LBL-38213
UC-401
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Submitted to Journal of Chemical Physics

Three-Body Interactions in Fluids from Molecular Simulation: Vapor-Liquid Phase Coexistence of Argon

R.J. Sadus and J.M. Prausnitz

December 1995

REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library.
LBL-38213
Copy 1

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-38213
UC-401

Three-body interactions in fluids from molecular simulation: vapor-liquid phase coexistence of argon

Richard J. Sadus and J. M. Prausnitz

Department of Chemical Engineering
University of California
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

December 1995

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Three-body interactions in fluids from molecular simulation: vapor-liquid phase coexistence of argon

Richard J. Sadus

Computer Simulation and Physical Applications Group, School of Computer Science and Software Engineering, Swinburne University of Technology, PO Box 218, Hawthorn, Victoria 3122, Australia

J.M. Prausnitz

Chemical Engineering Department, University of California, and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA.

Abstract.

Gibbs-ensemble molecular simulations are reported for the vapor-liquid phase coexistence of argon using the two-body Lennard-Jones potential. During the simulation, the possible effect of three-body interactions on the pressure and configurational energy of the vapor and liquid phases is estimated by performing calculations with three-body potentials. The intermolecular potentials used for the three-body calculations incorporate the influence of both three-body dispersion and three-body repulsion interactions. The results show that three-body repulsion makes a significant contribution to three-body interactions in the liquid phase. The effect of three-body dispersion is offset substantially by three-body repulsion.

I. Introduction

Fluid-phase transitions are a direct consequence of intermolecular interactions. Historically, however, prediction of vapor-liquid equilibria has relied almost exclusively on approximate theoretical models or on empirical equations of state rather than on rigorous models for intermolecular interaction at high fluid densities. The advent of new molecular simulation techniques[1] such as the Gibbs ensemble method[2] provides an opportunity to apply directly our knowledge of intermolecular potentials to the prediction of phase equilibria of fluids. The advantage of molecular simulation over other predictive methods is that comparison of simulation results with experimental data provides an unambiguous test for the accuracy of theory, particularly for the intermolecular potential used in the simulation. For a one-component fluid, the only assumption made concerning molecular interactions is the choice of intermolecular potential.

It is commonly assumed that the outcome of molecular interactions can be adequately attributed to the effect of two-body interactions alone.. Accurate two-body potentials have been developed[3] for some of the noble gases and the influence of three- or more-body interactions has been incorporated as "density effects" in some models.[4] Consequently, the role of three- or more-body interactions is inadequately documented. Calculations using three-body interactions are typically limited to those based on the triple-dipole dispersion term of Axilrod and Teller;[5] those calculations commonly contribute 5-10% of the pairwise additive energy of the liquid phase. These results suggest that pairwise calculations alone cannot fully account for the effects of intermolecular interactions. Several simulation studies[6] for phase coexistence of both one-component and two-component fluids using pairwise potentials but no work on deviations from pairwise additivity has been reported.

The purpose of this work is to examine the role of three-body interactions on the vapor-liquid coexistence of simple fluids. The Gibbs ensemble[2] is used to simulate vapor-liquid coexistence for argon and the results are compared with experimental data. Vapor-liquid coexistence is simulated using the conventional Lennard-Jones pairwise potential. However, during the simulation the effect of three-body interactions on the pressure and configurational energy of the fluid is estimated by calculations using three-body potentials. The effect of three-body dispersion interactions are calculated using the Axilrod-Teller term.[5] The contribution of

repulsive three-body interactions is also included using an electrostatic distortion potential developed by Sherwood et al.[7]

II. Intermolecular Potentials and Calculation Details

The Lennard-Jones potential was used to calculate interactions between pairs of molecules separated by a distance r_{ij}

$$u(ij) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1}$$

where the ε and σ parameters are characteristic of the strength of intermolecular interaction and molecular size, respectively. The parameters (ε/k = 119.8 K, σ = 0.341 nm) for argon used in this work are not "effective" parameters for dense argon. Instead, they are based on analysis of gas-phase virial coefficient data.[8] More accurate pair-potentials for argon are available.[3] However, the Lennard-Jones potential is simple to implement and it can be used to predict[2] accurately the coexistence curve of argon with the exception of the near-critical region.

