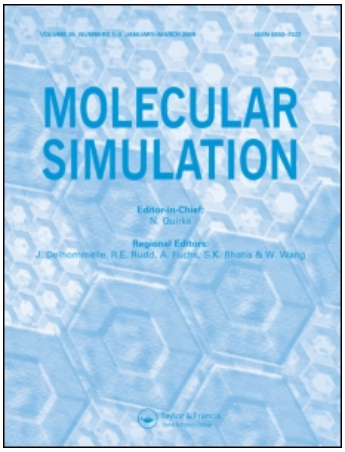

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Conference Reports

P. Cummings[a]; D. Frenkel[b]; K. E. Gubbins[c]; I. Nezbeda[d]; W. R. Smith[e]
[a] Oak Ridge Natl. Lab., [b] FOM, Amsterdam [c] Cornell University, Ithaca [d] Academy of Sciences, Prague [e] Univ of Guelph, Guelph

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CONFERENCE REPORTS

FOURTH LIBLICE CONFERENCE ON THE STATISTICAL MECHANICS OF LIQUIDS

June 6–10, 1994, Lake Milovy, Czech Republic

This report gives a summary of the events of the Fourth Liblice Conference on the Statistical Mechanics of Liquids held in the Czech Republic in early June, 1994. It attracted many of the leading experts in the field, which intersects chemistry, physics, chemical engineering, and applied mathematics. The meeting was the fourth in a series which began in 1983, as a private initiative of Ivo Nezbeda and his colleagues from the Academy of Sciences in Prague, Czech Republic, and continued in 1987 and 1990. This meeting was chaired by I. Nezbeda and co-chaired by K. Gubbins (Cornell) and D. Henderson (Mexico City).

Typically, the meeting venue is outside main residential areas. This time it was held in a remote resort in the heart of the Czech-Moravian Highlands, and had its standard format: an opening lecture on Monday evening given by a renowned specialist, followed by eight morning, three evening sessions, and a poster session.

An integral part of this particular meeting was the workshop "Novel Trends in the Simulation of Complex Liquids" sponsored by CECAM (European Center for Atomic and Molecular Computations) and chaired by D. Frenkel (FOM Amsterdam).

The conference was opened with a review talk "Teaching an Old Dog New Tricks: Some Recent Monte Carlo Stunts", given by J. Valleau (Toronto), and focussing primarily on the latest development of techniques for computing the chemical potential. Two of Tuesday's morning sessions were taken up by the CECAM workshop, within which 14 contributions were presented. The following evening session dealt with purely theoretical topics. Wednesday's morning sessions were devoted to inhomogeneous fluids. Polar, ionic, and associating fluids covered the following two sessions and the CECAM workshop continued on Thursday morning. The panel discussion took place on Thursday evening. The last two sessions on Friday were devoted to normal and chain-molecule fluids.

In addition to the total of 48 oral presentations, 78 posters, covering the above topics, were shown. The closing speech was delivered by E. Glandt who briefly summarized the main ideas which emerged during the meeting and invited all participants to the fifth conference which will be held in June 1998.

CECAM WORKSHOP AND THE PANEL DISCUSSION

The workshop covered both methodological and applied aspects of computer simulations and the contributions therein may be grouped as follows:

Simulation of phase equilibria, including systems with chemical reaction
liquid crystals and liquid crystalline polymers
fluids in confined media
massively parallel simulations

The Gibbs ensemble simulation technique (GEMC) and recent related advances were reviewed by T. Panagiotopoulos (Cornell). In particular, he addressed the problem of finite size corrections to critical behavior, and described a method to extrapolate grand-canonical ensemble Monte Carlo results to infinite system sizes. He also discussed simulations of liquid-vapor coexistence in systems of chain molecules, using the incremental chemical potential scheme of Kumar *et al.*, B. Smit (SHELL Amsterdam) later discussed how the Configurational Bias MC (CBMC) method could be used to perform GEMC simulations of liquid-vapor coexistence in systems of long alkanes up to C_{48}. He also discussed several other problems that had become tractable with CBMC, ie the problem of alkanes in zeolites. Another contribution that focussed on phase behavior was due to D. Kofke (Buffalo), who discussed the Gibbs-Duhem integration technique to trace out coexistence curves. He discussed the generalization of the technique to trace coexistence curves as a function of the Hamiltonian of the system. In particular, he showed how the melting pressure of simple models with an $-n$ potential could be followed as a function of n. Somewhat surprisingly, he found that the dependence on n is not monotonic. The problem of simultaneous phase and reaction equilibria has received considerable attention during the past few years, and was discussed by W. Smith (Guelph) who focussed primarily on a new reaction ensemble technique developed by him and B. Triska. This easily treats several cases which have proven difficult in the past, including multiple reactions and reactions that do not conserve the total number of molecules. He also showed how the Gibbs ensemble technique could be viewed as a special case of the reaction ensemble approach.

