

Trends in the equilibrium theory of polyatomic fluids

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Abstract. The thermodynamics of polyatomic fluids is determined by the interactions between the polyatomic particles subject to the constraints imposed by the bonding within the polyatomic structure. One aspect of this work is the determination of the intermolecular potential function and the other is the calculation of multipoint correlation functions based on these potential functions. Trends in the calculation of these multipoint correlation functions are discussed and a semiempirical method of obtaining effective interactions is applied to the thermodynamics of fatty acid mixtures at the air/water interface.

Keywords. Correlation functions; interaction sites; effective diameters.

1. Introduction

The equilibrium structure of liquids is most conveniently described in terms of interparticle correlation functions (Percus 1964; Friedman 1985). In monatomic liquids, the atom-atom pair distribution function $g(r_{12})$ [or $g(12)$ or $g(r)$ or simply g] plays a central role and most thermodynamic quantities can be expressed as functionals of $g(r)$. Here $r_{12} = r = 12$ is the separation between particles 1 and 2. If one particle is held at the origin of a reference coordinate frame, the value of $g(r)$ at a distance r from the origin is the ratio of the local density at r and the bulk system density. The fluctuations in density appear as damped oscillations in $g(r)$. At large values of r , the influence of the particle at the origin diminishes and $g(r)$ approaches unity. The total correlation function $h(r) = g(r) - 1$ is related to the direct correlation function $c(r)$ through the Ornstein-Zernicke relation (1) which may be iterated as shown in (2)

$$h(12) = c(12) + \rho \int c(13)h(32) d3 = c(12) + \rho c * h, \quad (1)$$

$$= c(12) + \rho \int c(13)c(32) d3 + \rho^2 \int c(13)c(34)c(42) d3 d4 + \dots \quad (2)$$

The number density of particles is given by ρ , the integration variable is the coordinate of particle 3 and the convolution integral in (1) over the connecting coordinate is denoted by $*$.

By a graphical analysis $c(12)$ can be shown to be a sum of diagrams of the type shown in (3),

$$c(12) = \text{graph 1} + \text{graph 2} + \text{graph 3} + \text{graph 4} + \dots \quad (3)$$

Here, the white or unshaded circles represent coordinates 1 and 2 which are held fixed and a black circle represents multiplication by ρ and integration with respect to a position variable. A line connecting the circles is the Mayer f bond defined as $f(12) = \exp[-u(12)/k_B T] - 1$, where $u(12)$ is the pair potential between particles 1 and 2; k_B , the Boltzmann constant; and T , the system temperature. The sum in (3) is over all graphs which are at least doubly connected (except for the first one) i.e. wherein there are at least two independent paths connecting any pair of circles. The function $f(12)$ decays to zero at large r as $u(12)$ goes to zero. Since $c(12)$ is a collection of highly connected graphs, $c(12)$, is a more short ranged function (for non-ionic systems) than $h(12)$ and so it is a good function to be approximated by, e.g. the first few terms of (3). Some common approximations are the Percus-Yevick (PY), (4), and the hypernetted chain (HNC), (5), approximations for c .

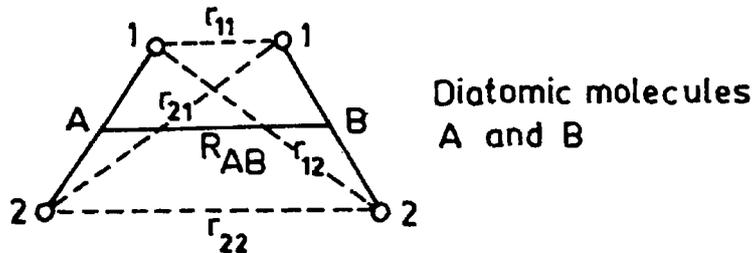
$$c = [\exp(-\beta u) - 1](1 + h - c), \quad (\text{PY}), \quad (4)$$

$$c = \exp(-\beta u - h - c) - h + c - 1. \quad (\text{HNC}), \quad (5)$$

Integral equations such as the ones shown above, along with perturbation theories, molecular dynamics and Monte Carlo computer simulations, form the main apparatus for the evaluation of the distribution functions and thermodynamic quantities for atomic fluids (Hansen and McDonald 1976).

