Akademie věd České republiky

Teze doktorské disertační práce
k získání vědeckého titulu „doktor věd"
ve skupině věd chemických

Molecular-Level Computer Simulation of Phase and Reaction Equilibria

Komise pro obhajoby doktorských disertací
v oboru chemické inženýrství

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Místo a datum: Praha 6. 10. 2003

Abstract

The accurate prediction of reaction and phase equilibria for complex chemical systems is an important problem in chemical engineering. These phenomena occur simultaneously during the industrially critical process of reactive distillation. In a series of papers, we have shown that molecular-level computer simulation is an alternative predictive approach to traditional (macroscopic) approaches and that the simulations do require less experimental input data than the traditional approaches. We have studied phase equilibria by our modification of the Gibbs Ensemble Monte Carlo method and by the Gibbs-Duhem integration technique combined with the molecular dynamics method; the methods have been applied to both model and real systems. Further, we have studied reaction equilibria in one- and two-phase systems by the Reaction Ensemble Monte Carlo simulation method. We have dealt with systems related to reactive-distillation processes and plasmas. Finally, we have developed a new Monte Carlo method for direct prediction of fluid systems at fixed total internal energy or enthalpy. We have applied the method to the prediction of the adiabatic temperature in reactors and to the prediction of the temperature change during Joule-Thomson processes.

1   Introduction

Phase and reaction equilibrium calculations for complex chemical systems are traditionally carried out by means of empirically-based thermodynamic equation of state and/or liquid-state activity-coefficient models. The main goal of such calculations is the prediction of the pressure-temperature-composition behavior of the mixture. In order to implement these approaches, particular experimental data concerning the behavior of each constituent pure fluid is required. These data are then combined with the mixture model; in addition, a mixture parameter appearing in the theory is often evaluated by means of an experimental measurement on the mixture. Given this input information, the system behavior is then calculated using standard thermodynamic relations. The accuracy of these approaches in predicting the experimental data varies; as with nearly all empirically-based methods, the path to further progress is not always clear.

The alternate approach to the calculation of phase and reaction equilibria involves modelling the intermolecular interactions between

the constituent molecules of the system followed by phase and reaction equilibrium calculations using various computer simulation techniques. In addition, computer simulation approaches can calculate the volumetric properties of the mixture, which are often difficult to determine experimentally.

Molecular-based simulation approaches have a considerable advantage over the empirically-based approaches in that predictions may be made in the absence of experimental data of any kind, provided one can construct an intermolecular potential model for the system. Such models can now be constructed by relatively straightforward means to within reasonable accuracy. They can be computed either by *ab initio* calculations or by a combination of *ab initio* calculations and an adjustment of some model parameters to conveniently chosen experimental property data. The latter approach usually performs better for the thermodynamics of the systems and our utilization of this approach for hydrofluorocarbon compounds is illustrated in Refs. [1, 2, 3].

2   What are Computer Simulations?

Computer simulations are in many respects very similar to real experiments. In a real experiment, we first prepare a sample of the material that we wish to study. Then, we connect the sample to some measuring instrument, and we measure the property of interest during a certain time interval. Since our measurement is subject to statistical noise, then the longer we average the more accurate our measurement becomes. In a computer simulation, we follow exactly the same approach. First, we prepare a sample *i. e.*, we select a model system typically consisting of several hundred particles. Then, we either solve Newton's equations of motion (in the molecular dynamics method) or we use the Metropolis algorithm (in the Monte Carlo method) for the system in hand until the properties of the system no longer change with time (*i. e.*, we equilibrate the system). After equilibration, we perform the actual measurement. In fact, some of the most common mistakes that can be made when performing a computer simulation are very similar to those that can be made in real experiments (*e. g.*, the sample is not prepared correctly, the measurement is too short, the system undergoes an irreversible change during the experiment, or we do not measure what we believe we are measuring). Computer simulations typically give us information about the positions and momenta of the particles in the system. This information is then converted to observable quantities such as the

pressure or the internal energy using standard statistical-mechanics relations.

