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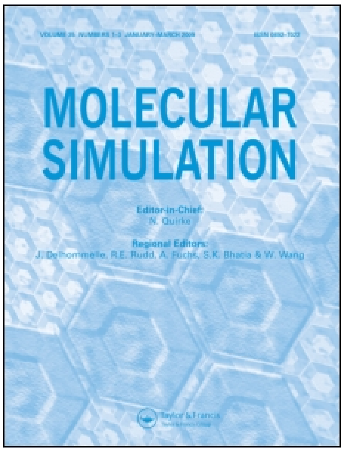

## Molecular Simulation

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# JOULE-THOMSON INVERSION CURVES BY MOLECULAR SIMULATION

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A method to determine Joule-Thomson inversion curves, using isobaric-isothermal Monte Carlo molecular simulations, is presented. Volumetric data obtained through the simulations is interpreted by means of thermodynamic relations to obtain the locus of points in which the isenthalpic derivative of temperature with respect to pressure vanishes. The procedure is exemplified for a Lennard-Jones fluid and the low-temperature branch of the inversion curve is obtained. In general, Joule-Thomson inversion curves obtained by molecular simulation may be used either as an unambiguous test for equations of state in the supercritical and high-pressure regions or for the prediction of real fluid behavior, should the potential be well known. Examples of both applications are presented.

*Keywords:* Inversion curve; Monte Carlo simulations; Lennard-Jones potential; refrigerants; equation of state

## 1. INTRODUCTION

The passing of a fluid through a restriction, with its resulting decrease in pressure is usually followed by a change in temperature. In an adiabatic process, this change can be quantified by means of the Joule-Thomson coefficient, $\mu_J$, defined as

$$\mu_J = \left(\frac{\partial T}{\partial P}\right)_h, \tag{1}$$

where $T$ and $P$ refer to temperature and pressure and the derivative is taken at constant enthalpy, $h$. Depending on the state conditions $\mu_J$ may be either positive or negative. The locus of points where $\mu_J = 0$ is called the inversion curve.

The inversion curve is one of the most important parameters needed in engineering to evaluate the performance of a refrigerant. Unfortunately, the experimental determination of inversion curves requires the very precise measurement of volumetric properties at conditions up to five times its critical temperature and twelve times its critical pressure. These harsh experimental conditions have hindered the publication of data for even simple fluids and mixtures. A method to circumvent these deficiencies has been to average the available experimental data using two-parameter corresponding-states principles to correlate them [1, 2].

On the other hand, the prediction of inversion curves is a particularly severe test of any equation of state (EOS). For a pressure-explicit EOS, the inversion condition requires not only a correct representation of the $P(v, T)$ function but also of its first derivatives. Previous work by Colazo *et al.* [3] attempted to obtain information on the functional form of cohesion factors of common cubic EOS from inversion curves and found difficulties in obtaining appropriate data. Song and Mason [4] proposed a fundamentally based EOS that is applied to the Lennard-Jones fluid. Nevertheless, upon testing their EOS, they report that they are unable to find inversion curve data for the Lennard-Jones fluid. They state that, in general, the quality of the high-pressure thermodynamic property prediction from a fundamentally based EOS can be adequately tested if inversion data could be obtained [4].

When the underlying physical situation and the intermolecular potentials are reasonably well known, computer simulations are a convenient method of extrapolating experimental data to other conditions of difficult experimental access. Using this premise, this work attempts to fill the abovementioned voids by presenting a method of calculating Joule-Thomson inversions curves for well defined fluids from Monte Carlo molecular simulations. The procedure is exemplified by providing the first reported inversion curve for a Lennard-Jones (LJ) fluid. The resulting data is then used for two complementary purposes: a) The inversion curve is compared to that predicted by EOS developed for the same potential. In this way, theoretical developments may be evaluated unambiguously, since the simulations provide true experimental data for a given potential. b) The inversion curve is scaled to reproduce experimental data for simple fluids, for which the LJ potential is a first order approximation. Given a reasonably accurate potential, the simulations provide the inversion curve for a given fluid, eliminating the necessity of costly experiments.