In the study of molecular liquids, we need to specify the centre of mass R as well as the orientational coordinates Ω for each molecule. The pair distribution function between molecules A and B is now a functional of the potential $u(R_{AB}, \Omega_A, \Omega_B)$ where R_{AB} is the separation between the centres of mass of molecules A and B. These potentials are difficult to determine empirically or by quantum chemical calculations and it is customary to write the total pair potential as a sum of site-site interaction potentials (Chandler 1982).

$$u_{AB}(R_{AB}, \Omega_A, \Omega_B) = \sum_{\alpha A, \beta B} u_{\alpha A, \beta B}(r_{\alpha\beta}). \quad (6)$$



Here $r_{\alpha\beta}$ is the distance between site α on molecule A and site β on molecule B. These sites are normally taken as the atomic centres on molecules A and B. One of the typical forms for the site-site potential is the 12-6-1 potential defined by

$$u_{\alpha A, \beta B}(r_{\alpha\beta}) = C_{\alpha A, \beta B} r_{\alpha\beta}^{-12} - D_{\alpha A, \beta B} r_{\alpha\beta}^{-6} + q_{\alpha A} q_{\beta B} r_{\alpha\beta}^{-1}, \quad (7)$$

where C and D are the coefficients similar to the Lennard-Jones potential and $q_{\alpha A}$ and $q_{\beta B}$ are the charges on the sites α and β on molecules A and B .

The integral equation (1) for the site-site total correlation function is written as (Chandler and Anderson 1972)

$$h_{\alpha A, \beta B} = \sum_{\substack{\delta, \lambda \\ \text{(sites)}}} \omega_{\alpha A, \delta A} * c_{\delta A, \lambda B} * \omega_{\lambda B, \beta B} \\ + \sum_S \sum_{\substack{\delta, \lambda \\ \text{(sites)}}} \omega_{\alpha A, \delta A} * c_{\delta A, \lambda S} * \rho_S h_{\lambda S, \beta B}. \quad (8)$$

The total intramolecular equilibrium site-site pair correlation function is denoted by ω , ρ_S denotes the density of each species S in a multicomponent liquid and $*$ denotes the convolution integral over intermediate coordinates as in (1). The quantity ω is defined in terms of $S_{\alpha\gamma}(r)$, the equilibrium pair correlation function between distinct sites in the liquid state

$$\omega_{\alpha A, \gamma B}(r) = \delta_{\alpha\gamma} \delta(r) + (1 - \delta_{\alpha\gamma}) S_{\alpha\gamma}(r). \quad (9)$$

Here, $\delta_{\alpha\gamma}$ is the Kronecker δ and $\delta(r)$ is the Dirac delta function.

In addition to the Ornstein-Zernicke equation (8), one needs closure relations like (4) and (5) to solve for the site-site pair correlation functions. The integral equation for the interaction site models (ISM) has been solved for nonionic systems such as N_2 and CCl_4 with the PY closure (Chandler 1978) and for polar and ionic systems like HCl , Br_2 and ions in water using the HNC closure (Rosky 1985). Another approach to molecular liquids is via computer simulations, wherein care has to be taken so that the intramolecular distances have to remain constant within some tolerance during the simulation (Rychaert 1977).

In the next section a semiempirical method to describe the thermodynamics of monolayers at the air/water interface is outlined. When the interacting molecules in the molecular liquid are complex (Wiegel and Cox 1980), the methods outlined above are not very easy to apply and this necessitates the search for methods which can be readily used by the experimentalist.

2. Method and Results

In complex molecular fluids a convenient approximation is to look for orientationally averaged intermolecular potentials and then use the formalism of atomic fluids to calculate the thermodynamic quantities. The orientationally averaged or median $u_0(r)$ potential may be evaluated from

$$\int d\Omega \text{sign}[u(r, \Omega) - u_0(r)] = 0. \quad (10)$$

Here Ω denotes relative orientational coordinates between molecules A and B , the sign function takes the sign of the argument and $u(r, \Omega)$ is the true anisotropic potential. Such a procedure has worked well for simple systems like the diatomic fluid N_2 (Johnson *et al* 1984).

