres of *different diameter.*

A realistic spherical pair potential differs from the HS potential in two aspects: first, it is *attractive* for large separations, and second, it is *not* infinitely steep at short separations. This leads directly to various versions of thermodynamic perturbation theory, whereby the Helmholtz free energy F of the realistic system (with number density $\rho = N/V$) is obtained by a perturbation expansion around a suitably selected reference system, say around the HS reference system with F_{HS}:

$$F = F_{HS} + \frac{\rho^2 V}{2}\int_0^\infty u_1(r) g_{HS}(r) 4\pi r^2 dr + \cdots \qquad (1)$$

Here we have assumed that the potential energy is pair-wise additive and that the pair potential is of the form $u(r) = u_{HS} + u_1(r)$, where $u_1(r)$ is the attractive perturbation contribution. The pair distribution function $g_{HS}(r)$ refers to the HS system. Substantial improvement results when the HS system is replaced by one whose constituent particles interact only through a repulsive but not infinitely steep potential (soft spheres)[2]. Perhaps the most successful approach is due to Weeks, Chandles and Anderson[20]. The WCA decomposition of the Lennard-Jones potential

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (2)$$

is shown in Fig.1: u(r) is separated into a part $u_0(r)$ representing the repulsive forces, and into a part $u_1(r)$ representing the attractive forces (which provide a relatively smooth background potential at high densities; see Kohler, Wilhelm and Posch[2]).

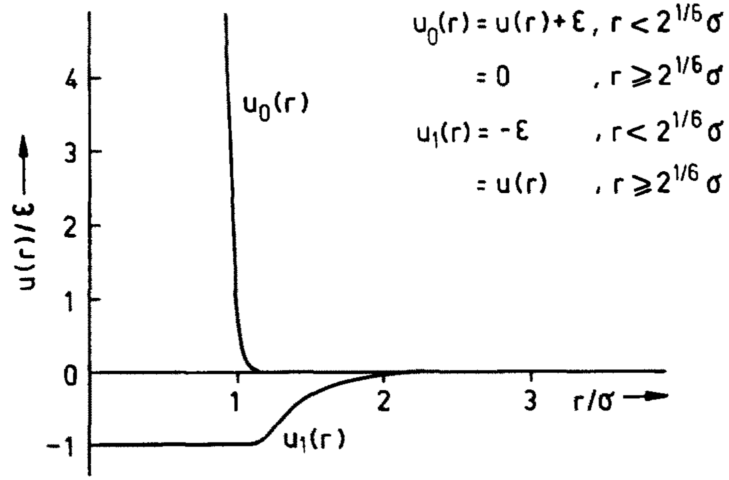

Fig. 1. WCA decomposition of the Lennard-Jones (12,6) potential, u(r), into a part representing all the repulsive forces, $u_0(r)$, and a part representing all the attractive forces, $u_1(r)$. After Weeks, Chandler and Andersen, ref. 20.

The next step concerns the incorporation of nonspherical *shape* into the formalism. Two requirements have to be met by any reference fluid. First of all, its properties should be accurately known, and second its structure (i.e. the pair correlation function) should resemble as close as possible that of the real fluid. No truly satisfactory general approach for nonspherical fluids is as yet available.

Relinquishing the second requirement, two different choices of *spherical* reference potentials have been proposed. One was introduced by Barker[21] and Pople[22], see also Stell[23]. These authors separate the pair potential into an isotropic, effective reference part defined by

$$u_0(r) \equiv \langle u(\vec{r},\omega_1,\omega_2)\rangle_{\omega_1,\omega_2} \tag{3}$$

and an anisotropic perturbation part, which may be expressed as the sum of electrostatic terms, induction terms and so forth. Here, $u(\vec{r},\omega_1,\omega_2)$ is the full pair potential for the fluid of interest, and ω_i indicates the relative orientation of molecule i. This approach has been extended to mixtures, notably by Gubbins and collaborators[13]. The other choice defines the effective reference potential by

$$\exp\left[-u_0(r)/k_BT\right] \equiv \left\langle \exp\left[-u(\vec{r},\omega_1,\omega_2)/k_BT\right]\right\rangle_{\omega_1,\omega_2} , \quad (4)$$

where k_B is Boltzmann's constant, and T is the temperature. This RAM (reference average Mayer-function) expansion was introduced by Perram and White[24].

A considerable part of recent research activity has been directed towards establishing convenient *nonspherical* reference systems. They should bring about a much faster convergence of the free energy perturbation expansion. Reliable equations are now at hand for thermodynamic properties of a variety of hard convex body fluids, such as hard dumbbells or spherocylinders, as well as for the corresponding site-site correlation functions used in interaction-site model (ISM) theories. Work along these lines is illustrated by refs. 25-31.

