Molecular Simulation of Joule-Thomson Inversion Curves[1]

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ABSTRACT

A method to determine Joule-Thomson inversion curves, using isobaric-isothermal Monte Carlo molecular simulations, is presented. The usual experimental practice to obtain the locus of points in which the isenthalpic derivative of temperature with respect to pressure vanishes is to process volumetric data by means of thermodynamic relations. This experimental procedure requires the very precise measurement of volumetric properties at conditions up to five times the fluid's critical temperature and twelve times its critical pressure. These harsh experimental conditions have hindered the publication of data for even simple fluids and mixtures. By using molecular simulation, these problems may be circumvented, since the computational effort is roughly independent of the actual value of the pressure or the temperature. 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. Both applications are exemplified for a Lennard-Jones fluid for which the complete inversion curve is obtained.

1 INTRODUCTION

The Joule-Thomson (JT) coefficient, μ_J, is defined as the isenthalpic derivative of temperature, *T*, with respect to pressure, *P*;

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

where *T* and *P* refer to temperature and pressure and the derivative is taken at constant enthalpy, *h*. Depending on the state conditions μ_J may be either positive or negative, implying the respective cooling or heating of a fluid when passing through a restriction. The locus of points where $\mu_J = 0$ is called the Joule-Thomson inversion curve.

Inversion curves are usually determined for refrigerants, where the knowledge of the region of positive JT coefficients is important. Recently, [1] reservoir fluid abnormalities have been explained by evaluation of JT coefficients.

The experimental determination of inversion curves requires 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. Most data available cover only the low temperature branch of the inversion curve. It is generally accepted that the available experimental data is well correlated by a two-parameter corresponding-states principles [2,3], albeit recent research suggests that deviations may be significant [4] and for polar fluids, especially refrigerants, another parameter must be used to account for non-conformity due to the presence of multipolar moments.

This lack of experimental data is particularly troubling to theoreticians since 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. For example, Colazo et al. [5] attempted to obtain information on the functional form of cohesion factors of common cubic EOS from inversion curves and found only a scarce data base available in the literature. Song and Mason [6] proposed a fundamentally-based EOS whose applicability was exemplified representing the P-v-T properties of a Lennard-Jones fluid. Nevertheless, they report that they were unable to find inversion curve data for the Lennard-Jones fluid. This is

unfortunate, since the quality of the high-pressure thermodynamic property prediction from an EOS can be adequately tested if inversion data could be obtained [6].

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 above-mentioned voids by presenting an alternative method of calculating Joule-Thomson inversions curves for well defined fluids from Monte Carlo molecular simulations. The procedure is exemplified for a Lennard-Jones (LJ) fluid, but it is general in nature, thus, if the intermolecular potential for a fluid is considered appropriate, the JT inversion curve may be found, eliminating the necessity of costly experiments.

II METHODOLOGY

The Joule-Thomson coefficient may be related to volumetric data by means of exact thermodynamic relations, such as

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

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 extreme of an isobar. Once P-v-T data is available, (preferably in the form of an isobar), it may be processed to obtain the inversion point. In a laboratory experiment, exact constant pressure can rarely be sustained, and the determination of inversion points requires some sort of data-fitting procedures. In a molecular simulation,

variables may be unambiguously set in an exact manner, thus, by performing Monte Carlo simulations in the isobaric-isothermal ensemble (MC-NPT) we can obtain as a result of the simulation, among others, an average density. A review of the method may be found in standard references (e.g. ref. [7]), thus only the particular details of this application will be specified here [8].

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. 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, φ_{ij} was used,

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

where ε and σ 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 [7] long range corrections were applied, although for this particular application they may be neglected. The system was left to equilibrate a minimum of $3\cdot10^3$ cycles ($1.5\cdot10^6$ configurations). Averages of the system volume were taken for at least 10^4 cycles ($5\cdot10^6$ configurations). The simulation result is expressed as an average equilibrium volume v^*. Further simulation details, including cross-checking of the results and numerical tables are presented elsewhere [8].

The JT inversion curve has two branches when plotted as pressure *versus* temperature. The low-temperature inversion points are easily found by the above mentioned methods. The high-temperature ones are very difficult to pin-point, due to the statistical errors inherent to the MC method and are subject to a higher uncertainty. This uncertainty is a limitation of the

method used and can not be improved by reasonable increases in system size or simulation length [8].

III RESULTS

Figure (1) 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 [6], 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 the intermolecular potential to predict the complete P(v,T) behavior. The simulation results are also compared to the van der Waals EOS, which presents a marked deviation, usually ascribed its cubic dependence in volume and to the lack of temperature dependence of the cohesion factor. The results of a virial expansion truncated after the third virial coefficient gives again only a qualitative result. The high pressures involved implies a dense fluid state, where mullet-body interactions must be taken into account to properly model it. Also, in figure (1), the prediction of a mullet-constant EOS [9] is also plotted. This EOS is an extended virial equation, fitted to a large data base of available simulation data. As is expected, it follows the simulation results closely, although some differences are noted at high pressures.