This procedure becomes quite tedious and has not been tested for molecules with a large number of internal degrees of freedom. In systems of dimensionality less than three, like monolayers or a one-dimensional system, the extent of averaging is considerably reduced. Now we shall analyse the role of intermolecular interactions on the thermodynamics of fatty acid monolayers at the air/water interface.

Experimental surface pressure area isotherms for a few fatty acids (curves A to D) are shown in figure 1. The isotherm calculated for a simple fluid such as a hard disk system of diameter 3.5 Å by any of the methods outlined in the introduction (in this case from the solutions of the Yvon-Born-Green equation) is also shown in the figure for comparison (curve E). The thermodynamics of even the soft core atomic systems where the interatomic potentials are continuous (such as a Lennard-Jones potential) is known to be very similar to that of curve E. The dissimilarity between the two-dimensional hard core model and the displayed experimental data is simply an indication of the dominant influence of the orientational dependence of the potential. In the semiempirical method presented here we use corresponding states or scaling ideas and define an effective size parameter σ_{eff} at a given surface pressure as:

$$\rho \sigma_{\text{eff}}^2 = \rho_R \sigma_R^2. \quad (11)$$

Here ρ_R and σ_R are the densities and diameters of the reference hard disk fluid and ρ is the density of the actual system. The effective diameters σ_{eff} for some acids as a function of density obtained from (11) are shown in figure 2 (curves A to C). This parameter is a representation of the orientational forces between the molecules. When the system density increases, the molecules on the average come closer and an increase in the extent of nonbonding interactions is represented by an increased effective diameter. It is also found that the effective diameters of bent molecular

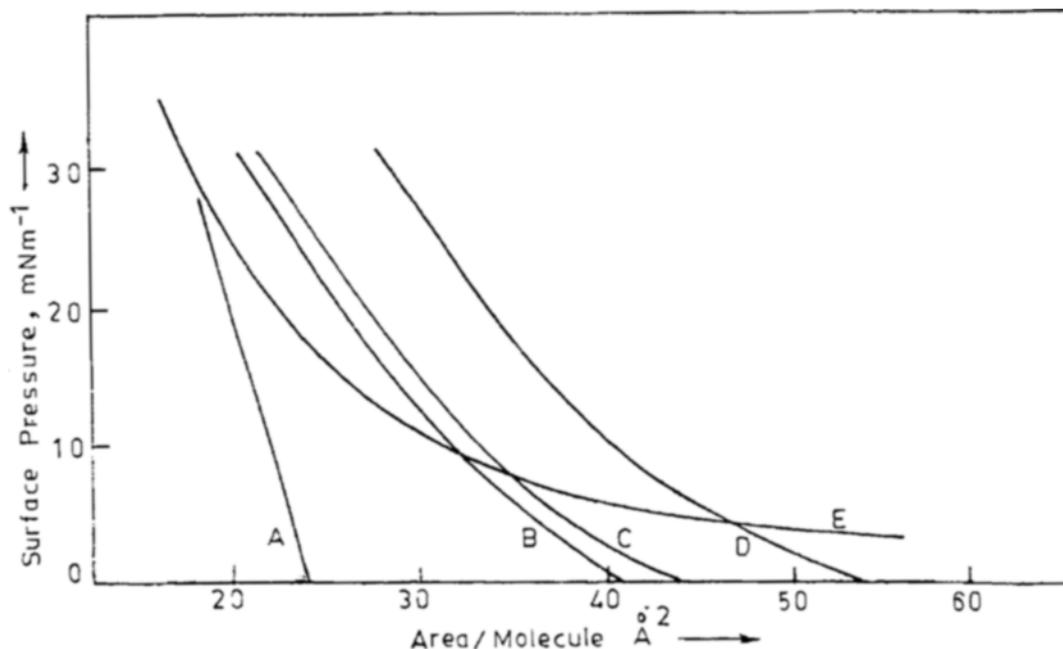


Figure 1. Pressure area isotherms for arachidic acid (curve A), oleic acid (D), 2:3 mixture of oleic and arachidic acids (B), and 52:48 mixture of oleic and arachidic acids (C). Curve E is the pressure area isotherm for hard disks with $\sigma = 3.5 \text{ \AA}$.