Two contributions to three-body interactions were used in the simulations. The Axilrod-Teller term[5] accounts for the contribution of three-body dispersion interactions:

$$u^{disp}(ijk) = \nu\frac{\left(1+3\cos\theta_i\cos\theta_j\cos\theta_k\right)}{\left(r_{ij}r_{ik}r_{jk}\right)^3} \tag{2}$$

where θ refers to the inside angles of a triangle formed by three molecules i, j and k (see Fig. 1) and ν is the non-additive coefficient. This potential is negative for near-linear configurations and positive for acute triangular arrangements. Accurate values of the non-additive coefficient ν are available[9] for all of the pure noble gases and many combinations of the noble gases. For argon, ν = 7.3382×10^{-90} Jcm[9].

Sherwood et al.[7] recognised that three-body repulsions are significant at small interatomic separations. They developed two approximate models for three-body repulsive interactions at small interatomic separations. Their electrostatic distortion model is particularly suitable for our

simulations because both angle-dependent terms and the pair separations are already evaluated in calculation of the Axilrod-Teller term. For a one-component fluid, we have

$$u^{rep}(ijk) = \frac{4\varepsilon\sigma^{21}}{9}\left[\frac{\cos 2\theta_i}{(r_{ij}r_{ik})^9 r_{jk}^3} + \frac{\cos 2\theta_j}{(r_{ij}r_{jk})^9 r_{ik}^3} + \frac{\cos 2\theta_k}{(r_{ik}r_{jk})^9 r_{ij}^3}\right] \tag{3}$$

where ε and σ are the Lennard-Jones parameters. Eq. (3) was obtained[7] by considering the effect of a third body on the repulsion between the pairs of atoms that constitute the triplet illustrated in Fig. 1. The different contributions to Eq. (3) represent the effect of a third atom on the repulsion experienced by the three pairs of atoms. The contribution[7] of three-body repulsion to the non-additivity of the third virial coefficient may be equivalent to 45% of the magnitude of the Axilrod-Teller term. The contribution from Eq. (3) was evaluated for each triplet of atoms which had at least one pair-separation $< \sigma$. The total contribution of three-body interactions becomes

$$u(ijk) = u^{disp}(ijk) + u^{rep}(ijk) \tag{4}$$

The energy (E) and pressure (P) were evaluated using

$$E = \langle E_2 \rangle + \langle E_3 \rangle \tag{5}$$

$$E_2 = \sum_i \sum_{j>i} u(ij) \tag{6}$$

$$E_3 = \sum_i \sum_{j>i} \sum_{k>j>i} u(ijk) \tag{7}$$

$$P = kT\langle \rho \rangle + \langle P_2 \rangle + \langle P_3 \rangle \tag{8}$$

$$P_2 = -\frac{1}{3V}\sum \left(r_{ij}\partial / \partial r_{ij}\right) u(ij) \tag{9}$$

$$P_3 = -\frac{1}{3V}\sum_{i<j<k}\left(r_{ij}\partial / \partial r_{ij} + r_{ik}\partial / \partial r_{ik} + r_{jk}\partial / \partial r_{jk}\right)\mu(ijk) \tag{10}$$

where T, V, ρ and k denote temperature, volume, density and the Boltzmann constant, respectively. Subscripts 2 and 3 refer to the contribution of two-body and three-body interactions, respectively and the angle brackets indicate ensemble averages. The chemical potential was determined during attempted particle interchanges using the formula proposed by Smit et al.[10]

$$\mu_i = -kT\ln\left\langle \frac{V_I}{N_{I,i}+1}\exp(-\beta\Delta U_{It})\right\rangle \tag{11}$$

where ΔU_{It} is the configurational energy change of region I during attempted particle transfers, N is the number of particles in the region.