3   Computer Simulation of Phase Equilibria

3.1   Modified Gibbs Ensemble Monte Carlo Method

In 1987, Panagiotopoulos suggested the first direct method for the simulation of phase equilibria, the Gibbs Ensemble Monte Carlo method. In this method, each coexistence phase is represented by a separate simulation box and phase equilibrium conditions (equality of temperature, pressure and chemical potentials) are achieved by a combination of unique Monte Carlo moves. The Gibbs Ensemble Monte Carlo method has not been considered to be competitive to the traditional approaches in their predictive accuracy of the vapor-liquid equilibrium properties, primarily a result of the fact that simulated vapor pressures of pure fluids are very sensitive to the details of the underlying intermolecular potential model. We circumvented the problem of accurately obtaining the simulation pure-fluid vapor pressures by incorporating the experimental pure-fluid vapor pressure data into the original Gibbs Ensemble Monte Carlo method as described in Ref. [4]. Refs. [4, 5] showed that the modified Gibbs Ensemble Monte Carlo method improved the accuracy of the vapor-liquid equilibrium prediction for mixtures; the simulation results were in very good agreement with the traditional approaches as well as the experimental results. Unlike macroscopic thermodynamic-based approaches such as the Wilson and the UNIFAC approximations, no experimental information concerning the mixtures was required.

3.2   Gibbs-Duhem Integration Method

In 1993, Kofke proposed a direct computer simulation method for phase equilibrium calculations, the Gibbs-Duhem integration method. The method combines the best elements of the Gibbs Ensemble Monte Carlo technique and thermodynamic integration. For pure substances, given the conditions of coexistence at a single coexistence point, simultaneous but independent isothermal-isobaric ensemble simulations of each phase can be carried out in succession in order to trace out the entire coexistence curve. For mixtures, given the conditions of coexistence for the pure substances at the special temperature and pressure, simultaneous but independent semi-grand ensemble simulations are similarly

carried out in succession to determine the entire phase envelope. In both cases, simulation parameters are adjusted during the simulation run in order to satisfy the Clapeyron-type equation. The Clapeyron-type equation is a first-order nonlinear differential equation that prescribes how the pressure must change with respect to the temperature in order to maintain coexistence for the case of pure substances, while similarly it prescribes how the pressure must change with respect to the species fugacity fractions in the case of mixtures. The Clapeyron-type equation is solved by the predictor-corrector method and the integrand is evaluated using the simulations.

Kofke's original works combined the Gibbs-Duhem integration approach with the Monte Carlo method and applied the method to model atomic fluids. In Refs. [6, 7, 8, 9, 10, 11, 12], we used the Gibbs-Duhem integration approach with the molecular dynamics method (the molecular dynamics method can determine dynamic properties of the coexistence phases while the Monte Carlo method cannot) and applied the approach to both idealized models as well as real systems. In Refs. [6, 7, 8], the method was utilized to generate vapor-liquid equilibrium data for polar and nonpolar molecular model fluids. Subsequently, these data were used in the description of the vapor-liquid equilibria of alternative refrigerants [9]. Further, we applied the method to the prediction of the vapor-liquid equilibria of chlorine modelled with an anistropic potential [10]; simulation results were in excellent agreement with experiments. Ref. [11] dealt with an application of the Gibbs-Duhem integration technique to vapor-liquid equilibria of model molecular mixtures. Finally, we adopted the Gibbs-Duhem integration approach for solid-fluid equilibrium calculations in Ref. [12]. In Ref. [12], we combined the approach with the Parrinello-Rahman molecular dynamics method for solid-phase simulations and predicted solid-fluid equilibria for a model molecular system.

4   Simulation of Reaction Equilibria

In 1994, Smith and Tříska, and Johnson *et al.* independently proposed the first direct method for the simulation of reaction equilibria, the Reaction Ensemble Monte Carlo method. After specifying the system stoichiometry and the thermodynamic constraints, the method only requires a knowledge of the species intermolecular potentials and their ideal-gas properties. The method's simplicity allows it to be readily used for situations involving any number of simultaneous reactions as well as

reactions occurring within or between phases. In collaboration with the author of the method Prof. W. R. Smith, we used the method to predict reaction and phase equilibria for the reacting mixtures: Br_2+Cl_2+BrCl; isobutene+methanol+MTBE [13, 14]. The simulation results were in very good agreement with those given by the traditional approaches. In contrast to these approaches, no experimental information concerning the mixtures was required.