Available experimental data are often correlated by means of two-parameter corresponding states principles. While the data used certainly may be conformal, e.g. noble gases, methane, nitrogen, etc., the most useful application of inversion curves is for fluids which present deviations from simple corresponding states law. Recent interest is focused on high P and T reservoir fluids and refrigerants. In these cases, at least a three parameter corresponding states principle should be invoked. One such recent correlation is presented by Castillo *et al.* [4]. It presents a reduced correlation function of critical pressures, temperatures and acentric factor. In figure two we scale the simulation results using an accepted LJ critical pressure and temperature, $T^* = 1.31$ and $P^* = 0.1264$, respectively, in reduced units [10]

and an acentric factor of ω= -0.03195 obtained from the vapor pressure curve reported in [7]. Both correlations agree amongst themselves and with the simulation data in the low temperature branch of the inversion curve. The high-temperature branch shows discrepancies amongst the models and with the simulation data. Some of the differences may be ascribed to the inability of the LJ potential to model real fluid behavior and some to the inaccuracies inherent in the determination of inversion curve points in the high temperature branch from simulations [8]. Nevertheless, the results also suggest deficiencies in the existing correlations and serve as a reference for qualitative behavior in this region.

IV CONCLUSIONS

In this work we present the Joule-Thomson inversion curve for a Lennard-Jones fluid obtained by isothermic-isobaric Monte Carlo simulations. The data may be used to evaluate the accuracy of a given theoretical EOS in order to improve upon the theoretical developments. Alternatively, if the intermolecular potential of a pure fluid is reasonably well known, molecular simulations give an exact result for the thermophysical properties at experimentally inaccessible conditions. This method is particularly promising for fluid mixtures.

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Figure Captions

Fig. 1 Inversion curves for a Lennard-Jones fluid. Circles are the simulation results. Solid line is the EOS of Johnson *et al.* [9], dotted line is the EOS of Song and Mason [6]; three dashed-dotted line is the van der Waals EOS, dashed-dotted line is the virial expansion truncated after the third virial term.

Fig. 2 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. dashed line is the correlation of Gunn *et al.* [2], solid line is the correlation of Castillo *et al.* [4].