III. Simulation Details

The NVT-Gibbs ensemble[2] was used to simulate the coexistence of liquid and vapor phases. 300 molecules were partitioned between two boxes to simulate the vapor and liquid phases. The temperature of the entire system is held constant and surface effects are avoided by placing each box at the centre of a periodic array of identical boxes. Equilibrium is achieved by attempting molecular displacements (for internal equilibrium), volume fluctuations (for mechanical equilibrium) and particle interchanges between the boxes (for material equilibrium). The Gibbs-ensemble method has recently been reviewed.[6]

The simulations were performed in cycles with each cycle typically consisting of 300 attempted displacements, a single volume fluctuation and 10-2000 interchange attempts. The maximum molecular displacement and volume changes were adjusted to obtain, where possible, a 50% acceptance rate for the attempted move. The number of attempted particle interchanges depends on the achievement of a satisfactory acceptance rate (5-10%). Ensemble averages were accumulated only after the system had reached equilibrium. The equilibration period was 40000 cycles (approximately between 20 and 80 million configurations) and a further 40000 cycles were used to accumulate the averages. The calculations were truncated at intermolecular separations

greater than half the box length and appropriate long-range corrections[1] were used to obtain the full contribution of pair interactions to energy and pressure. The full (untruncated) three-body potential was calculated to avoid uncertainties that arise when calculating three-body long-range corrections from unknown pair-distribution functions. The configurational properties were updated after each successful move.

Ideally, the contributions of both two-body and three-body interactions to the configurational energy of the fluid should be updated for each attempted move. However, it is currently not computationally feasible to include three-body interactions in the acceptance criterion because of the very large increase in computing time required to recalculate accurately triplet interactions. Consequently, only changes to two-body interactions contributed to the acceptance criterion and the predicted phase coexistence curve is not affect by three-body forces. Instead, the effect of three-body interactions to the energy and the pressure were estimated by re-calculating their contribution periodically during the course of the simulation. Three-body effects were calculated at intervals of 100 cycles.

The uncertainties in the ensemble averages were calculated by dividing the post-equilibrium results into ten sections. The estimated errors represent the standard deviations of the section averages. A typical run required 2 hours of CPU time on a CRAY C90 processor.

IV. Results and Discussion

The coordinates of the coexistence curve for the Lennard-Jones fluid are given in Table I. The normal convention was adopted for the reduced density ($\rho^* = \rho\sigma^3$), temperature ($T^* = kT/\varepsilon$), energy ($E^* = E/\varepsilon$), chemical potential ($\mu^* = \mu/\varepsilon$) and pressure ($P^* = P\sigma^3/\varepsilon$). The data in Table I are generally in good agreement with previous work.[2] Fig. (2) compares the simulation data with experimental density-temperature data[11] for argon. At low temperatures, both simulations agree well with experiment for both the vapor and liquid portions of the coexistence curve. Phase separation was not detected at temperatures greater than $T^* = 1.25$.

There are few examples in the fluid-phase literature of three-body calculations for dense fluids. The available simulation results are confined almost exclusively to those using the Axilrod-Teller potential. Barker et al.[12] demonstrated that the Axilrod-Teller potential makes a significant contribution (5-10%) to the overall energy of liquid argon. Monson et al.[13] reported that three-

body interactions make a substantial contribution to the configurational energy of diatomic fluids; their calculations indicate that the non-additive corrections for molecules such as chlorine are much larger than those for argon. Sherwood and Prausnitz[14] have documented the contribution of the three-body dispersion potential to the third viral coefficient. Later, Sherwood et al.[7] reported that the third virial coefficient is also sensitive to three-body repulsion interactions. Recently, Miyano[15] used the Axilrod-Teller potential as the basis of an effective triplet potential and simulated the saturated vapor and liquid densities, enthalpies of vaporization and second virial coefficients of argon. The Axilrod-Teller potential has also been applied[16] to the simulation of the shear viscosity of liquid argon. However, no simulations with three-body interactions have been reported for the phase coexistence of either pure fluids or fluid mixtures.

The contributions of three-body interactions to the ensemble averages for pressure and configurational energy are summarized in Table II. Three-body interactions do not make a significant contribution to the energy of the vapor phase. The magnitude of both three-body dispersion and repulsion to the configurational energy increases with rising density. In the liquid phase, the three-body repulsion energy (E^*_{3brep}) is typically 45% of the three-body dispersion energy (E^*_{3bdisp}). This is consistent with previous estimates.[7] The contribution from three-body repulsion is opposite to that of dispersion. Therefore, three-body repulsions substantially reduce the total three-body energy ($E^*_3 = E^*_{3bdisp} + E^*_{3brep}$) of the fluid. The contribution of three-body dispersion to pressure (P^*_{3bdisp}) is cancelled (within the uncertainty of the simulation) by the contribution of three-body repulsion (P^*_{3brep}).