## 2. THERMODYNAMIC RELATIONS

Direct experimental measurement of inversion curves is difficult and unreliable. At near-inversion conditions, the vanishing of the Joule-Thomson coefficient means that even very large pressure differences will result in small temperature differences, hence, extremely precise temperature measurements are needed to pin-point the inversion point. The preferred course of action in the laboratory is to determine volumetric data in the vicinity of expected inversion points and to use thermodynamic relations to relate these data to the inversion point. For example, $\mu_J$, may be expressed as

$$\mu_J = -\frac{1}{C_p}\left(\frac{\partial h}{\partial P}\right)_T = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right] = \frac{RT^2}{C_pP}\left(\frac{\partial Z}{\partial T}\right)_P, \tag{2}$$

where $C_p$ is the constant-pressure heat capacity, $Z$ is the compressibility factor $Z = Pv/RT = PV/NkT$, $v$ is the specific volume, $R$ is the ideal gas constant, $N$ is the number of molecules, and $k$ is Boltzmann's constant. The inversion condition is guaranteed when

$$T\left(\frac{\partial v}{\partial T}\right)_P - v = 0, \tag{3}$$

or equivalently when

$$\left(\frac{\partial Z}{\partial T}\right)_P = 0, \tag{4}$$

Both equations (3) and (4) relate to extrema of an isobar.

Additionally, to obtain the inversion curves from a pressure-explicit EOS, it is convenient to solve (analytically or numerically) for the following equivalent condition,

$$T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T = 0. \tag{5}$$

## 3. SIMULATION DETAILS

The Monte Carlo simulations were performed in the isobaric-isothermal (MC-NPT) ensemble which allows the *a priori* specification of the pressure and temperature of the system. A review of the method is given in standard references (e.g., ref. [5]), thus only the particular details of this application will be specified here.

A total of $N = 500$ molecules were initially placed in a random configuration in a cubic simulation box. Periodic boundary conditions and minimum image conventions were applied. Molecules are subject to random translation moves, where the maximum displacement is fixed in order to obtain approximately a 30% acceptance probability of a given move. Every $N$ attempts to displace molecules, a volume change was attempted and a cycle was completed. The changes in volume are limited in magnitude in order to obtain a 30% acceptance probability of a given change.

The Lennard-Jones potential, $\phi_{ij}$ was used,

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

where $\varepsilon$ and $\sigma$ are the characteristic energy and length parameters, respectively. The method may nevertheless be used with more complex potential functions. This choice of potential allows the definition of a reduced temperature $T^* = kT/\varepsilon$, a reduced pressure $P^* = P\sigma^3/\varepsilon$ and a reduced volume $v^* = V/N\sigma^3$. The potential cutoff distance $r_c$ was set to half the box size (typically $r_c \approx 5\sigma_{LJ}$) and the usual [5] long range corrections were applied, although for this particular application they may be neglected. The initial density of the system was chosen close to that expected, predicted by an EOS [6]. Tests were done at different starting configurations and densities, all giving the same average equilibrium properties. The system was left to equilibrate a minimum of $3 \cdot 10^3$ cycles ($1.5 \cdot 10^6$ configurations). Averages of the system volume were taken for at least $10^4$ cycles ($5 \cdot 10^6$ configurations). Low density systems required longer runs (up to two times longer) to achieve acceptable statistics. To summarize, given a temperature $T^*$ and a pressure $P^*$ the simulation result is expressed as an average equilibrium volume $v^*$ from which other volumetric properties may be calculated. Additionally, one may obtain the average reduced configurational energy, $e^* = E/N\varepsilon$ and enthalpy, $h^* = e^* + P^*v^*$.