P. Cummings (Oak Ridge) gave an overview of the work performed in his research group in recent years aimed at predicting phase equilibria in pure water and aqueous mixtures (water/methanol and water/methano/NaCl mixtures) using GEMC methods. The results pointed to deficiencies in the intermolecular potentials. He also described the use of molecular dynamics (MD) simulation to study pure supercritical water and supercritical aqueous solutions. It was shown that simple point charge models fitted to ambient conditions have limited utility at supercritical state points. Both the GEMC and MD results suggest that water–water potentials needed to include polarizability to be applicable over the wide range of state conditions covered by vapor–liquid equilibrium and supercritical states.

Within the liquid crystal and liquid crystalline polymer topic, B. Mulder (FOM Amsterdam) reviewed recent advances in the theoretical description of liquid crystalline polymers. He showed how it is possible to generalize techniques previously used to describe main chain liquid crystal polymers, in order to treat more complicated systems like side-chain liquid crystal polymers in such a way that the influence of parameters like backbone- and spacer- length and flexibility can be systematically explored. E. Miguel (Sevilla) reported on recent simulations of the Gay-Berne model. This model has been shown to exhibit a variety of liquid crystalline phases. He showed that his simulations reveal isotropic, nematic and several smectic (A, B, hexatic-B?) phases.

R. Hoyst (Warszawa) discussed the peculiar properties of wedge dislocation in smectics. Due to the strong coupling with the surface free energy, these dislocations are repelled by the surface. He reviewed the possibility of dislocation un-binding in the context of the Nelson-Toner theory.

Another topic that arose in several talks was the numerical simulation of fluids in confined media. This problem was discussed by W. Steele (Penn State U), who reported on simulations of a fluid in straight and modulated "corrugated" pores. He discussed both the structure of the confined fluid and the adsorption isotherm, as a function of the pore shape. Liquid-vapor coexistence in pores and the effect of the pore diameter on the location of the coexistence point was the topic of E. Piotrovskaya's (St. Petersburg) contribution. She showed how, from such a simulation, one can deduce the curvature corrections to the liquid-vapor interfacial tension. Another aspect of molecules in confined media is their unusual dynamics. J. Talbot (Purdue) considered the motion of non-spherical molecules in the presence of fixed obstacles (Lorentz gas). His simulation seem to indicate that the dynamical behavior of such a molecular Lorentz gas is quite different from that of its atomic counterpart. Another contribution that focussed on the dynamics was given by J. Fischer (Bochum), who considered the dynamics of liquid evaporation from a free surface.

Two contributions were mainly focused on the problems associated with massively parallel simulation. J. Perram (Odense) discussed strategies for the parallel simulation of polymers, while I. Snook (Melbourne) discussed his experience with parallel simulations of large atomic systems. The message of both talks was that, in order to benefit from parallelism, a complete rethinking of the problem and a willingness to adopt existing parallelization techniques, is essential.

The panel discussion "Perspectives for CECAM initiatives on simulation on complex fluids" was chaired by N. Quirke (BIOSYM Orsay) and the panel speakers were K. Gubbins (Cornell), A. Haymet (Sydney), P. Cummings (Oak Ridge), J. Perram (Odense), and D. Frenkel (FOM Amsterdam). Apart from discussion attempting to identify topics as possible subjects for future CECAM activities, a number of speakers expressed their interest in improved intermolecular potentials, both for small molecules (water, alcohols) and for macro-molecules. It was also stressed that there is a great need for workshop style training, meetings that provide the participants with hands-on experience with state-of-the-art computational techniques.

THEORETICAL TOPICS

In this session, chaired by J. Fischer (Bochum), five contributions were delivered. Y. Rosenfeld (Beer-Sheva) discussed his concept of the "ideal liquid". To illustrate, he considered in detail the case of a one-component plasma. J. Percus (New York) delivered a stimulating lecture on entropy functionals. P. Monson (Amherst) described his recent work with X. Cottin on the development of a cell theory for the thermodynamic properties of solid solutions. Applications to binary hard sphere mixtures forming both substitutionally disordered and substitutionally ordered ('compounds') solid solutions were considered. This approach correctly describes the trends in the solid-fluid phase diagrams as the molecular size ratio between the species is changed.