The substantial degree of cancellation between three-body repulsion and three-body dispersion interactions means that the overall contribution of three-body interactions to the fluid is small compared with two-body interactions. The total three-body energy (E^*_3) typically contributes < 2.0% and < 0.5% to the overall energy (E^*) of the liquid and vapor phases, respectively.

V. Conclusions

The contribution of both three-body dispersion and repulsion interactions must be included to simulate accurately the effect of three-body interactions on the phase coexistence properties of simple fluids. A substantial number of triplets in the liquid phase have at least one intermolecular

pair separation less than σ; therefore, three-body repulsion is significant. In contrast, very few repulsive triplets are found in the vapor phase. Because the effect of three-body dispersion interaction is largely offset by three-body repulsion, reasonably accurate results can be obtained by only using two-body potentials. The accuracy of results using only two-body potentials is probably not because three-body interactions are unimportant, but because the effect of three-body dispersion and three-body repulsion cancel to a large extent.

Acknowledgments

RJS thanks the Australian Department of Industry, Science and Technology for an Australia-USA Bilateral Science & Technology Collaboration Program grant. The project was also supported by a Swinburne Small Research Grant. JMP gratefully acknowledges support from the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy. Allocations of supercomputing time were granted by the San Diego Supercomputer Center, the Pittsburgh Supercomputer Center, the Australian National University Supercomputer Facility and the Swinburne University of Technology Cray facility.

References

[1] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, 1987.

[2] A. Z. Panagiotopoulos, N. Quirke, M. Stapleton and D. J. Tildesley, Mol. Phys. **63**, 527 (1988).

[3] See for example R. Aziz, Mol. Phys. **38**, 177 (1979).

[4] B. Smit, T. Hauschild and J. M. Prausnitz, Mol. Phys. **77**, 1021 (1992).

[5] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

[6] A. Z. Panagiotopoulos, Mol. Sim. **9**, 1 (1992).

[7] A. E. Sherwood, A. G. de Rocco and E. A. Mason, J. Chem. Phys. **44**, 2984 (1966).

[8] G. C. Maitland, M. Rigby, E. B. Smith and W. A. Wakeham, *Intermolecular Forces, Their Origin and Determination*, Clarendon Press, Oxford, 1981.

[9] P. J. Leonard and J. A. Barker in H. Eyring and D. Henderson (Eds), *Theoretical Chemistry, Advances and Perspectives, Vol 1.*, Academic Press, New York, 1975.

[10] B. Smit, Ph. de Smedt and D. Frenkel, Mol. Phys. **68**, 931 (1989).

[11] N. B. Vargaftik, *Handbook of Physical Properties of Liquids and Gases*, Hemisphere, Washington, D.C., 1975.

[12] J. A. Barker, R. A. Fisher and R. O. Watts, Mol. Phys. **21**, 657 (1971).

[13] A. Monson, M. Rigby and W. A. Steele, Mol. Phys. **49**, 893 (1983).

[14] A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. **41**, 429 (1964).

[15] Y. Miyano, Fluid. Phase Equilib. **95**, 31 (1994).

[16] S. H. Lee and P. T. Cummings, J. Chem. Phys. **101**, 6206 (1994).

TABLE I. Gibbs-ensemble simulation of the vapor-liquid phase coexistence of a one-component fluid (argon) using the Lennard-Jones potential.

	Vapor				Liquid			
T*	ρ*	P*	E*	μ*	ρ*	P*	E*	μ*
1.25	0.128 ± 0.015	0.096 ± 0.005	-1.01 ± 0.13	-3.64	0.507 ± 0.014	0.096 ± 0.007	-3.48 ± 0.09	-3.69
1.20	0.099 ± 0.020	0.077 ± 0.008	-0.83 ± 0.17	-3.67	0.560 ± 0.017	0.081 ± 0.017	-3.84 ± 0.10	-3.66
1.15	0.081 ± 0.005	0.064 ± 0.003	-0.70 ± 0.04	-3.66	0.612 ± 0.012	0.067 ± 0.012	-4.21 ± 0.09	-3.64
1.10	0.057 ± 0.002	0.047 ± 0.001	-0.50 ± 0.03	-3.72	0.641 ± 0.005	0.055 ± 0.016	-4.42 ± 0.03	-3.72
1.05	0.041 ± 0.003	0.035 ± 0.002	-0.39 ± 0.04	-3.78	0.671 ± 0.009	0.034 ± 0.020	-4.65 ± 0.07	-3.76
1.0	0.028 ± 0.004	0.024 ± 0.003	-0.26 ± 0.04	-3.89	0.701 ± 0.007	0.028 ± 0.030	-4.89 ± 0.05	-3.92