We further demonstrated the generality of the method for predicting the thermodynamic behavior of chemically reacting plasmas using a molecular-level model based on the underlying atomic and ionic interactions. We first modified and applied the Reaction Ensemble Monte Carlo method for the test case of a helium plasma in Ref. [15]. In Ref. [16], we then calculated new results for the thermodynamic properties of argon and air plasmas; these are complex systems involving 7 and 26 reactions, respectively. We calculated the plasma thermodynamic properties for temperatures up to 100,000 K. We also evaluated the contributions of different aspects of the model to the calculated thermodynamic properties. We compared the essentially exact simulation results with those obtained from the Debye-Hückel approximation to assess its accuracy. For argon and air plasmas, we have found that the accuracy of the Debye-Hückel approximation results, although reasonable, is generally worse than was observed for the helium plasma at a similar pressure. This was likely due to the effect of larger molecular sizes in the case of the argon and air plasmas. Also, based on the findings for the helium plasma, we expect that the errors of the Debye-Hückel results for both the argon and air plasmas will increase with increasing pressure.

5 Simulation at Fixed Total Internal Energy or Enthalpy

Calculations of the properties of fluid systems at fixed total internal energy or at fixed total enthalpy are other important problems in chemical engineering. Two examples are: (i) adiabatic flash (Joule-Thomson expansion) calculations for non-reacting pure fluids and for mixtures at fixed total enthalpy and pressure; and (ii) adiabatic flame-temperature calculations for reacting mixtures at either fixed total internal energy and volume, or at fixed total enthalpy and pressure. For such problems the main objective is to calculate the system (absolute) temperature and other system properties.

In Ref. [17], we presented a new methodology for performing Monte Carlo simulations at fixed total internal energy or at fixed total enthalpy, for both non-reacting and reacting systems. The resulting method is the first to enable the direct solution of such problems. In Ref. [18], we applied the method to the predictions of temperature changes for the alternative refrigerant HFC-32 undergoing the Joule-Thomson expansions in single- and two-phase regions. In Ref. [19], we further illustrated our methodology on an adiabatic calculation involving the ammonia synthesis reacting system.

6 Conclusion

It is now 40 years since the first computer simulation of a liquid was carried out at the Los Alamos National Laboratory in the United States. The Los Alamos computer, called MANIAC, was at that time one of the most powerful available. The first method for phase equilibrium simulations was proposed in 1987 and the first method for the simulation of reaction equilibria was suggested in 1994. In recent years, computer simulation has become a standard tool for predicting the macroscopic properties of systems. Rapid development and availability of fast computers, progress in *ab initio* calculations of the interaction potentials as well as the development of new simulation techniques enable us to study larger and more complex systems and their phase behavior. However, we must be mindful that the intent of computer simulation is not only to provide us numerical results for the system properties but also to provide a molecular-level understanding of the system based on the interactions of the constituent molecules making up the system. Therefore, the computer simulation of model systems plays a critical role in understanding and assessing the effects of various types of molecular forces on the system properties. The computer simulation should not be regarded as a competitor of experimental and macroscopic approaches but rather their partner. A partner that brings a deep-molecular insight into the system properties. We hope that we have contributed to some extent to this effort.

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Abstracts of Papers

Effective potentials for liquid simulation of the alternative refrigerants HFC-32: CH_2F_2 and HFC-23: CHF_3

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Abstract

Site–site potentials for use in liquid simulations of difluoromethane and trifluoromethane are constructed using effective interactions. These rigid molecules have interaction centres at the atomic sites coinciding with gas-phase monomer geometries. Atomic interactions consist of van der Waals (vdW) and Coulombic parts. The potential functions are adjusted to give simulated liquid properties for temperatures between 0.5 (T/T_C) and 0.9 (T/T_C) on the saturated liquid curves.

The proposed potentials are used in constant pressure–constant temperature (NPT) and constant temperature (NVT) molecular dynamics (MD) simulations of saturated liquid difluoromethane and trifluoromethane. The simulated results of thermodynamic properties and radial distribution functions are compared with experiments where available and the advantages of our potential are discussed.