D. Evans (Canberra) presented one of the few talks on nonequilibrium statistical mechanics, and discussed relations between phase space stability and thermophysical properties. Finally, S. Labik (Prague) spoke about recent work with Smith and Malijevsky on a new integral equation hierarchy for the background correlation functions of hard-body fluids. It yields the most accurate first-principles equation of state for hard-sphere systems, and very accurate pair and triplet background correlation functions.

INHOMOGENEOUS FLUIDS

The session on Inhomogeneous Fluids was chaired by W. Steele (Penn State U) and was opened by a talk by M. Rosinberg (Paris), who described the recent work he and his colleagues have done on extending density functional theory to inhomogeneous polyatomic fluids. Several talks were concerned with the effects of confinement on fluid behavior. S. Sokolowski (Lublin) spoke on the effect of pore closure on capillary condensation, again using density functional theory. K. Gubbins described recent simulation work on adsorption of both simple fluids and water in model carbon (graphitic and activated) pores. While these last two talks were concerned with precisely characterised model pores, E. Glandt (Philadelphia) described recent work of his on molecular fluids in random media.

G. Stell (Stony Brook) described simulations of quenched-annealed systems. The last three talks in this session were concerned with the behavior of charged interfaces. L. Blum (Puerto Rico) described theoretical and experimental work on structured charged interfaces. A. Haymet (Sydney) discussed the behavior of water and electrolytes near charged surfaces, and recent results for wholly molecular theories of electrical double layers were the topic of the last talk by G. Torrie (Kingston).

POLAR, IONIC AND ASSOCIATING FLUIDS

The contributions in these sessions, chaired by J. Perram and K. Gubbins, were approximately equally balanced between molecular simulation (Patey, van Leeuwen, Kusalik and Mezei) and integral equations (Nishimura, Yakub, Holovko and Blum). Haymet presented both molecular simulation and integral equation results for a new model of liquid water. Debenedetti's presentation concerned a lattice model theory for associating fluids.

G. Patey (Vancouver) described the first demonstration that dipolar forces alone can create an orientationally ordered liquid phase. MD simulations were used to show that strongly interacting dipolar spheres (both soft and hard) can form a ferroelectric phase (the first time that the existence of a ferroelectric nematic phase has been established for a model fluid) and that liquid crystals with columnar order could be obtained. The influence of boundary conditions and "dynamically induced" transitions was discussed. M. van Leeuwen (SHELL Amsterdam) presented the results of GEMC simulation results for the prediction of vapor-liquid equilibrium in pure methanol

using three three-site united-atom models published in the literature. The GEMC calculations proved quite sensitive to details of the intermolecular potentials, none of which was completely satisfactory. P. Kusalik (Dalhousie) reviewed the difficulties encountered in determining the dielectric constant of polar liquids from computer simulation. He showed that an examination of the distribution of fluctuations of the total dipole moment of the sample can be very useful in understanding long-standing problems, such as system-size and boundary condition effects. Knowledge of the functional form of this distribution can lead to significant reductions in the computational resources required to estimate the dielectric constant. In a wide-ranging talk, M. Mezei (New York) addressed several aspects of modeling liquid water. He discussed dimer potential surfaces and aspects of intramolecular potentials in the context of the existence of low-energy trifurcated structures and the importance and conformation dependence of the basis-set-superposition error and the zero-point vibration energy. He also described recently derived analytical expressions for the average contribution of molecules beyond a cutoff sphere and results on the free energy of solvation of sodium and lithium ions, indicating that the Born correction is still about a factor of two in error in the 10–14 Å range. The discussion was concluded with a demonstration of the feasibility of generating effective pairwise additive potentials based on the configurational energy of representative assemblies of molecules.

While simultaneously entertaining the audience with reflections and slides from a trip to the Antarctic to collect samples of a protein from a particular fish found near water/ice interfaces, A. Haymet (Sydney) described a model for water, called CF1, which is a modification of Stillinger's central force model designed to make the pressure be closer to that of real water. Classical MD simulations of the CF1 model were used to calculate the dissociation of water with the quite satisfactory result of pH = $8.5\ pm 0.7$ at ambient conditions. MD calculations of the structure of the bulk water were then used as input to an approximate integral equation theory for the structure and properties of water next to a planar interface. Predictions from the theory include the oxygen and hydrogen density profiles perpendicular to the interface, the mean electrostatic potential, the potential of zero charge and the differential capacitance.