TABLE II. The contribution of three-body interactions to the configurational energy and pressure of the coexisting vapour and liquid phases of a one-component fluid (argon).

Vapor Phase Properties				
T*	E*3bdisp	E*3brep	P*3bdisp	P*3brep
1.25	0.043 ± 0.003	-0.005 ± 0.001	0.007 ± 0.002	-0.006 ± 0.002
1.20	0.0058 ± 0.0008	-0.0017 ± 0.0005	0.0017 ± 0.0004	-0.0012 ± 0.0005
1.15	0.0037 ± 0.0008	-0.0010 ± 0.0004	0.0009 ± 0.0003	-0.0006 ± 0.0002
1.10	0.0024 ± 0.0003	-0.0008 ± 0.0003	0.00041 ± 0.00007	-0.0003 ± 0.0001
1.05	0.0014 ± 0.0001	-0.0004 ± 0.0001	0.00017 ± 0.00002	-0.00013 ± 0.00002
1.0	0.00080 ± 0.00009	-0.0003 ± 0.0002	0.000074± 0.000009	-0.00005 ± 0.00004
Liquid Phase Properties				
T*	E*3bdisp	E*3brep	P*3bdisp	P*3brep
1.25	0.094 ± 0.024	-0.041 ± 0.012	0.15 ± 0.05	-0.15 ± 0.05
1.20	0.129 ± 0.004	-0.059 ± 0.006	0.22 ± 0.01	-0.24 ± 0.03
1.15	0.145 ± 0.004	-0.062 ± 0.003	0.27 ± 0.01	-0.27 ± 0.01
1.10	0.169 ± 0.003	-0.074 ± 0.003	0.326 ± 0.006	-0.33 ± 0.01
1.05	0.186 ± 0.002	-0.083 ± 0.002	0.377 ± 0.004	-0.39 ± 0.01
1.0	0.205 ± 0.003	-0.089 ± 0.002	0.432 ± 0.008	-0.44 ± 0.01

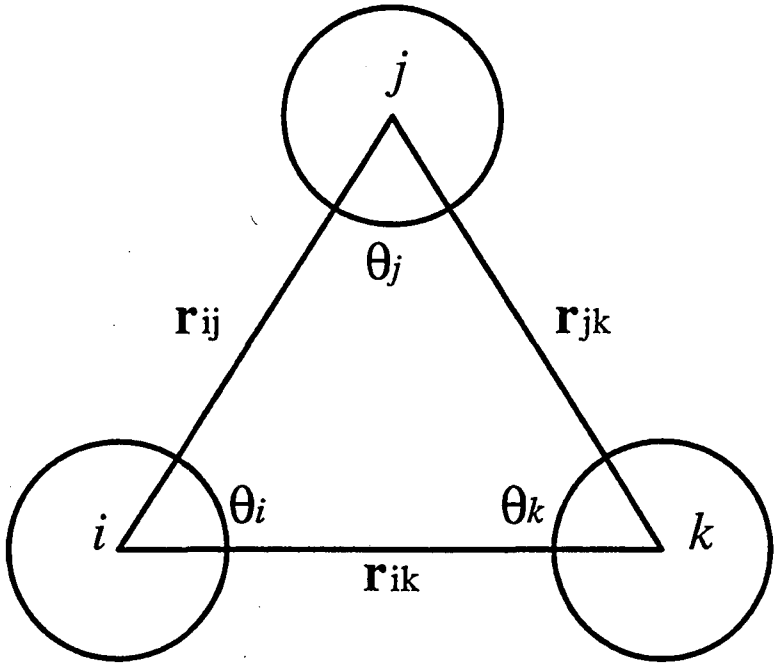

FIG 1. Triplet configuration of atoms i, j and k in Eq. (2) and Eq. (3).