Keywords: Computer simulation; Molecular interactions; Alternative refrigerants; Radial distribution functions; Saturated liquid properties

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Effective potentials for liquid simulation of the alternative refrigerants HFC-134a (CF_3CH_2F) and HFC-125 (CF_3CHF_2)

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Abstract

Isotropic atom–atom potentials for use in liquid simulations of 1,1,1,2-tetrafluoroethane (HFC-134a; CF_3CH_2F) and pentafluoroethane (HFC-125; CF_3CHF_2) are constructed using effective interactions. These semirigid molecules have interaction centres at the atomic sites and internal rotation about the C–C bond. Intermolecular interactions consist of repulsion–dispersion and Coulombic parts. The internal rotation about the C–C bond is described by a small angle cosine Fourier expansion in the dihedral angle. The potential functions are adjusted to give simulated liquid properties for temperatures between 0.5 (T/T_C) and 0.9 (T/T_C) on the saturated liquid curves.

The proposed potentials are used in constant pressure–constant temperature and constant volume–constant temperature molecular dynamics simulations of saturated liquid HFC-134a and HFC-125. Simulated results for thermodynamic, structural and dynamic properties are presented, and compared with experimental data where available.

Keywords: Autocorrelation functions; Molecular interactions; Molecular simulation; Pentafluoroethane; Radial distribution functions; Refrigerants; Saturated liquid properties; 1,1,1,2-Tetrafluoroethane

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Molecular dynamics simulations of fluorinated ethanes

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Differences in thermodynamic properties are investigated by means of constant pressure–constant temperature molecular dynamics simulations for three isomeric pairs of fluorinated ethanes: CHF_2CHF_2 (HFC-134) and CF_3CH_2F (HFC-134a); CF_3CH_3 (HFC-143) and CHF_2CH_2F (HFC-143a); and CH_2FCH_2F (HFC-152) and CHF_2CH_3 (HFC-152a). These semi-rigid molecules have interaction centres at the atomic sites and internal rotation about the C–C bond. Intermolecular interactions consist of repulsion–dispersion and Coulombic parts. Molecular dynamics simulations were performed at the normal boiling points and the accord between simulated and experimental values of the potential energy and molar volume is very good. A great difference was found between the repulsion–dispersion and Coulombic contributions to the potential energy for every isomeric pair. A detailed analysis of the repulsion–dispersion and Coulombic interactions was carried out and was discussed in relation to the thermodynamic properties. A comparison of the radial distribution functions, autocorrelation functions and self-diffusion coefficients for these substances is also presented.

Accurate Computer Simulation of Phase Equilibrium for Complex Fluid Mixtures. Application to Binaries Involving Isobutene, Methanol, Methyl *tert*-Butyl Ether, and *n*-Butane

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We have developed a new method, called the reaction Gibbs ensemble Monte Carlo (RGEMC) method, for the computer simulation of the phase equilibria for multicomponent mixtures, given an intermolecular potential model for the constituent molecular species. The approach treats the phase equilibrium conditions as a special type of chemical reaction and incorporates knowledge of the pure-substance vapor pressure data into the simulations. Unlike macroscopic thermodynamic-based approaches like the Wilson and the universal quasichemical functional group activity coefficients (UNIFAC) approximations, no experimental information concerning the mixtures is required. In addition to the *PTxy* phase equilibrium data, the volumetric properties of the mixture are calculated. We developed intermolecular potential models based on the optimized potentials for liquid simulations (OPLS) of Jorgensen and used the RGEMC method to predict phase equilibrium data for the binary systems isobutene + methyl *tert*-butyl ether (MTBE) and the binaries formed by methanol with isobutene, MTBE, and *n*-butane. The predictions are excellent, and of comparable accuracy to those obtained using the Wilson and the UNIFAC thermodynamic-based approaches, even though such approaches use experimental mixture information.

Accurate vapour–liquid equilibrium calculations for complex systems using the reaction Gibbs ensemble Monte Carlo simulation method

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Abstract

The reaction Gibbs ensemble Monte Carlo (RGEMC) computer simulation method [J. Phys. Chem. B 103 (1999) 10496] is used to predict the vapour–liquid equilibrium (VLE) behaviour of binary mixtures involving water, methanol, ethanol, carbon dioxide, and ethane. All these mixtures contain molecularly complex substances, and accurately predicting their VLE behaviour is a considerable challenge for molecular-based approaches, as well as for traditional engineering approaches. The substances are modelled as multi-site Lennard–Jones (LJ) plus Coulombic potentials with standard mixing rules for unlike site interactions. No adjustable binary-interaction parameters and no mixture experimental properties are used in the calculations; only readily-available pure-component vapour-pressure data are required. The simulated VLE predictions are compared with experimental results and with those of two typical semi-empirical macroscopic-level approaches. These latter are the UNIFAC liquid-state activity-coefficient model combined with the simple truncated virial equation of state, and the hole quasi-chemical group contribution equation of state. The agreement of the simulation results with the experimental data is generally good and also comparable with and in some cases better than those of the macroscopic-level empirical approaches. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: VLE; Computer simulations; Mixtures; Water; Ethane; Carbon dioxide; Ethanol; Methanol

