

CHEMPOR'85

4th INTERNATIONAL CHEMICAL ENGINEERING CONFERENCE

University of Coimbra

Coimbra — Portugal

April 15-19, 1985

CHEMPOR'85

4.^A CONFERÊNCIA INTERNACIONAL DE ENGENHARIA QUÍMICA

Universidade de Coimbra

Coimbra — Portugal

Abril 15-19, 1985

CHEMPOR '85

4th INTERNATIONAL CHEMICAL ENGINEERING CONFERENCE

University of Coimbra

Coimbra - Portugal

April 15-19, 1985

CHEMPOR '85

4ª CONFERÊNCIA INTERNACIONAL DE ENGENHARIA QUÍMICA

Universidade de Coimbra

Coimbra - Portugal

Abril 15-19, 1985

ACKNOWLEDGEMENTS

AGRADECIMENTOS

The Conference is sponsored by
A Conferência realiza-se sob o patrocínio de

- Fundação Calouste Gulbenkian
- The British Council
- INIC - Instituto Nacional de Investigação Científica
- JNICT - Junta Nacional de Investigação Científica e Tecnológica
- LNETI - Laboratório Nacional de Engenharia e Tecnologia Industrial
- Câmara Municipal de Coimbra
- CNP - Companhia Nacional de Petroquímica, EP
- Indústrias Lever Portuguesa, Lda.
- União de Bancos Portugueses
- CIRES - Companhia Industrial de Resinas Sintéticas, SARL
- Siderurgia Nacional, EP
- EPSI - Empresa de Polímeros de Sines, SARL
- Companhia Portuguesa de Petróleos BP, SARL
- SAPEC - Produits et Engrais Chimiques du Portugal
- Sociedade Nacional de Sabões
- Shell Portuguesa
- Sociedade Portuguesa do Acumulador TUDOR
- Indústrias Textéis Somelos, SARL
- Universidade de Coimbra

Their contribution, financial or otherwise, is gratefully acknowledged.
Agradece-se a contribuição, financeira ou outra, das entidades referidas.

ORGANIZING COMMITTEE

COMISSÃO ORGANIZADORA

President	Dr. T.R. Bott	(University of Birmingham, UK)
Vice-President	Prof. J.J.B. Romero	(University of Minho, Portugal)
Secretary	Prof. L.Q. Lobo	(University of Coimbra, Portugal)
Members	Prof. J.A.A.M. Castro	(University of Coimbra, Portugal)
	Prof. A.E.G. Medina	(University of Oporto, Portugal)
	Prof. C.A. Nieto de Castro	(University of Lisbon, Portugal)
	Dr. C.P. Nunes	(CNP - Companhia Nacional de Petroquímica, Portugal)
	Prof. J.D.R.S. Pinheiro	(University of Minho, Portugal)
	Prof. M. Margarida L.F.L. Rebola	(University of Coimbra, Portugal)
	Prof. L.J.S. Soares	(University of Minho, Portugal)

Secretariat

Secretariado

Miss M. Regina Seguro

Mr. M.G. Costa Ferreira

SCIENTIFIC PROGRAMME

BLOCK 1 - THERMOPHYSICAL PROPERTIES

SESSION TP1: Plenary lecture

The need for new developments in Thermodynamics

Jorge C.G. Calado (Cornell, USA, and T. Lisboa, PORTUGAL)

SESSION TP2: Communications

- 01 *Computer Simulation and Theoretical Studies of Liquid Mixtures: Brute Force vs. Insight*
K.E. Gubbins (Cornell, USA)
- 02 *Prediction of VLE Data for Two-Component Mixtures from Heats of Mixing and the Complete Local Concentration Model*
N. Chiou and D. Yarbrough (Tennessee, USA)
- 03 *Prediction of VLE and LLE by the ASOG Method*
A. Arce, A. Blanco, J.M. Correa, M.R. Mendez and J. Tojo (Santiago and Vigo, SPAIN)
- 04 *Some Difficulties on the Application of the UNIFAC Model for the Prediction of LLE Compositions*
M.G. Bernardo Gil and L.J.S. Soares (Lisboa and Minho, PORTUGAL)
- 05 *VLE of Polar Mixtures: A New Generalized Correlation*
S. Persio Ravagnani and S.G. d'Ávila (Campinas, BRASIL)