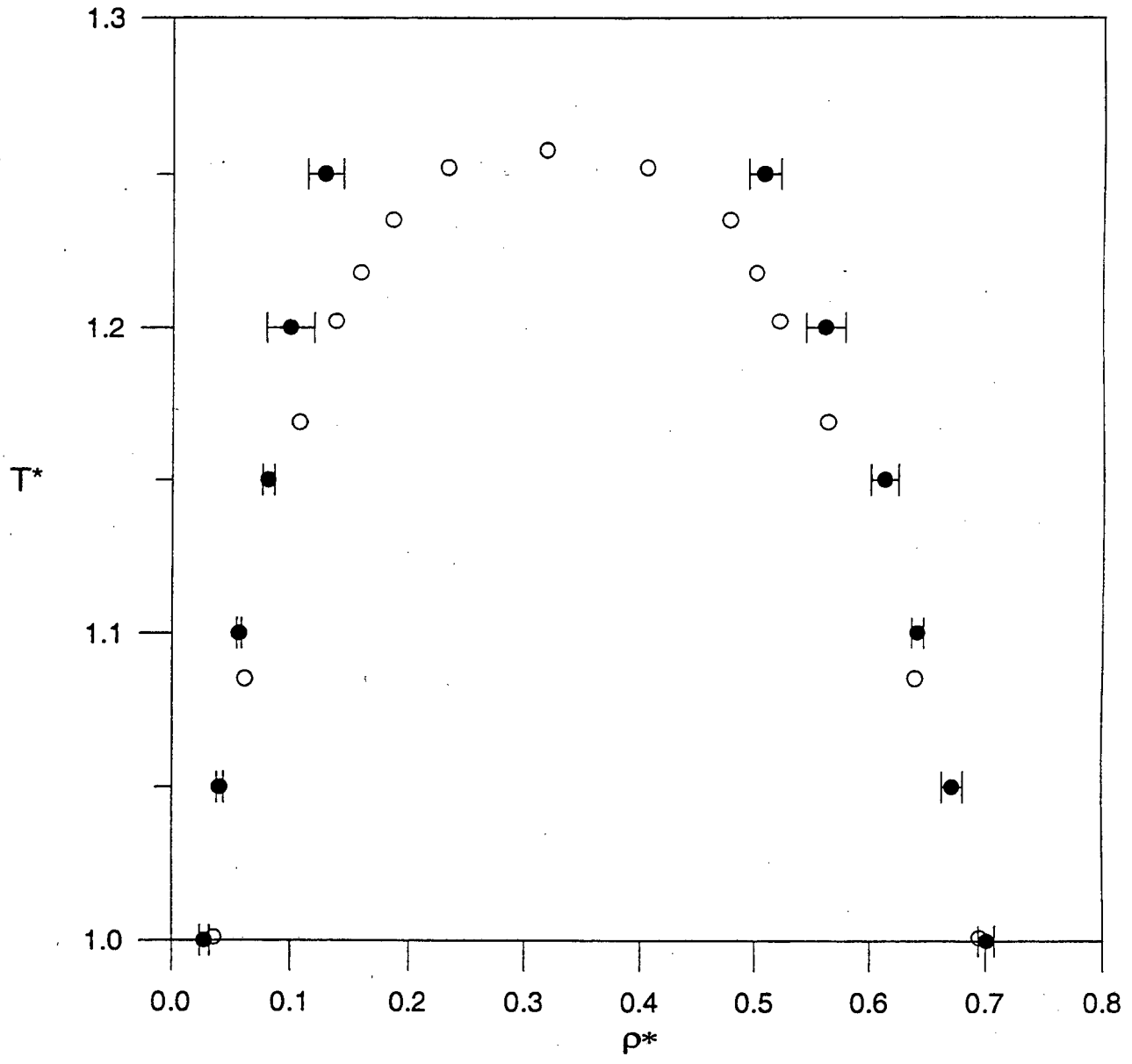

FIG 2. Comparison of the experimental phase diagram for argon (O) with Gibbs-ensemble simulations (●).

LAWRENCE BERKELEY NATIONAL LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL & ELECTRONIC INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720