DIRECT EVALUATION OF VAPOUR-LIQUID EQUILIBRIA BY MOLECULAR DYNAMICS USING GIBBS-DUHEM INTEGRATION

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An application of the Gibbs-Duhem integration [D. A. Kofke, *J. Chem. Phys.*, **98**, 4149 (1993)] for the direct evaluation of vapour-liquid equilibria by molecular dynamics is presented. The Gibbs-Duhem integration combines the best elements of the Gibbs ensemble Monte Carlo technique and thermodynamic integration. Given conditions of coexistence at one coexistence point, simultaneous but independent NPT molecular dynamics simulations of each phase are carried out in succession along saturation lines. In each simulation, the saturated pressure is adjusted to satisfy the Clapeyron equation. The Clapeyron equation is a first-order nonlinear differential equation that prescribes how the pressure must change with the temperature to maintain coexistence. The Clapeyron equation is solved by the predictor-corrector method. Running averages of enthalpy and density of each phase are used to evaluate the right-hand side of the Clapeyron equation. The Gibbs-Duhem integration method is applied to a two-centre Lennard-Jones fluid of elongation 0.505. The starting coexistence point was taken from published data or was determined *via* the Widom test particle insertion method. Implementation of the Gibbs-Duhem integration with a thermodynamic model for the vapour phase is also presented.

KEY WORDS: Vapour-liquid equilibria, molecular dynamics, Gibbs-Duhem integration.

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Vapour–liquid equilibria for dipolar two-centre Lennard-Jones fluids by Gibbs–Duhem integration

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Abstract

Vapour–liquid equilibria for dipolar two-centre Lennard-Jones fluids having elongations $L = 0.22$, 0.3292, 0.505 and 0.67, and axial dipole moments $\mu^{*2} = 2$, 4, 8 and 12 are determined by the Gibbs–Duhem integration method. Starting coexistence points of the Gibbs–Duhem integrations are obtained by the Maxwell construction. Critical temperatures and densities are estimated from the law of rectilinear diameter and the critical scaling relation. Calculated vapour pressures as well as vapour and liquid densities are correlated by Wagner equations. The dipole moment increases the critical temperature and pressure, and affects slightly the critical density. The dipole moment provokes deviations from the principle of corresponding states. The temperature–density coexistence envelope is broadened and the slope of the vapour pressure curve increases with the dipole moment. Application of vapour–liquid equilibria of the dipolar two-centre Lennard-Jones fluids to real fluids is demonstrated on the alternative refrigerant HFC-134a. © 1997 Elsevier Science B.V.

Keywords: Critical properties; Molecular simulation; Polar fluids; Principle of corresponding states; Real fluids; Vapour–liquid equilibria

VAPOUR – LIQUID EQUILIBRIA OF DIPOLAR TWO-CENTRE LENNARD-JONES FLUIDS FROM A PHYSICALLY BASED EQUATION OF STATE AND COMPUTER SIMULATIONS

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The paper is concerned with the model fluid consisting of two-centre Lennard-Jones molecules with embedded axial dipole moment (2CLJD), particularly with its vapour–liquid phase equilibrium behaviour as calculated from different molecular simulation methods and from an analytical equation of state. The focus of the present study is the parameter region of large elongations (L in the range from 0.505 to 1.0) and large dipole moments (μ^{*2} in the range from 9 to 12) of the 2CLJD fluid. In order to assess the performance of independent molecular simulation methods and to examine the validity of a physically based equation of state of the augmented van der Waals type within this parametric region, we have calculated the 2CLJD model fluid properties along the vapour–liquid coexistence locus by the Gibbs ensemble Monte Carlo method, Gibbs-Duhem integration technique looking at the effect of different starting state points, the NpT plus test particle method, and from the equation of state. Within the entire region examined, fairly good mutual agreement of the independent simulation methods is observed. The equation of state represents a good compromise between the results of different simulation methods at intermediate elongations but fails at large elongations. The extended base of pseudoexperimental data is prerequisite for further equation of state development.

