

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1999 issue.

NOTES

Determination of potential parameters for alkanes

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In recent years, several groups¹⁻⁵ have been developing potential models for alkanes by using Gibbs ensemble simulations.⁶ By using these new force fields good agreement between simulation and experiment was found for the vapor-liquid equilibria of alkanes.

Another possibility for determining potential models for *n*-alkanes is through second virial coefficient calculations. The evaluation of B_2 for alkanes started with the work of Lal and Spencer for butane and pentane.⁷ Later, Lopez Rodriguez and Freire⁸ performed calculations for *n*-alkanes by using a different force field for each alkane. In 1991, Lopez Rodriguez *et al.*⁹ proposed a methodology to obtain potential parameters of *n*-alkanes from second virial coefficient calculations. Lopez Rodriguez *et al.* showed⁹ that experimental values of B_2 of *n*-alkanes could be described by a unique force field provided that the energy of methyl groups is much larger (by a factor of more than two) than that of methylene groups. Several groups have used second virial coefficients for obtaining force fields⁸⁻¹³ for alkanes. A good description of this type of work can be found in two recent papers.^{14,15}

Therefore, there are at least two routes for determining potential parameters for alkanes, either liquid simulations or second virial coefficient calculations. It is well known for argon and other simple substances that parameters describing the gas phase do not describe the liquid phase as well.¹⁶ Three body forces are responsible for this difference. The calculation of B_2 is at least one order of magnitude faster than the determination of vapor-liquid coexistence. Therefore, a reasonable strategy for finding potential parameters for flexible molecules (alkanes or other) in the liquid state is first to perform second virial calculations and then proceed to refinement of the parameters by using some selected simulations in the liquid state. An example of this strategy is the work of Siepmann *et al.*,^{3,4} who used our potential parameters obtained from second virial coefficients⁹ as a starting point for determining liquid state parameters. Both sets of parameters are shown in Table I. As can be seen both sets of parameters are rather similar. Unfortunately both our 1991

and their 1993, and 1995 papers contained computer errors, so it is not clear whether parameters obtained from gas phase would be similar to the parameters obtained from the liquid phase. Fortunately these errors have been corrected. In fact, in 1993 we corrected an error in our 1991 code and repeated the calculations by also using a new fitting criterion. The conclusions of our 1991 paper were not modified, but the potential parameters changed. The new set of parameters for *n*-alkanes was published in 1993¹⁰ and is shown in Table I. These parameters reproduce with an accuracy of about 5% the experimental values of the second virial coefficients of alkanes from *n*-butane to *n*-octane for temperatures in the range 300–580 K. Also, Nath *et al.*¹ recently performed Gibbs ensemble simulations and proceeded to a new determination of the parameters of *n*-alkanes for reproducing the vapor-liquid equilibria of *n*-alkanes. The proposed parameters are shown in Table I. As can be seen, the parameters proposed by Nath are similar to those of our 1993 force field. The largest difference is for the CH₂-CH₂ interaction energy, the difference being about 8%. Therefore, the conclusion that parameters obtained from second virial coefficients calculations are similar (although not identical) to those obtained to fit liquid properties now also has a solid basis for *n*-alkanes.

In Fig. 1 the second virial coefficients of Nath *et al.*,¹ and our 1993 force field are compared with experimental data. Since all these models use quite similar values of σ , the

TABLE I. Some recent force fields for *n*-alkanes. For the torsional potential used in each model see the original references.

Model	σ_{CH_3}	σ_{CH_2}	ϵ_{CH_3}	ϵ_{CH_2}	Pub.year	Ref.
Lopez Rodriguez <i>et al.</i>	3.923	3.923	121.6	46.1	1991	9
Siepmann <i>et al.</i>	3.93	3.93	114	47	1993,1995	3,4
Lopez Rodriguez <i>et al.</i>	3.923	3.923	104	49.7	1993	10
Vega and Lopez Rodriguez	3.923	3.923	104	47.5	1996	12
Nath <i>et al.</i>	3.91	3.93	104	45.8	1998	1

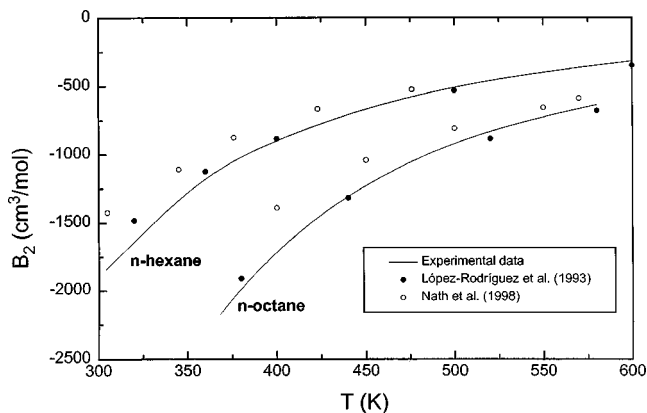


FIG. 1. B_2 of *n*-hexane and *n*-octane as obtained from experiment (Ref. 20) (solid line), from our 1993 force field (Ref. 10) (filled circles) and from the model of Nath *et al.* (Ref. 1) (open circles).

difference in B_2 values is mainly due to differences in ϵ . Our 1993 force field describes the experimental data satisfactorily, whereas the results of Nath *et al.* are too high. As expected, a good pair potential for the liquid phase is not as good for the gas phase. It is likely that our 1993 force field, which is good for the gas phase, does not perform so well for the liquid phase. In particular it is expected that our 1993 field will yield critical temperatures higher than experiment. Therefore, for alkanes, differences in the interaction energy parameter of about 8% should be expected in the gas and liquid phases.

In 1996, some of us performed calculations of the second virial coefficients of long alkanes at high temperatures¹² with the purpose of estimating the critical temperature of polymethylene.¹⁷ This goal led us to propose a new force field describing the experimental values of the second virial coefficient of alkanes at high (i.e., $T \geq 580$ K) temperatures. The parameters proposed by us are shown in Table I. As can be seen, the model proposed by Nath *et al.* is similar to that presented previously by us. In fact, differences are about 0.3% for σ_{CH_3} , 0.18% for σ_{CH_2} , 0% for ϵ_{CH_3} , and 3.5% for ϵ_{CH_2} from our 1996 force field. For long chain molecules the critical temperature and the Boyle temperature (where $B_2 = 0$) are similar (in fact, they are identical in the limit of

infinitely long chains).^{18,19} Therefore, it is not so surprising that force fields which describe well the second virial coefficient of chains at high temperatures are similar to those force fields which yield good predictions for the critical temperature.

Our conclusions are that, for chain molecules, force fields obtained from second virial calculations do not necessarily describe the liquid phase, but provide an useful starting point to this purpose (with a low computational effort). Furthermore, force fields obtained from second virial calculations for long chains at high temperatures are quite similar to those obtained to match the experimental values of the critical temperatures.

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