The next "turn of the screw" is brought about by the *flexibility* of most of the real molecules, which results from the existence of two or more energetically and kinetically easily accessible molecular conformations. Typical examples are the n-alkanes n-$C_\ell H_{2\ell+2}$, with n-butane (ℓ=4) being the first member of this series showing *trans-gauche* equilibrium (Fig.2).

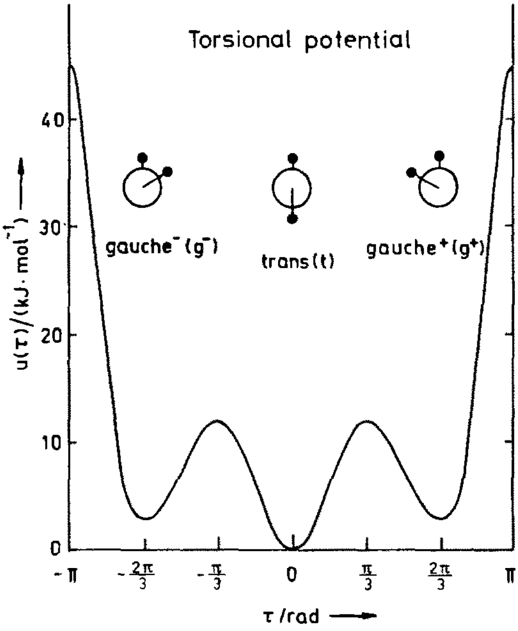

Fig. 2. Torsional potential u(τ) as function of dihedral angle τ for n-butane[32], eq. 21: u_0/k_B = 1116 K, u_1/k_B = 1462 K, u_2/k_B = -1578 K, u_3/k_B = -368 K, u_4/k_B = 3156 K, u_5/k_B = -3788 K. Thus, $u(2\pi/3) - u(0) = \Delta u_{gt}$ = 2.93 kJ/mol.

Incorporation of this molecular aspect into a rigorous statistical-mechanical theory of fluids is much less advanced. A *fortiori* this is the case for *associated*, i.e. hydrogen-bonded liquids (and solutions), such as the alcohols. Fig.3 summarizes schematically the most important aspects to be considered in the description of pure liquids and liquid mixtures on the molecular level as well as on the bulk level. The principal obstacles for treating reasonably complex fluids of practical, that is to say chemical engineering, interest are:

(a) uncertainty about the appropriate *intermolecular potential* and, in the case of mixtures, insufficient knowledge about the potential between unlike molecules (combining-rules)[11,33];

(b) the difficulties encountered when two or more of the characteristic molecular aspects, say shape anisotropy and a permanent electric multipole moment, are present simultaneously[34];

(c) our meager knowledge of *many-body effects*, for instance many-body induction effects[35,36], correlation of molecular orientation (CMO)[14,37-39], and solvent effects upon conformational equilibria[39,40].

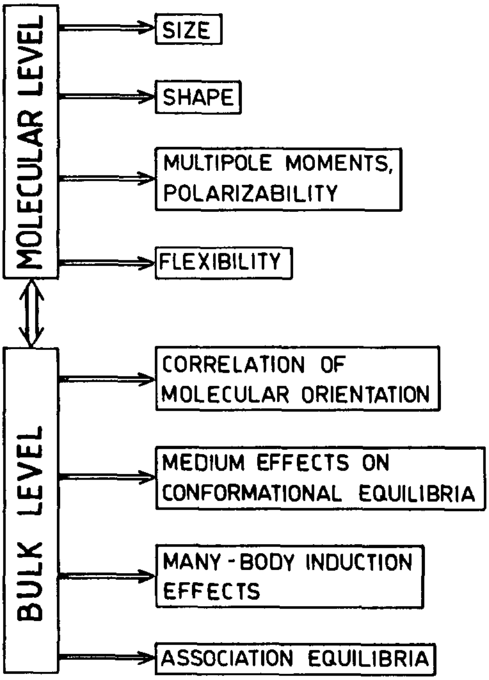

Fig. 3. Some important aspects for the description of fluids on the molecular and the bulk level (schematic).