SESSION TP3: Communications

- 06 *Binary Parameter Values for VLE Calculations*
Y. Adachi and B.C.-Y. Lu (Ottawa, CANADA)
- 07 *Thermodynamics of Liquid Mixtures - A Unified Approach for Predicting Isothermal VLE and Viscosity from Heat of Mixing*
T.R. Kubendran, M.R.V. Krishnan and G.S. Laddha (Anna/Madras, INDIA)

- 08 *Sensitivity of Separation Process Design to Phase Equilibria and Operation Parameters*
A.M. Sereno and S. Macchietto (Porto, PORTUGAL and London, UK)
- 09 *An Exercise on the Influence of the Uncertainty in the Calculation of VLE on the Costs and Performance of Distillation Columns*
M. Margarida L.F.L. Rebola, A.G.M. Ferreira and L.Q. Lobo (Coimbra, PORTUGAL)
- 10 *Thermal Properties of Binary Mixtures at Infinite Dilution*
P. Alessi, M. Fermeglia and I. Kikic (Trieste, ITALY)
- 11 *The Use of Infinite Dilution Activity Coefficients in Process Design*
J.C. Bastos, M.E. Soares and A.G. Medina (Porto, PORTUGAL)
- 12 *Computer Simulation of Aromatics Extraction*
A.M. Sereno and A.G. Medina (Porto, PORTUGAL)

SESSION TP4: Communications

- 13 *Use of Isothermal Microcalorimetry for the Characterization of Thermal Power Occuring in Technically Important Materials and Products*
J. Suurkuusk and I. Wadsö (Lund, SWEDEN)
- 14 *Thermodynamics of Phase Transitions in Some Organic Polyols*
M. Concelção P. Lima and C.D. Maycock (Coimbra, PORTUGAL)
- 15 *Expansivities of Pure Organic Compounds at Moderate Temperatures*
J. Ortega, J.S. Matos, J. Trujillo, M.I. Paz-Andrade and E. Jimenez (Las Palmas and Santiago, SPAIN)
- 16 *Thermal Expansion Coefficients of Mixtures: Benzene + 1-Pentanol and + 2-Pentanol at Moderate Temperatures*
J. Ortega and M.I. Paz-Andrade (Las Palmas and Santiago, SPAIN)
- 17 *Excess Molar Volumes of Binary Mixtures: Ethyl Formate + Isomers of Hexanol at 298.15 K*
J. Ortega, J.S. Matos, M.I. Paz-Andrade and R. Bravo (Las Palmas and Santiago, SPAIN)
- 18 *Excess Molar Volumes of Binary Mixtures: Ethyl Acetate + Isomers of Hexanol at 298.15 K*
J. Ortega, J.S. Matos, M.I. Paz-Andrade, and R. Bravo (Las Palmas and Santiago, SPAIN)