Vapor–Liquid Equilibria of Alternative Refrigerants by Molecular Dynamics Simulations[1]

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Alternative refrigerants HFC-152a (CHF_2CH_3), HFC-143a (CF_3CH_3), HFC-134a (CF_3CH_2F), and HCFC-142b (CF_2ClCH_3) are modeled as a dipolar two-center Lennard–Jones fluid. Potential parameters of the model are fitted to the critical temperature and vapor–liquid equilibrium data. The required vapor–liquid equilibrium data of the model fluid are computed by the Gibbs–Duhem integration for molecular elongations $L = 0.505$ and 0.67, and dipole moments $\mu^{*2} = 0, 2, 4, 5, 6, 7$, and 8. Critical properties of the model fluid are estimated from the law of rectilinear diameter and critical scaling relation. The vapor–liquid equilibrium data are represented by Wagner equations. Comparison of the vapor–liquid equilibrium data based on the dipolar two-center Lennard–Jones fluid with data from the REFPROP database shows good-to-excellent agreement for coexisting densities and vapor pressure.

KEY WORDS: alternative refrigerants; Gibbs–Duhem integration; HCFC-142b; HFC152a; HFC-143a; HFC-134a; Lennard–Jones two-center dipolar potential model; molecular simulations; vapor–liquid equilibria.

Vapor–liquid equilibrium, fluid state, and zero-pressure solid properties of chlorine from anisotropic interaction potential by molecular dynamics

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Abstract

Extensive examination of the anisotropic interaction potential of chlorine by Rodger et al. [P.M. Rodger, A.J. Stone, D.J. Tildesley, J. Chem. Soc., Faraday Trans. 2, 83 (1987) 1689–1702] (with interaction sites located at the positions of atoms in a molecule and the electrostatic part found by ab initio calculations) for its predictive power has been performed. We have calculated (i) the second virial coefficient by using a non-product algorithm, (ii) a series of liquid-phase state points in the temperature and pressure ranges of 200 to 400 K and 0 to 6.2 MPa, respectively, by the constant pressure–constant temperature molecular dynamics simulations, (iii) vapor–liquid equilibrium and heat of vaporization from the triple point (172 K) to 300 K by the Gibbs–Duhem integration method combined with simultaneous (but independent) constant pressure–constant temperature molecular dynamics simulations of the vapor and liquid phases, and (iv) the properties of the zero-pressure crystal structures by molecular dynamics technique due to Parinello and Rahman [M. Parrinello, A. Rahman, Phys. Rev. Lett. 45 (1980) 1196–1199]. Generally, good to excellent agreement of the calculated properties with the corresponding values for real chlorine was observed. The results obtained from the investigated interaction potential are equivalent to (or even better than) those reported for a more complicated potential by Wheatley and Price [R.J. Wheatley, S.L. Price, Mol. Phys. 71 (1990) 1381–1404]. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chlorine; Intermolecular potential; Molecular simulation; Vapor–liquid equilibria; Vapor pressure; Density

DIRECT EVALUATION OF VAPOUR-LIQUID EQUILIBRIA OF MIXTURES BY MOLECULAR DYNAMICS USING GIBBS-DUHEM INTEGRATION

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We present an extension of the Gibbs-Duhem integration method that permits direct evaluation of vapour-liquid equilibria of mixtures by molecular dynamics. The Gibbs-Duhem integration combines the best elements of the Gibbs ensemble Monte Carlo technique and thermodynamic integration. Given conditions of coexistence of pure substances, simultaneous but independent molecular dynamics simulations of each phase at constant number of particles, constant pressure, constant temperature and constant fugacity fraction of species 2 are carried out in succession along coexistence lines. In each simulation, the coexistence pressure is adjusted to satisfy the Clapeyron-type equation. The Clapeyron-type equation is a first-order nonlinear differential equation that prescribes how the pressure must change with the fugacity fraction of species 2 to maintain coexistence at constant temperature. The Clapeyron-type equation is solved by the predictor-corrector method. Running averages of mole fraction and compressibility factor for the two phases are used to evaluate the right-hand side of the Clapeyron-type equation. The Gibbs-Duhem integration method is applied to three prototypes of binary mixtures of the two-centre Lennard-Jones fluid having various elongations. The starting points on the coexistence curve were taken from published data.