The thermodynamic properties of pure liquids and liquid mixtures can be completely described by means of formal thermodynamics and an adequate equation of state (EOS). Ideally, the latter should be derived from a detailed, realistic description on the molecular level. As indicated above, for most liquids and liquid mixtures of practical importance this is not feasible. Thus while the link between intermolecular forces on the one side and macroscopic, measurable quantities on the other should be emphasized, this link will become by necessity the more empirical the more complex the system. Against this background several recent theoretical as well as experimental advances will be reviewed. Predominantly this article will be concerned with GVDW-based approaches applied to fluids of flexible organic molecules, that is to say to molecules exhibiting conformational equilibria of the kind found in n-alkanes and their derivatives. Alternative contributions, such as those based on the KGB (Kehiaian-Guggenheim-Barker)[15,41] or PFP (Prigogine-Flory-Patterson)[14,42-44] theory, will be discussed only briefly. These topics have been comprehensively reviewed recently in refs. 14, 15 and 38.

2. REVIEW OF GVDW THEORY[45,46]

A convenient statistical-mechanical starting point for a discussion of liquid-state properties is the canonical partition function $Q_N(T,V,N)$ for N molecules contained in a volume V. The link with thermodynamics is established through

$$F(T,V,N) = -k_B T \ln Q_N(T,V,N) \quad , \tag{5}$$

whence all thermodynamic quantities may be obtained by appropriate differentiation with respect to T, V or N. In particular, the EOS follows from

$$P = k_B T \left(\frac{\partial \ln Q_N}{\partial V} \right)_{T,N} \quad . \tag{6}$$

For a pure, reasonably simple fluid where to a good approximation the center-of-mass degrees of freedom (translation) are separable from the vibrational and rotational degrees of freedom

$$Q_N(T,V,N) = (N!)^{-1} \Lambda^{-3N} (q_r q_v q_e)^N Z_N(T,V,N) \quad . \tag{7}$$

Here, $\Lambda = (h^2/2\pi m k_B T)^{1/2}$ is the de Broglie wavelength associated with a molecule of mass m, h is Planck's constant, q_r, q_v and q_e are the molecular rotational, vibrational and electronic partition functions, respectively, and

$$Z_N(T,V,N) = \int \cdots \int \exp\left[-U_N(\vec{r}_1, \ldots, \vec{r}_N)/k_BT\right] d\vec{r}_1 \cdots d\vec{r}_N \tag{8}$$

is the configuration integral. For noncentral interactions the total potential energy U_N is also a function of the relative orientations of the molecules, and the integrals in eq. 8 have then to be modified accordingly.

When adopting the essential idea of the GVDW model of dense fluids[46], that is to say hard spheres embedded in an uniform negative background potential, eq. 7 transforms to

$$Q_N(T,V,N) = (N!)^{-1}(V_f/\Lambda^3)^N (q_r q_v q_e)^N \left[\exp\left(-\frac{\phi(T,V,N)}{2k_BT}\right)\right]^N , \tag{9}$$

where ϕ is the *mean potential*, and V_f is the *free volume* available to the center-of-mass motion of a single molecule: it accounts for hard-core molecular repulsion.

The generalized van der Waals partition function, eq. 9, is readily extended to mixtures yielding

$$Q_N(T,V,\{N_i\}) = \prod_i \left[N_i! \Lambda_i^{3N_i} (q_{r,i} q_{v,i} q_{e,i})^{-N_i}\right]^{-1} V_f^N(T,V,\{N_i\}) \times \left[\exp\left(-\frac{\phi(T,V,\{N_i\})}{2k_BT}\right)\right]^N , \tag{10}$$

where N_i denotes the number of molecules of component i, and $N = \sum N_i$.

3. APPLICATION TO FLEXIBLE-CHAIN FLUIDS

Evidently, the approximations indicated in eq. 7 may lead to significant errors for polyatomic liquids due to *density dependence* of some rotational and vibrational modes of molecular motion. A reasonable approximation, essentially due to Prigogine[42], is to assume that the rotational and vibrational partition functions may be factored into an external part, depending on temperature as well as on density, and an internal part, depending only on temperature[11]:

$$q_r q_v = (q_r q_v)_{int} \times (q_r q_v)_{ext} \ . \tag{11}$$

Further, the additional approximation may be made that the external contributions can be treated as equivalent to those from translational motions[47,48], viz.

$$(q_r q_v)_{ext} = \left[\frac{V_f}{V} \exp\left(-\frac{\phi}{2k_BT}\right)\right]^{c-1} , \tag{12}$$

where 3c is the number of *external* degrees of freedom per molecule. For simple, spherical molecules such as argon (or perhaps methane), c=1, whereas c > 1 for all other molecules. Thus for long-chain molecules, such as the n-alkanes, the parameter c reflects to a large extent their flexibility.