To find an inversion curve point, a series of simulations, generally from 5 to 10, were made at a fixed pressure and at temperatures in the vicinity of the expected value. With this table of isobaric data, either equation (3) or (4) may be used to find the inversion point. To use equation (3), the values of $v^*$ were fitted to a cubic polynomial in $T^*$,

$$v^* = a_0 + a_1 T^* + a_2 T^{*^2}, \tag{7}$$

where the application of equation (3) implies that the inversion temperature, $T^*_{\text{inversion}}$, corresponds to

$$T^*_{\text{inversion}} = \sqrt{\frac{a_0}{a_2}}. \tag{8}$$

An alternative path, is to convert the volumetric data to compressibility factors, $Z = P^* v^* / T^*$ and fit them to a polynomial in $T^*$

$$Z = \sum_{i=0}^{4} b_i T^{*^i}, \tag{9}$$

where the application of equation (4) implies that the inversion temperature corresponds to the positive root of

$$f = \sum_{i=1}^{4} i b_i T^{*^{i-1}} = 0. \tag{10}$$

It is clear that the coefficients $a_i$ and $b_i$ of equations (7–10) have no physical meaning whatsoever, and are only the result of empirical fits. However, the fact that there are two separate routes for obtaining the inversion temperature, equations (8) and (10), allows an independent check on the error and reliability of the results.

In principle, it is possible to obtain inversion curves from fluctuation formulas. For example, the derivative which appears in equation (3) may be related to the reduced thermal expansion coefficient, $\alpha_P^*$, defined as

$$\alpha_P^* = \frac{\varepsilon}{kv}\left(\frac{\partial v}{\partial T}\right)_P. \tag{11}$$

Thus, equation (3) may be re-written as $T^* \alpha_P^* - 1 = 0$. On the other hand, $\alpha_P^*$ may be obtained from the appropriate fluctuation formula in the NPT ensemble,

$$\alpha_P^* = N\langle 1/v^* \rangle \frac{\langle h^* v^* \rangle - \langle h^* \rangle \langle v^* \rangle}{T^{*^2}}, \tag{12}$$

where the brackets $\langle \ldots \rangle$ represent an ensemble average. The resulting data obtained by means of fluctuation formulae provide no advantage to the method we used, due to the large errors encountered in obtaining these numbers from small finite-size simulation cells.

## 4. RESULTS

In Figure 1, the compressibility factor as a function of reduced temperature is plotted for a typical isobar. In this type of plot, the low temperature inversion point corresponds to a well pronounced minimum (point a in Fig. 1) while the high temperature inversion point corresponds to a very flat maximum (point b in Fig. 1), almost indistinguishable in graphical form. In

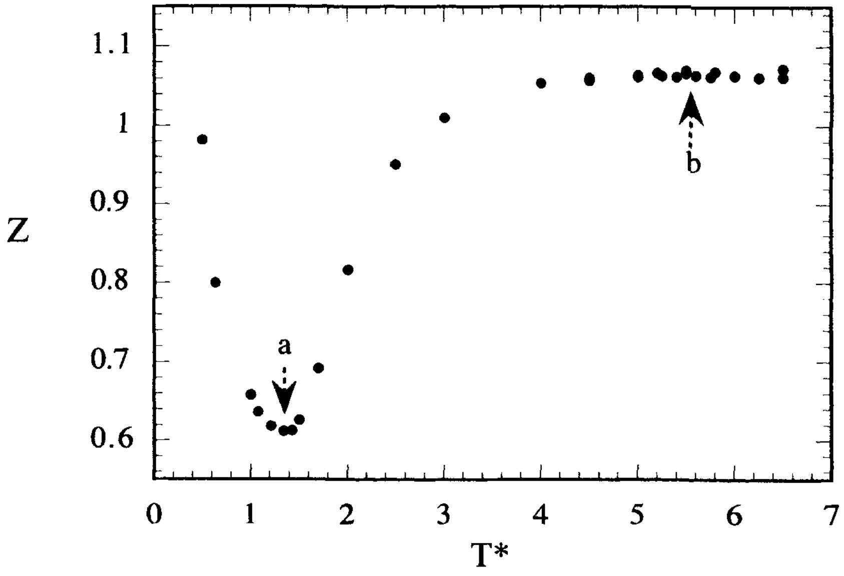

FIGURE 1 Compressibility factor, $Z$, as a function of reduced temperature $T^* = kT/\varepsilon$ at a reduced pressure $P^* = P\sigma^3/\varepsilon = 0.5$. The arrows point to the low-temperature minimum (a) and the high temperature maximum (b) of this isobar, both of which are inversion curve points.

these plots, one may find the inversion points by fitting the data to an equation similar to (9) and solving for (10) . The temperature obtained by this method and by using equations (7–8) disagree only within the estimated errors, indicating that either method is suitable for obtaining the inversion curve. We have used both methods in all points calculated and found the inversion point as an average of both results.