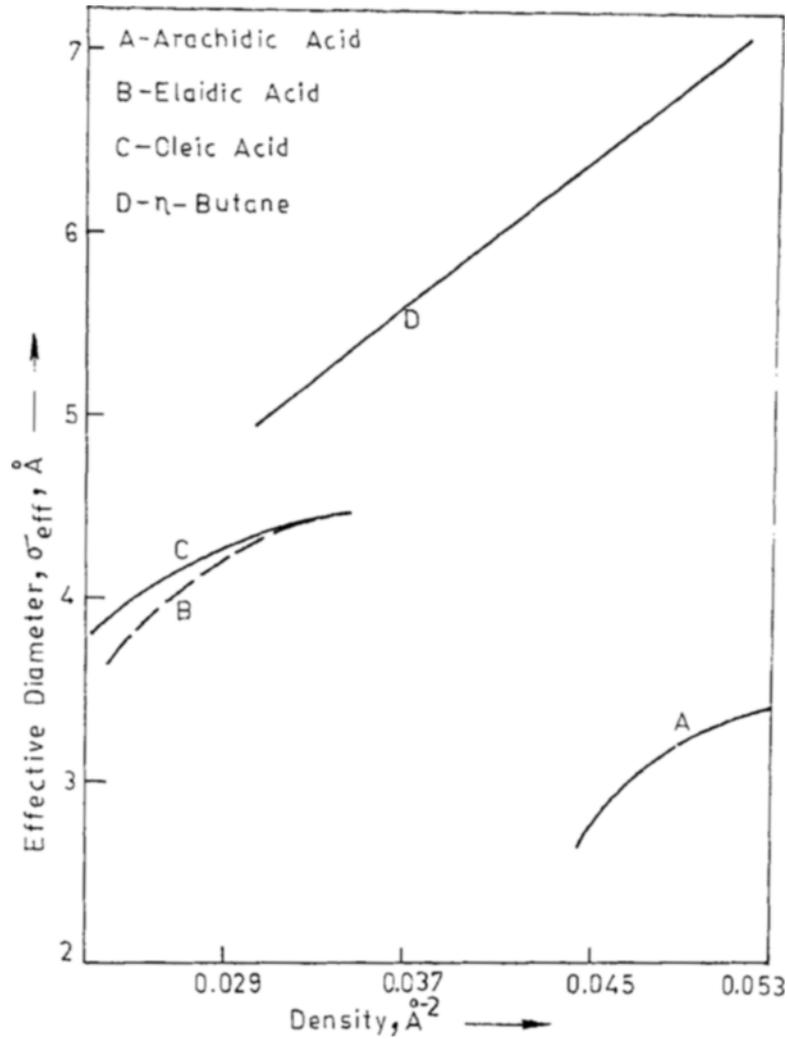


Figure 2. Effective diameter as a function of density for arachidic acid (curve A), elaidic acid (B) and oleic acid (C) and the calculated effective diameters for *n*-butane (curve D).

chains such as oleic acid (*cis*) are greater than the effective diameters of straight chains of elaidic acid (*trans*) due to an increased contact between bent chains (Nagalakshmi 1985; Nagalakshmi and Tembe 1987).

A practical utility of these effective diameters is in the calculation of the surface pressures of the mixtures from the effective diameters of the components σ_1 and σ_2 (Venkateshwara Rao 1986; Venkateshwara Rao and Tembe 1987). At a given density, the effective diameter of the binary mixture σ_{mix} is obtained from those of its components by the equation

$$\sigma_{\text{mix}}^2 = X_1 \sigma_1^2 + (1 - X_1) \sigma_2^2, \quad (12)$$

where X_1 is the mole fraction of component 1. Knowing σ_{mix} we can get ρ_R from (11) and thereby the pressure of the system. The pressures calculated from (12) are in fair agreement with experiment (Feher *et al* 1977; Venkateshwara Rao 1986).