The PHC partition function for a polyatomic pure fluid is thus

$$Q_N(\mathrm{PHC}) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \left[\frac{V_f}{V} \exp\left(-\frac{\phi}{2k_BT}\right)\right]^{Nc} q(T)^N , \tag{13a}$$

$$q(T) = (q_r q_v)_{int}\, q_e \ . \tag{13b}$$

For spherical hard particles, the free volume is accurately described by an expression derived[49] from the Carnahan-Starling equation[50]

$$V_f/V = \exp\left[-\frac{4\eta - 3\eta^2}{(1-\eta)^2}\right] , \tag{14}$$

where $\eta = \pi\rho\sigma^3/6$ with σ being the hard-sphere diameter. Prausnitz et al.[47,48], in their perturbed-hard-chain (PHC) theory, used the form of eq. 14 in conjunction with a *redefined* η , that is to say

$$\eta = \frac{\pi\sqrt{2}\,V_m^{0*}}{6V_m} = r\pi\rho\sigma^3/6 , \tag{15}$$

where V_m is the molar volume, $V_m^{0*} = N_A r\sigma^3/\sqrt{2}$ is the molar close-packed volume, r is the number of segments per molecule (r= 1 for a CH_2-segment), σ is the hard-core diameter per segment, $\rho = N_A/V_m$ is the number density of chains, and N_A is Avogadro's constant.

To account for molecular attractions, Alder's molecular dynamics results for the square-well fluid[51] were adopted for the mean potential, that is to say

$$\frac{\phi}{2k_BT} = \sum_n \sum_m \frac{A_{n,m}}{\tilde{T}^n \tilde{V}^m} , \tag{16}$$

with $\tilde{T} = T/T^* = ck_BT/\varepsilon^*q$, and $\tilde{V} = V_m/V_m^{0*} = \sqrt{2}/\rho r\sigma^3$ (ε^* is the interaction energy per unit area, and q is the molecular surface area). Insertion of eqs. 13,14 and 16 into eq. 6 yields the PHC equation of state in the GVDW form,

$$Z = PV_m/N_Ak_BT = Z_{HC} + Z_{ATTR}$$

$$= 1 + c\frac{4\eta - 2\eta^2}{(1-\eta)^3} - \frac{a(\tilde{T},\tilde{V})}{N_Ak_BTV_m} , \qquad (17)$$

where $a(\tilde{T},\tilde{V})$ is obtained by means of the square-well potential coefficients of eq. 16. The subscript HC indicates hard chains, and ATTR is for the attraction term. For hard spheres (c=1), Z_{HC} becomes identical with the Carnahan-Starling expression[50] for Z_{HS}. In order to improve agreement with experimental virial coefficients, an essentially empirical term was added to the partition function[48,52]. Eq. 17 has five independent parameters. For the calculation of pure-fluid properties only three are necessary: $T^* = \varepsilon^*q/ck_B$, V_m^{0*} and c. For about 45 common fluids ranging from ethane to eicosane, squalane and bicyclohexyl, these parameters were obtained from experimental vapor-pressure and PVT data. We note that (a) for a normal fluid the parameter c increases smoothly with the acentric factor, and (b) V_m^{0*} is closely related to the van der Waals volume V_{VDW} calculated from Bondi's group-contribution method[53].

Another approach, similar in spirit to the one just presented, is due to Chien, Greenkorn and Chao[54]. The *rotational* contributions of chain molecules to the *configurational* properties are explicitely introduced, resulting in the chain-of-rotators (COR) equation of state. Specifically, the EOS of hard dumbbells (i.e. chain molecules with two segments) as obtained by Boublik and Nezbeda[55] from computer simulations,

$$Z_{HD} = 1 + \frac{(3\alpha + 1)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1-\alpha^2)\eta^3}{(1-\eta)^3} , \qquad (18)$$

is used to obtain the external rotational partition function of a chain molecule. The quantity α is defined by

$$\alpha = \frac{(1 + l/\sigma)(2 + l/\sigma)}{2 + 3l/\sigma - (l/\sigma)^3} \quad \text{for } l/\sigma < 1 , \qquad (19)$$

where ℓ is the center-to-center distance and σ is the diameter of the constituent spheres of the dumbbell. Eq. 18 was used by Kohler et al.[25] and Fischer[26] in their perturbation theory for diatomics. The complete configurational partition function is obtained as

$$Q_{\mathrm{conf}}(\mathrm{COR}) = \frac{V^N}{N!}\left(\frac{V_f}{V}\right)^N \left\{\left(\frac{1}{1-\eta}\right)^{\alpha^2-1} \exp\left[-\frac{(\alpha^2+3\alpha-4)\eta-3\eta^2(\alpha-1)}{(1-\eta)^2}\right]\right\}^{Nc/2}$$

$$\times \exp\left\{-N\left[1+\frac{c}{2}\left(B_0+B_1\tilde{T}^{-1}+B_2\tilde{T}\right)\right]\sum_n\sum_m \frac{A_{n,m}}{\tilde{T}^n\tilde{V}^m}\right\} . \quad (20)$$