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DIRECT EVALUATION OF SOLID–LIQUID EQUILIBRIA BY MOLECULAR DYNAMICS USING GIBBS-DUHEM INTEGRATION

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An application of the Gibbs-Duhem integration [D. A. Kofke, *J. Chem. Phys.*, **98**, 4149 (1993)] for the direct evaluation of solid–liquid equilibria by molecular dynamics is presented. The Gibbs-Duhem integration combines the best elements of the Gibbs ensemble Monte Carlo technique and thermodynamic integration. Given conditions of coexistence at one coexistence point, simultaneous but independent constant pressure–constant temperature molecular dynamics simulations of each phase are carried out in succession along saturation lines. In each simulation, the saturated pressure is adjusted to satisfy the Clapeyron equation, a first-order nonlinear differential equation that prescribes how the pressure must change with the temperature to maintain coexistence. The Clapeyron equation is solved by the predictor–corrector method. Running averages of enthalpy and density of each phase are used to evaluate the right-hand side of the Clapeyron equation. The Gibbs-Duhem integration method is applied to a two-centre Lennard-Jones system with elongation 0.67. The starting coexistence point is determined as the point of intersection of solid and liquid isotherm branches in the pressure *vs* chemical potential plane.

The reaction ensemble method for the computer simulation of chemical and phase equilibria. II. The Br_2+Cl_2+BrCl system

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The reaction ensemble Monte Carlo (REMC) method [W. R. Smith and B. Tříska, J. Chem. Phys. **100**, 3019 (1994)] is used to study combined reaction and vapor–liquid equilibrium of the Br_2+Cl_2+BrCl system. The substances are modeled as nonpolar and dipolar two-site Lennard-Jones molecules with Lorentz–Berthelot mixing rules for unlike atoms. No parameters were fitted to any mixture properties in our calculations. The simulated data are compared with experimental results, and with previous simulation data for the mixture obtained by an indirect semigrand ensemble approach. The REMC method efficiently calculates the complete phase compositions, whereas only a limited subset is available experimentally. The agreement of the simulations with experiment is good. In the course of this work, we used the Gibbs ensemble Monte Carlo method (which may be regarded as a special case of the REMC method) to calculate the vapor–liquid equilibrium properties of pure BrCl; since this compound is chemically unstable, such data is experimentally inaccessible. © *1999 American Institute of Physics.*
[S0021-9606(99)50112-8]

Molecular Simulation of Multicomponent Reaction and Phase Equilibria in MTBE Ternary System

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Reaction and phase equilibria in the isobutene + methanol + MTBE ternary system were studied using the reaction-ensemble Monte Carlo (REMC) simulation method. The system was modeled at the molecular level by an OPLS force field. No adjustable binary cross-interaction parameters or mixture data of any kind were used in the simulation model, and only vapor-pressure data for the pure components was required as input. The REMC method also computes excess internal energies and molar volumes as a biproduct of the simulations. Both the nonreacting and reacting ternary systems were considered over the temperature range of practical interest at 5 bar. Results are compared with the calculations using two conventional thermodynamic approaches: the Wilson and UNIFAC free-energy models for the liquid phase, together with a truncated virial equation of state for the gas phase in both cases. Computer simulation results were similar to those of the thermodynamic approaches, and they are arguably more accurate.

Computer simulation of the thermodynamic properties of high-temperature chemically-reacting plasmas