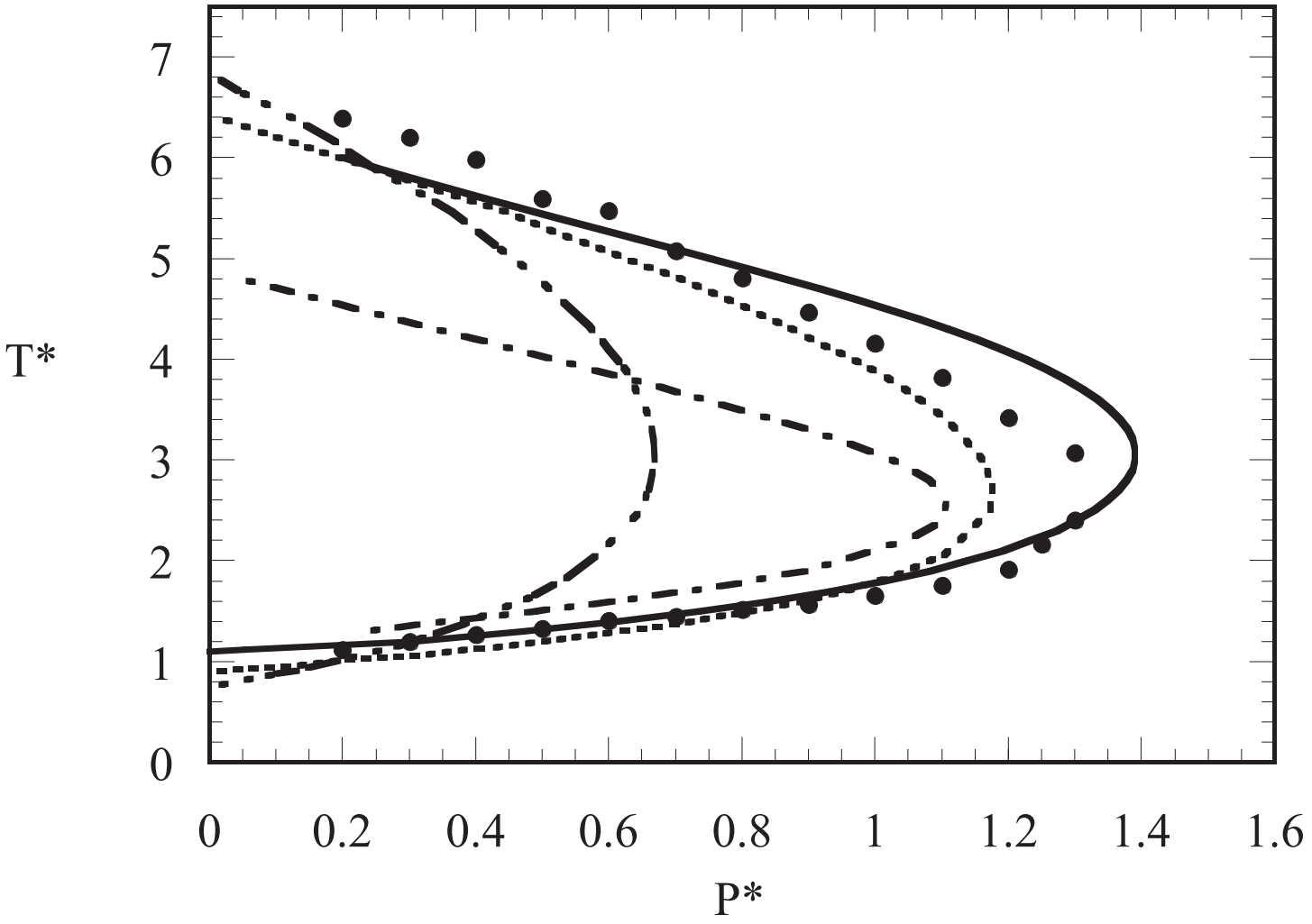
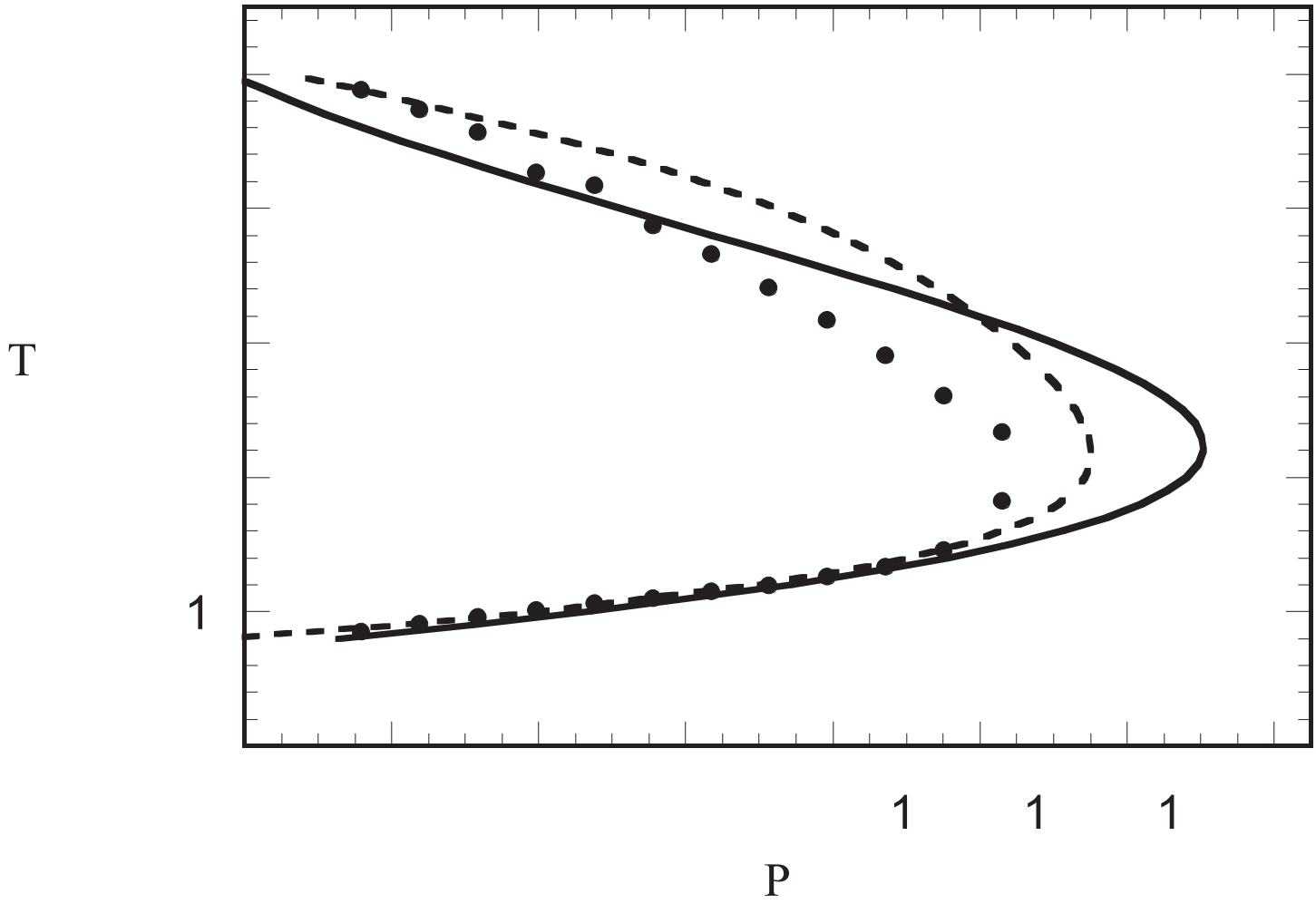


Figure 1



Figure