As before the flexibility of the chain is characterized by the parameter c, the free volume term V_f/V is again given by eq. 14 and the attractive term is similar to those used by Chen and Kreglewski[56] and Prausnitz[47,48], respectively. We note that in the limit of zero density the rotational contribution to the compression factor, Z_r, of elementary rotators approaches zero, it remains insignificant for the dilute gas state and increases rapidly only at high density.

Both the PHC and the COR equation use three characteristic parameters for each substance. For relatively simple fluids both equations perform equally well for vapor pressures, while the COR equation gives better liquid and vapor densities. With increasing chemical complexity of the molecules, the COR equation becomes superior to the PHC equation in all properties: the accuracy of calculated properties is improved, roughly by a factor of two.

PHC and COR theory have been extended to mixtures. Though no details will be presented here, a few remarks concerning the mixing rules for the characteristic parameters are indicated. As usual, they have a certain empirical flavor. For instance, in order to relate the mixture energy parameter to the pure-fluid values, the COR model uses the van der Waals one-fluid prescription in conjunction with a binary interaction parameter, which has to be determined from experimental data. Perhaps least satisfactory is the use of a linear additivity rule for the flexibility parameter, $c_{\mathrm{mix}} = \sum x_i c_i$. As indicated by the results presented below on mixtures containing n-alkanes, there is strong evidence that c_{mix} may deviate appreciably from this rule.

A promising route towards a quantitative understanding of solvent-induced changes of conformational equilibria is presented in ref. 12. Based on perturbation theory, it utilizes the semiempirical hard-convex-body (HCB) EOS of Boublik[55]. Specifically, a model for n-butane is discussed with rigid C-C bonds and fixed bond angles; the conformational equilibrium is characterized by the Scott-Scheraga potential[32] (see Fig.2)

$$u(\tau) = \sum_{i=0}^{5} u_i \cos^i\tau \quad (21)$$

for a single n-butane molecule in the absence of intermolecular interactions (τ is the dihedral angle). This type of semiempirical potential has been extensively used in computer simulation studies of model n-alkanes[57-59]. In the dense fluid state $u(\tau)$ has to be augmented by a contribution due to the influence of *all* the adjacent particles; in other words, a potential of mean torsion is introduced,

$$w(\tau) = u(\tau) + t(\tau,\rho) \ . \tag{22}$$

The corresponding normalized conformational distribution function is

$$p(\tau) = \frac{\exp\left[-w(\tau)/k_B T\right]}{\int_{-\pi}^{\pi} \exp\left[-w(\tau)/k_B T\right] d\tau} \tag{23}$$

Since $\lim_{\rho\to 0}[t(\tau,\rho)] = 0$, for vanishingly small densities $p(\tau)$ approaches the perfect-gas state distribution function.

By treating a fluid of flexible molecules as a mixture of *formally* rigid conformers with variable composition, the link with perturbation theory is established. The thermodynamic properties of the hard-core reference fluid may be evaluated from a suitable HCB EOS[55] using generalized shape functions. For instance, the generalized volume is now

$$\langle \hat{V} \rangle = \sum_i x_{i,\mathrm{solvent}} \hat{V}_i + x_{n\text{-}C_4H_{10}} \int_{-\pi}^{\pi} p(\tau)\, \hat{V}(\tau)\, d\tau \ , \tag{24}$$

with corresponding expressions for the surface area and the mean curvature integral. Here, x denotes the mole fraction, and $\hat{V}(\tau)$ represents the molecular volume of a τ-conformer. We note, that in this approach the frequently invoked rotational-isomeric-state approximation is *not* used. In fact, the population in the *trans* and *gauche* states is now defined by

$$x_t \equiv \int_{-\pi/3}^{\pi/3} p(\tau)\, d\tau \qquad \text{and} \qquad x_g = 1 - x_t \ . \tag{25}$$

Results obtained so far on pure liquid n-butane and n-butane dissolved in tetrachloromethane appear to be at least as accurate as those obtained from the Chandler-Pratt theory[60,61]. For instance, the ratio x_g/x_t at 291.5 K is predicted to shift from 0.52 for the perfect-gas state to 0.80 for liquid n-C_4H_{10}, which is in very good agreement with the computer simulation data of Ryckaert and Bellemans[57], and Rebertus, Berne and Chandler[58]. However, no condensed-phase effects on the conformer population of pure n-butane were found by Jorgensen et al.[62,63] in their recent Monte Carlo simulations.