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The Reaction Ensemble Monte Carlo (REMC) computer simulation method [W. R. Smith and B. Tříska, J. Chem. Phys. **100,** 3019 (1994)] is employed to predict the thermodynamic behavior of chemically reacting plasmas using a molecular-level model based on the underlying atomic and ionic interactions. Unlike previous plasma simulation studies, which were restricted to fairly simple systems of fixed composition, the REMC approach is able to take into account the effects of the ionization reactions. In the context of the specified molecular model, the computer simulation approach gives an essentially exact description of the system thermodynamics. We develop and apply the REMC method for the test case of a helium plasma. We calculate plasma compositions, molar enthalpies, molar volumes, molar heat capacities, and coefficients of cubic expansion over a range of temperatures up to 100 000 K and pressures up to 400 MPa. We elucidate the contributions of the Coulombic forces, ionization-potential lowering, and short-ranged interactions to the thermodynamic properties. We compare the results with those obtained using macroscopic-level thermodynamic approximations, including the ideal-gas (IG) and the Debye–Hückel (DH) approaches. For the helium plasma, the short-ranged forces are found to be relatively unimportant, but we expect these to be important for molecular systems. The DH theory is always more accurate than the IG approximation. The DH theory yields compositions that slightly underpredict the overall degree of ionization. For the molar heat capacity and the coefficient of cubic expansion, the DH theory is accurate at lower pressures, but at 400 MPa yields results that are up to 40% in error for the molar heat capacity. © *2000 American Institute of Physics.* [S0021-9606(00)50236-0]

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REMC computer simulations of the thermodynamic properties of argon and air plasmas

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The reaction ensemble Monte Carlo (REMC) computer simulation method (Smith, W. R., and Triska, B., 1994, *J. chem. Phys.*, **100,** 3019) is employed to calculate reaction equilibrium in multi-reaction systems using a molecular based system model. The compositions and thermodynamic properties of argon plasmas (7 reactions) and air plasmas (26 reactions) are studied using a molecular level model based on the underlying atomic and ionic interactions. In the context of the specified molecular model, the REMC approach gives an essentially exact description of the system thermodynamics. Calculations are made of plasma compositions, molar enthalpies, molar volumes, molar heat capacities, and coefficients of cubic expansion over a range of temperatures up to 100 000 K at a pressure of 10 bar, and the results are compared with those obtained using the macroscopic level ideal-gas and Debye–Hückel approximations.

Direct Monte Carlo simulation methods for nonreacting and reacting systems at fixed total internal energy or enthalpy

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(Received 5 February 2002; published 18 July 2002)

A Monte Carlo computer simulation method is presented for directly performing property predictions for fluid systems at fixed total internal energy, U, or enthalpy, H, using a molecular-level system model. The method is applicable to both nonreacting and reacting systems. Potential applications are to (1) adiabatic flash (Joule-Thomson expansion) calculations for nonreacting pure fluids and mixtures at fixed (H,P), where P is the pressure; and (2) adiabatic (flame-temperature) calculations at fixed (U,V) or (H,P), where V is the system volume. The details of the method are presented. The method is compared with existing related simulation methodologies for nonreacting systems, one of which addresses the problem involving fixing portions of U or of H, and one of which solves the problem at fixed H considered here by means of an indirect approach. We illustrate the method by an adiabatic calculation involving the ammonia synthesis reaction.

Direct molecular-level Monte Carlo simulation of Joule–Thomson processes

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We present an application of the recently developed constant enthalpy–constant pressure Monte Carlo method [SMITH, W. R., and LÍSAL, M., 2002, *Phys. Rev.* E, **66**, 01114] for the direct simulation of Joule–Thomson expansion processes using a molecular-level system model. For the alternative refrigerant HFC-32 (CH_2F_2), we perform direct simulations of the isenthalpic integral Joule–Thomson effect (temperature drop) resulting from Joule–Thomson expansion from an initial pressure to the representative final pressure of 1 bar. We consider representative expansions from single-phase states yielding final states in both single-phase and two-phase regions. We also predict the dependence of $T(P, h)$ and of the Joule–Thomson coefficient, $\mu(P, h)$, on pressure along several representative isenthalps, as well as points on the Joule–Thomson inversion curve. HFC-32 is modelled using a five-site potential taken from the literature, with parameters derived from *ab initio* calculations and vapour–liquid equilibrium data. The simulated results show excellent agreement with those calculated from an international standard equation of state.

Adiabatic Monte Carlo Simulation of Ammonia Synthesis Reaction[*]

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Abstract

We describe the implementation of a recently developed Monte Carlo algorithm for the molecular-based calculation of fluid properties at constant enthalpy [W. R. Smith, and M. Lísal, Phys. Rev. E **66**, 01114-1 (2002)]. We apply the algorithm to the calculation of the composition and adiabatic flame temperature for the industrially important ammonia synthesis reaction.