H. Nishimura (Tokyo) described his approach to solving the hypernetted chain approximation (HNCA) for dipolar hard spheres. As he explained the approximations he invoked, it became clear that he was describing the linearized HNCA. Moreover, to solve the linearized HNCA he had rediscovered the invariant expansion approach of Wertheim. E. Yakub (Odessa) presented an integral equation theory for chemically associating molecules under the assumption that the number of other molecules to which each molecule can bond is limited. This property of saturation in the chemical bonding is explicitly introduced into the theory in a similar fashion to that proposed by Wertheim and extended by Kalyuzhnyi and Stell. M. Holovko (Lwow) presented the integral equation theory derived by him and Y. Kalyuzhnyi to account for association effects in ionic fluids. The theory is an extension of the Kalyuzhnyi and Stell formalism noted above and it involves separating the potential into associating and non-associating parts with each part handled by different approximations. Both numerical and analytical solutions of HNCA-like and MSA-like approximations were presented for models of 2-2 and highly asymmetric electrolyte solutions. L. Blum (Puerto Rico) described a simple potential model for water, originally proposed by Bratko, Blum and

Luzar, consisting of hard spheres with a point dipole and a potential well with the symmetry of a tetrahedral quadrupole. Structural results from the model were presented and the gon(−) and guu(−) were found to compare quite favorably with neutron scattering experiments. The agreement for goo(−) is not as good and reflects the hard core nature of the model.

P. Debenedetti (Princeton) described the use of a lattice model with orientation-dependent interactions to study the phase behavior and limits of stability of network-forming fluids, such as silica and water. These interactions give rise to a competition between bonded states of low energy, entropy, and density, and non-bonded states of high energy, entropy, and density. By suitable choice of the parameters, the mean-field solution of the model can be used to explain the anomalous behavior of supercooled water. The model's generality suggests that similar behavior can occur in other network-forming fluids.

NORMAL AND CHAIN-MOLECULE FLUIDS

These topics covered the last two sessions, which were chaired by W. Smith (Guelph) and E. Glandt (Philadelphia), respectively.

M. Wertheim (Haughton) gave a talk on the geometry of hard convex bodies in connection with the problem of determining the third virial coefficient and contributions to higher coefficients. He introduced geometric functionals of the pairs of hard bodies and discussed ways of their determination. D. Henderson (Mexico City) spoke on the bridge and correlation functions for hard spheres using inhomogeneous integral equations. T. Boublick (Prague) also dealt with the third virial coefficients of hard body fluids. In addition to the well-defined parameter of nonsphericity, he introduced another parameter in order to match the virial coefficient of both prolate and oblate bodies. R. Lustig (Aachen) concentrated on an 'exact' way of treating the "MD microcanonical ensemble" i.e. microcanonical ensemble in which the total momentum is conserved in contrast to the usual approach which uses the canonical expressions. The problem of simulating the systems of molecules with a surface adhesion was addressed by B. Borstnik (Ljubljana) who presented a variant of molecular dynamics tailored to this special case. J. Vrabec (Bochum) described the extension of the NpT + test particle simulation to mixtures. The method was applied to the system argon + methane and good agreement with real experimental data was reported. F. del Rio (Mexico City) gave an overview of the development reached by his research group for the square-well fluid and square-well fluid mixtures. C. Hall (Raleigh) reviewed the development of a class of successful equations of state for hard-chain-molecule fluids based on the generalized Flory dimer theory, in which the pressure is calculated in terms of the chain insertion probability. The last two talks, presented by Y. Chiew (Piscataway) and M. Banaszak (Annandale) dealt with realistic chain-molecule fluids both from the point of theory and simulations. Theories for equations of state were discussed and a variational theory for Lennard-Jones chains was also presented. Good agreement between the theory and simulation data for pressure of Lennard-Jones chains is observed.

SOCIAL EVENTS

Following the conference opening lecture, a social mixer was held in the dining room of the hotel, giving an excellent opportunity for the conference participants and their guests to renew old and make new acquaintances. On Tuesday, a group of enthusiasts took the opportunity to admire the mountains and castles of Bohemia from the bird-eye view. On Wednesday afternoon, the conference attendees were taken by bus to the "Moravian Karst", where they toured the magnificant caves, and took a cruise on the underground river. The planned barbecue party on Thursday evening was held indoors due to the inclement weather, but this did not dampen the festivities. From Tuesday through Thursday, an excellent Accompanying Persons Program involved visits to historic sites in the surrounding countryside and to the city of Brno.

This report was written by
P. Cummings, Oak Ridge Natl. Lab.
D. Frenkel, FOM Amsterdam
K. E. Gubbins, Cornell University, Ithaca
I. Nezbeda, Academy of Sciences, Prague
W. R. Smith, Univ of Guelph, Guelph

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