SESSION TP5: Communications

- 19 *Partial Molar Volumes of Naphthalene Dilute in Supercritical Fluid Solvents*
E.J.S. Gomes de Azevedo and J.M. Prausnitz (T. Lisboa, PORTUGAL and Berkeley, USA)
- 20 *Excess Molar Volumes of Mixtures of n-Butyl Acetate with an n-Alkane*
E.F.G. Barbosa, J.C.G. Calado, E. Jimenez, I.M.S. Lamprela, L. Pias and M.I. Paz-Andrade (Lisboa, PORTUGAL and Santiago, SPAIN)
- 21 *VLE for Binary Systems Ethyl Formate with l-Propanol and 2-Propanol at 760 mm Hg*
J.A. Peña, J. Ortega, M.I. Paz-Andrade and J. Fernandez (Las Palmas and Santiago, SPAIN)
- 22 *VLE of the System Benzene - Cyclohexane - l, Propanol at 760 mm Hg*
A. Arce, A. Blanco, J.M. Correa and J. Tojo (Santiago, SPAIN)
- 23 *Interfacial Tensions in Hydrocarbon + Perfluorocarbon Mixtures: A Microcosm of Intermolecular Forces and Close-to-critical Endpoint Effects*
I.A. McLure and V.A.M. Soares (Sheffield, UK and Lisboa, PORTUGAL)
- 24 *A Microscopic Model for the Interfacial Properties of Mixtures of Oil, Water and Non-Ionic Surfactants*
M.M. Telo da Gama and K.E. Gubbins (Cornell, USA)

SESSION TP6: Communications

- 25 *The Transport Properties of Gases with Multipole Moments*
G.C. Maitland, R.D. Trengove and W.A. Wakeham (London, UK)
- 26 *On the Role of the External Effects in the Intermolecular Parameters Determination from Experimental Thermophysical Data*
Galina P. Dudchick and G.G. Kuleshov (Minsk, USSR)
- 27 *Calculation of Transport Collision Integrals for Lennard-Jones Gases*
E.V. Akhmatkaya and L.A. Pozhar (Kharkov, USSR)
- 28 *A General Relationship Between Dynamic Viscosity and Reduced Temperature for Liquids in the Reduced Temperature Range 0.4 to 0.8*
C. Baroncini, G. Latini and P. Pierpaoli (Ancona, ITALY)
- 29 *The Effect of Uncertainty in Diffusion Coefficients in the Design of Packed Columns*
M.L.S. Matos Lopes, C.A. Nieto de Castro and W.A. Wakeham (Lisboa, PORTUGAL and London, UK)

SESSION TP7: Communications

- 30 *Thermophysical Properties of Molten Salts*
J.P. Petitet, L. Denielou, R. Tufeu and B. LeNeindre (Paris, FRANCE)
- 31 *Thermal Conductivity of a Titanium-Aluminium-Vanadium Alloy*
J.E. Connett and J.M. Corsan (NPL, UK)
- 32 *Thermal Conductivity of Porous Catalysts*
K.A. Al-Halhouli, R. Hughes and P.R. Patnaik (Salford, UK)
- 33 *Calculation of Thermal Conductivity in Simple Gases and Their Binary Mixtures*
E.V. Akhmatskaya, L.A. Pozhar and V.N. Shchelkunov (Kharkov, USSR)
- 34 *Evaluation of Eddy Diffusivities in a Crystallization Column*
M. Lurdes Serrano and M. Fátima Farelo (T. Lisboa, PORTUGAL)
- 35 *Thermal Diffusion in Solids - An Overview*
M. Fátima Morgado and J.D. Pinheiro (Minho, PORTUGAL)

SESSION TP8: Workshop

Impact of thermophysical properties on technological innovation

BLOCK 2 - ENERGY CONSERVATION IN THE CHEMICAL AND ALLIED INDUSTRIES

SESSION EN1: Plenary lecture

Integrated Design of Processes and Service Systems.

Improving Energy, Capital and Flexibility

Bodo Linnhoff (Manchester, UK)

SESSION EN2: Communications

- 41 *The Relationship Between Energy Analysis and Operating Costs for Energy Conservation in Chemical Processes*
C.D. Grant and A.N. Anozie (Strathclyde, UK and Ife, NIGERIA)
- 42 *Improvements of the Energy System at an Oil Refinery by Optimization of the Heat Exchanger Network*
B. Sundén, H. Thersthol and C. Wernersson (Chalmers and Shell/Göteborg, SWEDEN)
- 43 *Energy Savings Through Improvements of a Heat Transfer System in a Petrochemical Plant - A Case Study*
C.P. Nunes and J. Vasconcelos (CNP, PORTUGAL)
- 44 *Energy Recovery in Distillation Columns with Direct Vapour Recompression. Application to the Distillation of the Ethanol-Water System*
Teresa M.K. Ravagnani and J.A.F.R. Pereira (Campinas, BRASIL)
- 45 *Thermally Integrated Distillation Columns: A Comparison of Different Control Schemes*
S. Bigini, A. Brambilla, G.F. Nencetti and C. Scali (Pisa, ITALY)