We conclude this section with a few remarks on the theory developed by Flory[43], which yields the well-known reduced EOS (in GVDW form)

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3}-1} - \frac{1}{\tilde{T}\tilde{V}} \, , \tag{26}$$

where all the quantities have their usual meaning. When applied to dense liquids, this equation is remarkably successful. However, at low densities it gives incorrect results and does *not* approach the perfect gas law. Specifically, with $P = P/P^* = PV^*_m/cRT$ the hard term, i.e. the first term on the *ℓhs* of eq. 26, is seen to be

$$Z_{H,FL} = \frac{c}{1-\eta^{1/3}} \; . \tag{27}$$

Here 3c denotes again some effective number of external degrees of freedom per molecule, and $\eta = V^*_m/V_m$ with V^*_m signifying the hard-core volume of N_A molecules. For hard spheres, $V^*_m = \pi\sqrt{2}V^{0*}_m/6 = 0.74048 \cdot V^{0*}_m$.

4. ORDER/DISORDER EFFECTS IN LIQUID MIXTURES (Y + AN n-ALKANE)

The influence of the molecular environment on conformational equilibria and hence on thermodynamic properties as well as on dynamic properties and chemical reaction rates is well documented[64,65]. Under isothermal conditions, the population of the various conformational states may be altered by changes of *density* as well as by *admixture* of another substance. Consequently, in mixtures of type (Y + an n-alkane) the shape and hence the size of the n-alkane (n-$C_\ell H_{2\ell+2}$), as characterized by the mean-square end-to-end distance, will depend on composition.

Traditional treatments of solvent-mediated shifts of conformational equilibria have focussed upon the dielectric energetics of changing low-order electric moments of flexible molecules, such as 1,2-dichloroethane. Qualitatively, the maxim applied that the more polar conformer will be stabilized in more polar media. While electrostatic aspects are undoubtedly important, the role of steric or packing effects in dense liquids has only been recently fully appreciated, in particular through the theoretical work of Chandler, Pratt and collaborators[60,61,66], see also above.

During the last decade, increasing effort has been invested in systematic experimental work on thermodynamic properties of mixtures of type (Y + an n-alkane)[10,14,15,38,39]. For a given substance Y, the focus has usually been upon the dependence of the principal thermodynamic excess quantities, such as excess molar enthalpy H_m^E, excess molar heat capacity $C_{P,m}^E$, excess molar volume V_m^E etc., either on the chain length ℓ of the n-alkane or on temperature, and has subsequently led to the detection of new effects[14,37-39,67]. These effects have been tentatively discussed in terms of destruction or creation of order, usually in conjunction with solute-induced conformational changes, all with respect to the situation existing in the pure liquid n-alkane. This kind of experimental studies is illustrated by our recent work on (a haloaromatic + an n-alkane)[68], see Figs. 4,5 and 6.

In general, order phenomena have been discussed in terms of deviations of observed excess quantities, say H_m^E and $C_{P,m}^E$,from predictions of reliable theories, such as the PFP theory or, with certain model-immanent restrictions, the KGB theory. In particular, the study of the ℓ-dependence and T-dependence[69] of these excess quantities has been illuminating. A lucid review of this topic has recently been presented by Patterson and collaborators[14], see also refs. 38

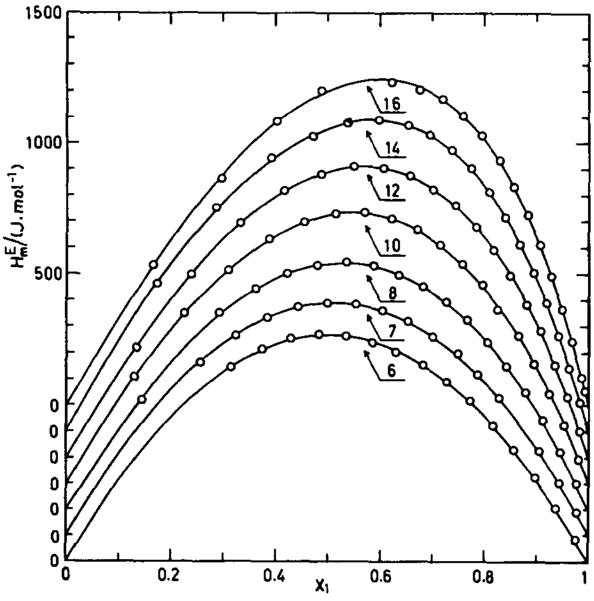

Fig. 4. Excess molar enthalpies H_m^E of $\{x_1C_6H_5F + x_2n\text{-}C_\ell H_{2\ell+2}\}$ at 298.15 K. Circles denote experimental points (ref. 68b), the numbers are values of ℓ.