The low-temperature inversion points are easily found by the above mentioned methods . The high-temperature ones are very difficult to pin-point, since the statistical errors inherent to the MC method hide the fine details. The large margin of error that this imprecision causes prompted us to refrain from publishing these points. The unsmoothed simulation data are presented in Table I. The data points span from a point close to the saturation curve to the maximum pressure for which a clearly defined inversion point is found.

Figure 2 shows the inversion curve data for a Lennard-Jones fluid. The results obtained are compared to those predicted by the EOS of Song and Mason [4], which was applied specifically to the Lennard-Jones potential. Since both the theory and the simulations pertain to the exact same potential, the discrepancies point to inaccuracies of the EOS . This type of test for an EOS is very stringent, and thus a qualitative agreement is recomforting, especially considering that the Song-Mason EOS relies on obtaining the second virial coefficient and two temperature dependent parameters from

TABLE I Unsmoothed .MC results of inversion points for a Lennard-Jones potential. Reduced pressure $P^* = P\sigma^3/\varepsilon$ is fixed, while reduced temperature $T^* = kT/\varepsilon$ is the average result of applying equations (8) and (10). The numbers in parenthesis indicate estimated error, e.g. 1.23(4) means 1.23 ± 0.004

| $P^*$ | $T^*$ |
|---|---|
| 0.2 | 1.117(0) |
| 0.3 | 1.201(1) |
| 0.4 | 1.264(3) |
| 0.5 | 1.330(8) |
| 0.6 | 1.402(8) |
| 0.7 | 1.446(5) |
| 0.8 | 1.519(2) |
| 0.9 | 1.570(4) |
| 1.0 | 1.658(3) |
| 1.1 | 1.754(7) |
| 1.2 | 1.92(1) |
| 1.25 | 2.16(3) |
| 1.3 | 2.40(2) |

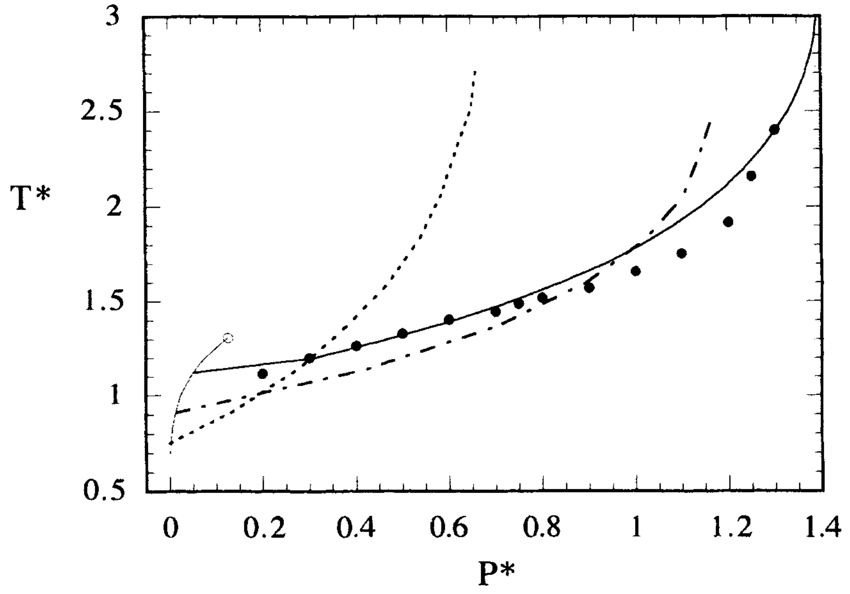

FIGURE 2 Inversion curves for a Lennard-Jones fluid. Circles are the simulation results. Solid line is the EOS of Johnson *et al.* [6], dashed-dotted line is the EOS of Song and Mason [4]; dashed-dotted line is the van der Waals EOS. Thin solid line is the LJ saturation curve, which end at the critical point (open circle).