SESSION EN3: Communications

- 46 *Extraction as an Energy-Saving Alternative to Rectification in the Recovery of Organic Compounds from Aqueous Solutions*
R. Billet and M. Pajak (Ruhr/Bochum, WEST GERMANY)
- 47 *Um Programa Global de Economias de Energia e Utilidades no Complexo Petroquímico de Sines*
C.P. Nunes and M.M. Palma (CNP, PORTUGAL)
- 48 *Thermodynamic Analysis of a Shale Oil Production Plant for Energy Conservation*
R. Mundstock, L.C. Casavechia and K. Rajagopal (PETROBRAS and Fed. Rio de Janeiro, BRASIL)

- 49 *Project of Energy Recovery from Flue Gases at Sociedade Nacional de Sabões*
A.R. Janeiro Borges, J.C. Galvão Teles and J. Braga (U.N. Lisboa, AM Lisboa and SNS, PORTUGAL)
- 50 *Temperature Profile-Basis for Heat Accounting*
M. Fehr (Uberlândia, BRASIL)
- 51 *Heat Recovery in Glass Fusion Furnaces - A Case Study*
A.A.B. Neves, M.N. Nina and J.F.P. Gomes (LNETI and T. Lisboa, PORTUGAL)

SESSION EN4: Communications

- 52 *Intensification of Design and Operation of Continuous Treatment Processes*
R. Burley (Heriot-Watt, UK)
- 53 *A Quasi Steady State Model for Low Density Polyethylene Pipeline Reactors*
J.A. Howell and S. Fayo de Azevedo (Swansea, UK and Porto, PORTUGAL)
- 54 *The Effect of Temperature on the Rate of Photodegradation (weathering) of Polymer Films*
M.S. Carvalho, J.J.C. Cruz Pinto and J.F.A. Ferreira (Minho, PORTUGAL)
- 55 *Transfert de Chaleur en Lit Fluidisé*
K. Alia, F. Bentahar, M. Benali, H. Ait-Sahlia and C. Dahmane (H. Boumediene, ALGERIA)
- 56 *Simulation of Industrial Chemical Processes. I - Synthesis of Phthalic Anhydride from O-Xylene in a Fixed Bed Reactor*
J.C. Oliveira and A.E. Rodrigues (Porto, PORTUGAL)

SESSION EN5: Communications

- 57 *Influence of the Intermolecular Potential on the Calculated Detonation Characteristics of Explosives with Positive Oxygen Balance*
O. Heuzé, H.N. Presles and P. Bauer (Poitiers, FRANCE)
- 58 *Determination of the Composition of Gaseous Mixtures*
O. Heuzé, P. Bauer and H.N. Presles (Poitiers, FRANCE)
- 59 *Ignition of White Pine and Cork Dust*
L. Araújo and J. Campos (Coimbra, PORTUGAL)
- 60 *Combustion Characteristics of Wood and Cork Dust Suspensions*
L. Lemos and J. Campos (Coimbra, PORTUGAL)

- 61 *Obtenção de Gás de Poder Calorífico Médio a Partir da Madeira*
Z.T. Makray and J.A.F.R. Pereira (Campinas, BRASIL)
- 62 *Energy Recovery in the Pyrolysis and Gasification of Wood Wastes for Local Energy Production*
S.S. Alves and J.L. Figueiredo (T. Lisboa and Porto, PORTUGAL)