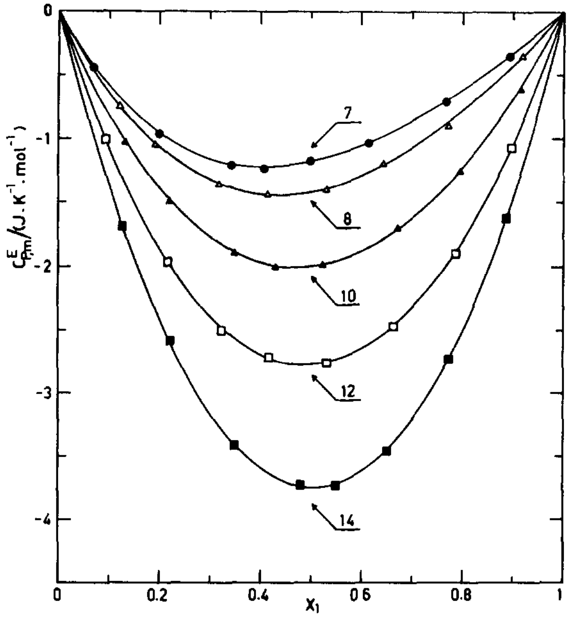

Fig. 5. Excess molar heat capacities $C^E_{P,m}$ of $\{x_1C_6H_5F + x_2n\text{-}C_\ell H_{2\ell+2}\}$ at 298.15 K. Experimental results are from ref. 68b, the numbers are values of ℓ.

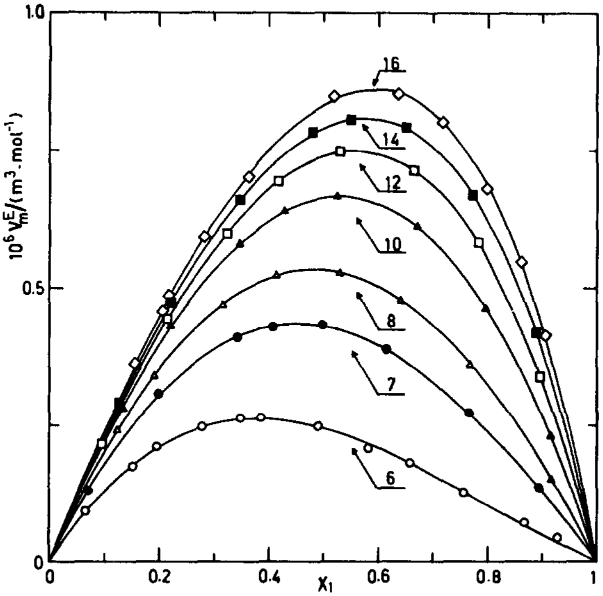

Fig. 6. Excess molar volumes V^E_m of $\{x_1C_6H_5F + x_2n\text{-}C_\ell H_{2\ell+2}\}$ at 298.15 K. Experimental results are from ref. 68b, the number are values of ℓ.

and 39. Thus, only a brief summary of the salient points will be given here.

If Y is a more or less globular molecule (e.g. $CC\ell_4$), mixing with an n-alkane of sufficient chain length and sufficiently high density will cause a net destruction of the (short-range) correlation of molecular orientation (CMO) presumed to exist in the pure hydrocarbon. It will manifest itself by positive contributions to H^E_m and S^E_m , and negative contributions to $C^E_{P,m}$ and $\partial V^E_m/\partial T$. Since the CMO increases with increasing ℓ, at a given temperature the magnitude of these contributions is expected to increase with chain length. A semiquantitative measure of this effect is provided, for instance, by the increase of the Flory interaction parameter X_{12} with ℓ, or alternatively, by the increase of the KGB interaction parameter h_{12} with ℓ.

According to Bendler's[70] fluctuation theory of enhanced segmental orientational order in liquid n-alkanes, the variation of (CMO) order with temperature should be analogous to that of the isotropic phase of liquid crystals. Specifically, for the *positive* enthalpic contribution due to the destruction of CMO

$$H^E_m(\mathrm{CMO}) \sim X_{12}(\mathrm{CMO}) \sim N_0 k_B T \left(\frac{T_0}{T - T_0}\right) \tag{28}$$

is obtained, where N_0 is the number of modes of fluctuation which are thermally excited, and T_0 is an ordering temperature lying somewhat below the n-alkane melting point. A similar expression was derived by Heintz and Lichtenthaler[38,71].