The next task is the evaluation of the effective areas from site-site pair potentials. For this, we take two *n*-butane molecules A and B which are placed on a planar surface. Molecule A is fixed. At a given distance r between the two chains, the

effective pair potential is obtained by averaging over the orientations of the molecule B. In the present calculation, site-site Lennard-Jones potentials with $\sigma = 2.4 \text{ \AA}$ and $\epsilon = 50 \text{ K}$ are used for all pairs of atoms. For each value of r , 72 conformations on molecule B were considered for obtaining the effective potential. The effective potential rises faster than the site-site potential in the repulsive region and decays to zero more rapidly in the attractive region. The repulsive parts of the effective and the site-site potentials are shown in figure 3. At each value of r a Lennard-Jones potential with a different value of σ is seen to have the same value as the effective potential. Taking r to be a measure of the average distance of molecular separation, the density may be obtained as $\rho \sim 1/r^2$. A plot of σ as a function of density for *n*-butane obtained from the data of figure 3 is shown in figure 2 (curve D). These effective diameters show the same qualitative trend as the experiment although the systems compared are of different chainlengths.

While there is need to optimise the number of configurations in the averaging procedure and even to use Boltzmann weighted averages, the semiempirical

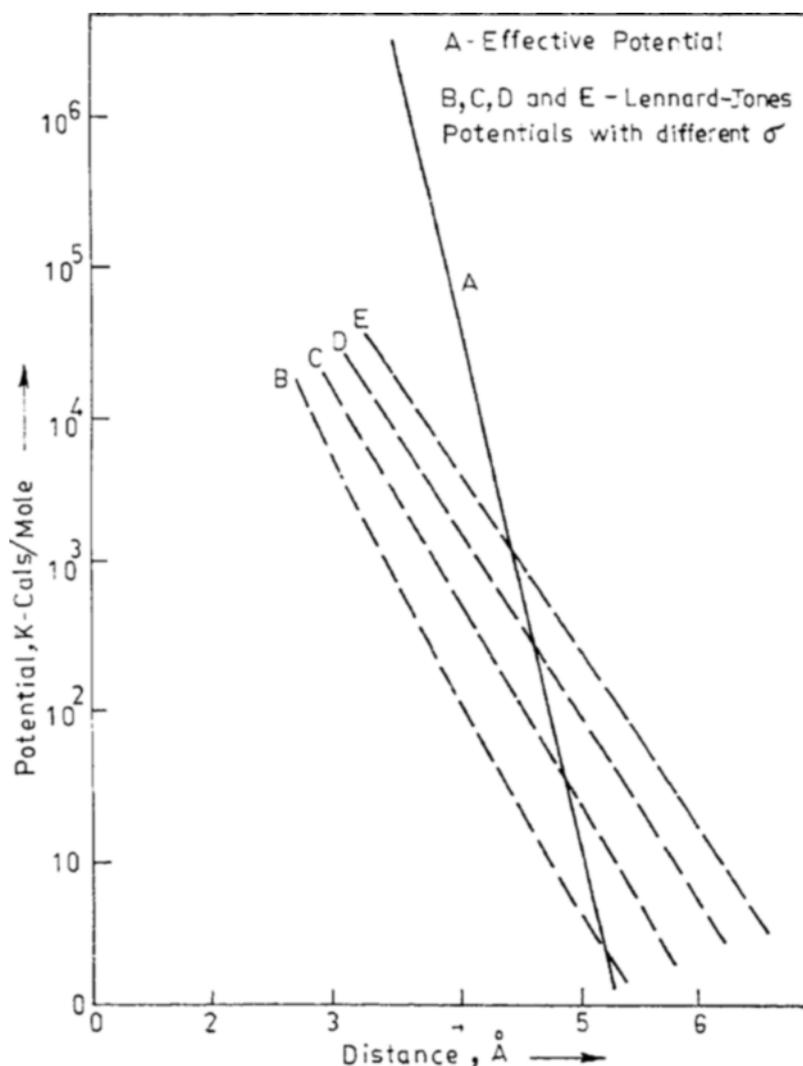


Figure 3. Rotationally averaged effective potential for *n*-butane (curve A) and Lennard-Jones potentials with different values of σ . The σ values for the curves are B (5.35 Å), C (6.0 Å), D (6.5 Å) and E (7 Å).

approach outlined here is useful for correlating the experimental data with effective size parameters which can be readily evaluated. The effective size as a function of the number of carbon atoms in the chains is being investigated. When the thermodynamics of the mixture does not match the thermodynamics obtained from σ_{mix} , additional parametrizations of molecular size with an effective diameter and an effective length may be needed. There is also need to systematically reduce the number of degrees of freedom in complex molecules so that the integral equations for interaction site models can be efficiently solved.

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