SESSION EN6: Communications

- 63 *The Use of Hot Wire Techniques in Fouling Tests. A Word of Awareness*
J.D. Pinheiro, L.F. Melo and R.T. Oliveira (Minho, PORTUGAL)
- 64 *Fouling in Heat Exchangers: A Study of the Mechanisms of Formation of Kaolin Deposits*
L.F. Melo and J.D. Pinheiro (Minho, PORTUGAL)
- 65 *Biofouling in Tubes - Some Trends and Perspectives*
J.D. Pinheiro, L.M.F. Melo and M.M.S. Pinheiro (Minho, PORTUGAL)
- 66 *An Improved Method to Estimate Kinetic Thermal Properties in the Design of Heat Exchangers*
V.G. Dovi, B. Canepa, P. Costa and L. Maga (Genova, ITALY)
- 67 *Parametric Pumping: An Energetically Efficient Separation Process*
C. Costa and A.E. Rodrigues (Porto, PORTUGAL)
- 68 *Analysis of Transient Thermal Measurements on Fibrous Insulations Obtained with an Unguarded Flat Tester*
D.W. Yarbrough, D.L. McElroy, T.W. Tong and J.K. Wood III (Oak Ridge, Tennessee and Kentucky, USA)
- 69 *Improving Thermal Insulation Performance in the Process Industries*
R.P. Tye (DYNATECH, USA)

SESSION EN7: Panel session

Energy Conservation in the Chemical and Allied Industries

COMPUTER SIMULATION AND THEORETICAL STUDIES OF LIQUID MIXTURES: BRUTE FORCE vs. INSIGHT

Keith E. Gubbins

School of Chemical Engineering
Cornell University

ABSTRACT

Recent advances in our understanding of the thermodynamics of molecularly simple liquid mixtures based on theory and computer simulation are reviewed. Perturbation theories based on spherical and nonspherical reference fluids are described, and examples are given of comparisons with experiment. Computer simulation studies of model fluid mixtures in which the molecules possess both nonspherical shape and electrostatic forces are proving useful in understanding the role of these molecular effects in thermodynamics, and are briefly discussed. Finally, a summary is given of recent work on the vapour-liquid interface for simple mixtures.

INTRODUCTION

The thermodynamic properties of mixtures can be studied by experiment, theory, or computer simulation (Fig. 1). In this review only the last two methods will be covered, with the emphasis on (a) comparison of theoretical and simulation results, and (b) comparison of theory and experiment. The discussion will focus on molecularly simple mixtures, e.g. the inert gases, CH_4 , CH_3OH , CO_2 , HCl , etc. We shall not deal

specifically with ionic fluids (electrolytes, fused salts, etc.), aqueous solutions or polymers.

For the thermodynamic properties, perturbation theory provides the most convenient compromise between rigour and ease of calculation at present. A survey of the existing theories is given in Section 2, with the emphasis on molecular rather than atomic fluids. These theories can be conveniently divided into those based on a reference fluid of spherical molecules, and those based on a reference of nonspherical molecules. The former are easier to use, but do not work well for strong orientation-dependent forces. The latter work better, but are more difficult to use. Most comparisons with experiment have so far been for the simpler spherical reference theories. Some examples of such comparisons are given in Section 3. Both the electrostatic and induction forces have a large effect on the thermodynamic properties. Comparatively few computer simulation studies have been reported so far on mixtures of simple model nonspherical molecules. This area is reviewed in Section 4, and results for models in which the molecules

have nonspherical shape (spherocylinders, dumbbells, etc.) and/or electrostatic forces are summarized. Finally, in Section 5 some recent results for the vapour-liquid interface of spherical Lennard-Jones mixtures are discussed.