the intermolecular potential to predict the complete $P(v, T)$ behavior. In Figure 2, the prediction of a recent multi-constant EOS [6] is also plotted. This EOS, while having some theoretical background relies mainly on a numerical fit of the available simulation data for its accuracy. As is expected, the EOS of Johnson *et al.* [6], follows the simulation results closely, although some differences are noted at high pressures. The agreement is not surprising due to the exhaustive data fitting employed to produce this EOS. For comparison purposes, the van der Waals result is also plotted. This equation, along with all other cubic EOS, suffer from deficiencies associated to their analytical structure. Nevertheless, the comparison with accurate inversion data allows the deduction of improved temperature-dependent cohesion factors [3].

Should the intermolecular potential of a molecule be known, simulations can be a relatively fast and economical way of obtaining inversion curve data. This can be particularly important in the screening of refrigerants and refrigerant mixtures. Simple molecules, such as the noble gases, may be well represented by means of a LJ potential. In Figure 3 the simulation data is

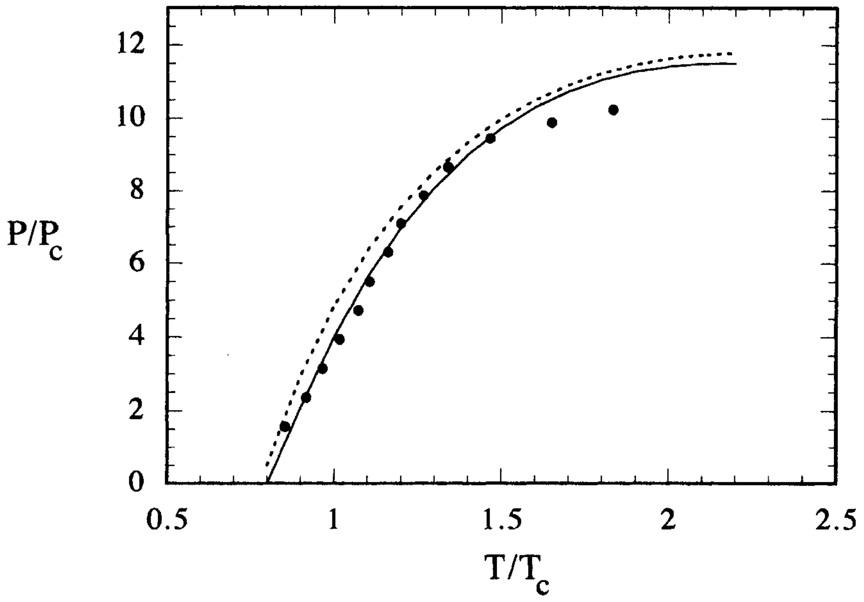

FIGURE 3 Inversion curve for simple fluids. The pressures and temperatures are reduced with respect to their critical values, i.e. a two-parameter corresponding states principle is invoked. Circles are simulation results. Solid line is the correlation of Gunn *et al.* [1], dashed line is the correlation of Miller [2].

scaled using an accepted LJ critical pressure and temperature, $T^* = 1.31$ and $P^* = 0.1264$, respectively, in reduced units [7]. The simulation results compare favorably to the currently used correlations for experimental data [1, 2]. Some discrepancy is observed in the higher pressure maximum of this curve which is not yet resolved. We speculate that some of the differences are due to the inadequacy of the LJ potential to model the repulsions seen in real fluids at extremely high pressures and temperatures, i.e. the repulsive part of the LJ model is too "hard" to model a real fluid.

## 5. CONCLUSIONS

This work presents a method for obtaining inversion curve data from molecular simulations. The usefulness of these data is twofold; both practical and theoretical. Inversion curves may be used to evaluate the thermophysical properties of certain fluids, particularly refrigerants and refrigerant mixtures should the intermolecular potentials be reasonably well known. Alternatively, the data may be used to evaluate the accuracy of a given theoretical EOS in order to improve upon the theoretical developments.

For illustration purposes, in this paper we have focused on the LJ potential. Nevertheless, the procedure may be applied to a more realistic potential model and/or extended to study mixtures.

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