If Y is a sufficiently anisotropic plate-like molecule, such as 1,2,4-trichlorobenzene[67] or 1-chloronaphthalene[68a], substantial *negative* contributions to H^E_m have been observed, and frequently H^E_m decreases with increasing ℓ. Tentatively, these results have been discussed in terms of creation of order of some sort in these mixtures[39] (intra- *and* intermolecular ordering). The corresponding decrease of X_{12}, or h_{12}, with increasing ℓ may be used to estimate the negative contribution due to order creation. Consistent with this hypothesis are the experimental $C^E_{P,m}$ data. For example, $C^E_{P,m}$ for (1-chloronapthalene + an n-alkane) at 298.15 K is positive for $\ell \geqslant 6$, and increases up to $\ell \approx 11$; for larger chain lengths $C^E_{P,m}$ decreases slightly.

Perhaps one of the most interesting results obtained recently is the highly unusual composition dependence of $C^E_{P,m}$ in the series (1,4-dioxane + an n-alkane)[72] and (an α,ω-dichloroalkane + an n-alkane)[73], see Fig.7. At present only a few other systems are known to show such W-shaped $C^E_{P,m}(x)$ curves[74-76]. Tentative interpretations communicated so far, consider significant preferential orientation between strongly polar molecules (molecular species) in conjunction with conformational changes. However, their exploratory character should be kept in mind.

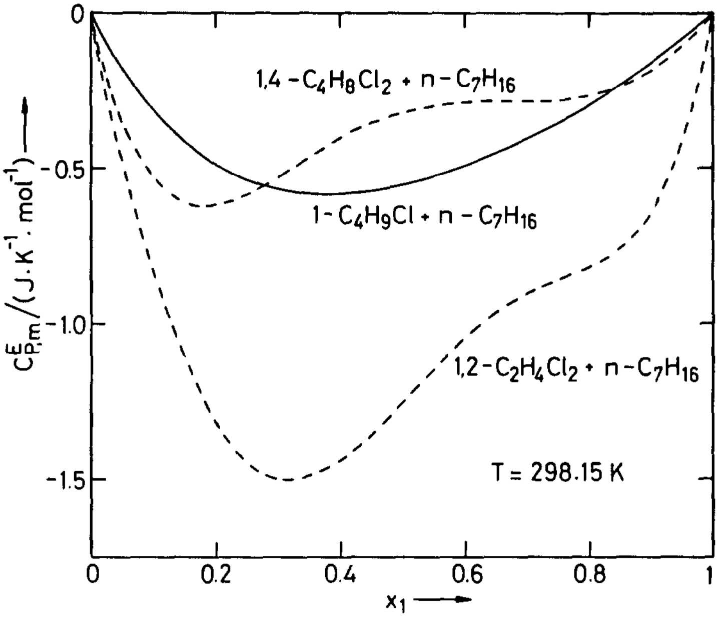

Fig. 7. Excess molar heat capacities $C^E_{P,m}$ of three mixtures of type (a haloalkane + an n-alkane)[73] at 298.15 K; x_1 is the mole fraction of the haloalkane.

5. CONCLUDING REMARKS

In this review we have endeavored to cover the main areas of current theoretical as well as experimental research on flexible-molecule fluids, pure and mixed. Through our discussion of the GVDW approach the importance of the flexibility parameter c has been demonstrated. In fact, this concept is responsible for the remarkable success of the PFP theory when applied to dense fluid mixtures containing polyatomic molecules, despite the unsatisfactory hard term in the EOS. This aspect is further illustrated by the successful use of the PFP theory, in a corresponding-states formulation, to interpret and predict excess volumes[14,77,78]. It may therefore serve as a "base-line" theory against which special effects can be discerned and discussed.

There remains, of course, the question whether any manageable model theory can comprehensively cover all aspects of flexible-molecule fluids with reasonable precision. While efforts of the kind presented in ref. 12 or in refs. 60, 61 and 66 are of the highest value for our understanding of the underlying physics, the possibility of their extension to treat quantitatively more complex systems remains to be demonstrated.

Results on aqueous solutions of flexible molecules have not been considered at all in this review. In recent years this field has advanced rapidly[10,11, 16-18,79,80], with the momentum for this progress coming from both the increasing interest in biophysics, biochemistry and biotechnology as well as from the technological advances in thermodynamic instrumentation. Undoubtedly, this progress has stimulated convergence of ideas, a process which, hopefully, will continue.

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