PERTURBATION THEORY

In perturbation theory the Helmholtz free energy A for the fluid mixture of interest is expanded about the value A_0 for some reference fluid in which the intermolecular potential energy is U_0 . The expansion is carried out in terms of the perturbation potential $U_p \equiv U - U_0$, where U is the intermolecular potential energy of the full system; the parameterization method varies with the particular theory used. For spherical molecules such perturbation theories are well established; for reviews see, for example, McDonald (1973), Smith (1973) and Gubbins et al. (1983). Of particular value are the Weeks-Chandler-Anderson (WCA) form of hard sphere perturbation theory and the van der Waals 1-fluid (vdW1) form of conformal solution theory. We do not dwell on these theories here, but shall focus our attention on theories for nonspherical molecules. For a more detailed review of these theories see Gray and Gubbins (1984).

Spherical Reference Molecules

Three different choices of spherical reference potentials have been suggested; we refer to these theories as the u -expansion, f -expansion, and

median potential theory. The median potential theory (see, e.g. MacGowan et al., 1984) fails for electrostatic forces, and we do not describe it further here.

The u -Expansion. This is the oldest of the perturbation theories for molecular fluids, and is the easiest to use. The reference pair potential $u_0(r)$ is defined by

$$u_0(r) \equiv \langle u(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} \quad (1)$$

where $u(r\omega_1\omega_1)$ is the full pair potential for the fluid of interest, ω_i is the orientation of molecule i ($\theta_i\phi_i$ for linear or $\theta_i\phi_i\chi_i$ for nonlinear molecules), and $\langle \dots \rangle_{\omega_1\omega_2}$ means an unweighted average over molecular orientations. With this choice the first-order perturbation term A_1 vanishes and the series for the Helmholtz energy becomes

$$A = A_0 + A_2 + A_3 + \dots \quad (2)$$

The second-order term A_2 involves integrals over the two- and three-body reference correlation functions. The third-order term A_3 is more complex in general, but for electrostatic forces reduces to integrals over two- and three-body reference correlation functions. These integrals have been evaluated and fitted to simple functions for a variety of intermolecular force types (Gubbins and Twu, 1978; Nicolas et al., 1979),

and detailed descriptions of the theory and its use have been given by Gubbins and Twu (1978), Twu and Gubbins (1978), and Moser et al. (1981).

Unfortunately, the series of eqn. (2) is slow to converge, and even the inclusion of A_3 is not sufficient to deal with strongly polar molecules such as alcohols or water. This led Stell et al. (1974) to propose a Padé approximant to the series,

$$A = A_0 + A_2/(1 - A_3/A_2) \quad (3)$$

This equation agrees well with computer simulation results for fluids with strong electrostatic forces, provided that the molecules possess spherical or near spherical cores. Typical results are shown in Fig. 2. Recently this theory has been extended to include quantum corrections (Clancy and Gubbins, 1981), nonaxial molecules (Gubbins et al., 1981) and induction effects (Wertheim, 1979; Venkatasubramanian et al., 1984).

The u -expansion is convenient and gives a good account of the effects of electrostatic forces on thermodynamic properties. It is much less satisfactory for molecules with highly nonspherical cores or for describing fluid structure.

The f -Expansion. In this expansion, also called the RAM (reference average Mayer function)

theory, the reference potential $u_0(r)$ is defined through an unweighted average over orientations of the Boltzmann factor $\exp[-u(r\omega_1\omega_2)/kT]$,

$$\exp[-u_0(r)/kT] = \langle \exp[-u(r\omega_1\omega_2)/kT] \rangle_{\omega_1\omega_2} \quad (4)$$

This reference potential includes an averaged contribution from the anisotropic part of the potential, and also gives the second virial coefficient exactly. Thus, the zeroth order f -expansion becomes exact in the low density limit. However, the potential $u_0(r)$ depends on temperature and must be calculated numerically for each new temperature or intermolecular potential function. Thus the f -expansion is less convenient to use than the u -expansion.

With this choice of reference the A_1 term again vanishes and the free energy series is again given by eqn. (2). Terms beyond A_2 have not been calculated. The fluid structure is usually obtained by expanding the pair function $y(r\omega_1\omega_2) \equiv \exp[u(r\omega_1\omega_2)/kT]g(r\omega_1\omega_2)$, i.e.

$$g_f(12) = \exp[-u(12)/kT] [y_0(r) + y_1(12) + \dots] \quad (5)$$

where $y(12) \equiv y(r\omega_1\omega_2)$, etc. Here $g(r\omega_1\omega_2)$ is the pair correlation function. The fluid structure calculated from the f -expansion is generally

better than from the u-expansion, though there are still considerable discrepancies. The structure results can be improved somewhat by using the 'reduced form' of the theory (Smith and Nezbeda, 1981, 1983), in which the pair correlation function is given by

$$g(12) = \frac{g_f(12)}{g_{f,000}(r)} g_0(r) \quad (6)$$

where the f-expansion is used to calculate the ratio $g_f(12)/g_{f,000}(r)$, where $g_f(12)$ is given by eqn. (5) and $g_{f,000}(r)$ is the $l=l', m=m' = 000$ spherical harmonic co-efficient of $g(12)$, defined in general by

$$g_{l,l',m,m'}(r) = 4\pi \langle g(12) Y_{lm}(\omega_1')^* Y_{l'm'}(\omega_2')^* \rangle_{\omega_1', \omega_2'} \quad (7)$$

where Y_{lm} is the spherical harmonic in the convention of Rose (1957), ω_i' is the orientation of molecule i in the intermolecular frame, and $\underline{m} \equiv -m$. The reference pair correlation function $g_0(r)$ that appears in eqn. (6) is calculated from the Percus-Yevick theory.

In Fig. 3 the f-expansion results are compared with simulation data for the structure of two simple model fluids, the hard dumbbell (HD), a simple model of nonspherical shape, and the hard dumbbell plus point charge quadrupole (HD+PCQ), a

model in which the molecules also possess strong electrostatic forces. The three harmonic coefficients of $g(12)$ shown are those that are most important for the thermodynamic properties. For the HD fluid the first-order theory gives good results for g_{220} and g_{221} , but is poor for g_{222} . For the HD+PCQ fluid the theory gives rather poor results for all three harmonics, and the first-order theory is no better than zeroth order. The pair correlation function for molecular centres, $g(r)$, is given quite accurately by the theory for these fluids (Wojcik and Gubbins, 1984b).

The results of the reduced form of the theory for the free energy are shown in Fig. 4 for the HD+PCQ fluid. The theory overestimates the electrostatic contribution to the free energy.

Nonspherical Reference Potentials

From the previous section it will have become clear that theories based on spherical reference molecules are unsatisfactory, particularly for fluids of molecules that are nonspherical in shape and also exert electrostatic forces. Most recent work in perturbation theory has been aimed at finding suitable reference fluids of nonspherical molecules. Expansions about such a fluid should be more rapidly convergent, but usually at the cost of added complexity. Reference fluids of hard, nonspherical molecules such as dumbbells or spherocylinders are often used, as accurate equations are now known for the thermodynamic

properties of such fluids.

Nonspherical reference perturbation theories can be conveniently divided into two types: (a) those that divide the full pair potential $u(r\omega_1\omega_2)$ into two parts, usually a repulsive and an attractive branch as in Weeks-Chandler-Andersen (WCA) theory for spherical molecules; this splitting is, of course, different for different molecular orientations; and (b) those that are restricted to interaction site model (ISM) potentials, where the full potential is the sum of site-site potentials $u_{\alpha\beta}(r)$ between molecular sites α and β , and where $u_{\alpha\beta}$ is divided, usually into repulsive and attractive branches. In both approaches the reference fluid properties are usually related to those of a fluid of hard molecules, e.g. dumbbells. In the theories of type (a) the reference fluid pair correlation function $g_0(r\omega_1\omega_2)$ is unknown, and must be estimated. This is often estimated using the f -expansion. This approach has been applied to fluids of two-centre Lennard-Jones (Kohler et al., 1979; Fischer, 1980; Quirke and Tildesley, 1983) and Gaussian overlap (Monson and Gubbins, 1983) molecules. The principal weakness in theories of this type is in the evaluation of the reference correlation function. An interesting variant of this theory is due to Boublik and his collaborators (Boublik, 1974, 1976, 1979, 1981; Pavlicek and Boublik, 1981),

who apply it to fluids in which the molecules obey a Kihara potential. In this model the molecules contain a hard convex core, and the intermolecular potential depends on the shortest distance $\rho = \rho(r\omega_1\omega_2)$ between molecular cores, rather than on the distance between molecular centres. The perturbation terms can then be simplified using the geometry of hard convex bodies, and it is found that A_1 involves only the correlation function $g_0(\rho)$ rather than the full pair correlation function $g_0(r\omega_1\omega_2)$. Here $g_0(\rho)$ is proportional to the probability that a molecular pair has a minimum distance ρ between cores. The accuracy of this theory has not yet been tested against computer simulation results, primarily because simulations of Kihara fluids would be very time consuming.

Theories of type (b) for ISM fluids have the advantage that one only needs to know the site-site correlation functions $g_0^{\alpha\beta}(r)$ for the reference fluid and not the full pair correlation function. Such theories have been proposed by Chandler and Andersen (1972), Tildesley (1980), Lombardero et al. (1981a), and Enciso and Lombardero (1981). The site-site correlation functions can be calculated using the reference interaction site model (RISM) theory of Chandler and Andersen (1972) or related theories. The theory gives good results for ISM fluids in the absence of electrostatic forces for both thermodynamics and structure (Tildesley, 1980).

The theories described above have for the most part been applied to either molecules having spherical shape plus electrostatic forces, or to molecules with nonspherical shape but no electrostatic forces. Real molecules usually have nonspherical shape and electrostatic forces, and the theories are usually poorer for such cases. To illustrate this we consider a fluid of hard dumbbells in which the molecules have embedded point charges arranged in a quadrupolar symmetry, i.e. positive charges q on each of the sphere centres, and a negative charge $-2q$ at the molecular centre. We call this the HD+PCQ model. One obvious reference fluid is one of hard dumbbells in the absence of point charges, so that the free energy series is

$$A = A_{HD} + A_1 + A_2 + A_3 + \dots \quad (8)$$

However, this reference system does not contain all the strong short-range forces, nor even all the repulsive forces, since the electrostatic forces will have repulsive regions for certain molecular orientations. If we include the repulsive part of the electrostatic forces in the reference potential, in addition to the HD part, eqn. (8) is modified to

$$A = A_{REP} + A_1 + A_2 + \dots \quad (9)$$

where A_{REP} is the free energy of the repulsive

force reference fluid. These two series have been recently studied by Wojcik and Gubbins (1984b) using Monte Carlo simulations in which the various terms A_{HD} , A_{REP} , A_1 , and A_2 are evaluated exactly. The results are shown in Fig. 4. The HD reference system gives especially poor results; the A_1 term alone greatly underestimates the electrostatic forces, while the inclusion of A_2 overestimates it. The REP reference system gives better results. The A_1 term alone still underestimates the effect of electrostatic forces, but the inclusion of A_2 now gives results that agree almost exactly with the Monte Carlo values for A . This series appears to warrant further study, although it is possible that yet better reference fluids may be found by including part of the strong attractive forces in the reference potential. The structure results for the REP fluid are intermediate between those for the HD and HD+PCQ fluids (Wojcik and Gubbins, 1984b).

Although the series of eqn. (8) is poorly convergent, it is possible that a Padé approximant to the series might give good results, as in the case of the u -expansion. Rasaiah et al. (1975) and Martina et al. (1979, 1981) have suggested the Padé

$$A = A_{HD} + A_1 + A_2/(1 - A_3/A_2) \quad (10)$$

To avoid the difficulty of calculating the HD correlation functions that appear in A_2 and A_3