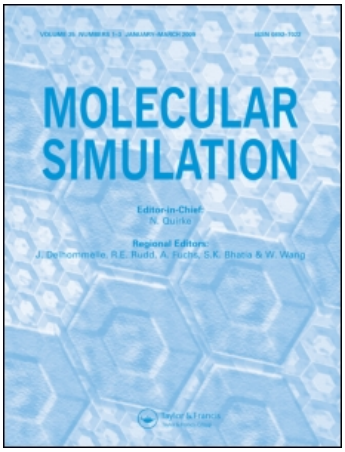

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The Extrapolation of Vapour–liquid Equilibrium Curves of Pure Fluids in Alternative Gibbs Ensemble Monte Carlo Implementations

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Extrapolation schemes based on Taylor series expansion to determine the vapour–liquid equilibrium (VLE) curves of pure molecular fluids are presented for the NpH and μVL versions of the Gibbs ensemble Monte Carlo (GEMC) simulations. The coexistence curves of the various configurational quantities can be expressed as Taylor series around the simulated equilibrium point as a function of pressure in the NpH version and chemical potential in the μVL version. The coefficients of the Taylor series are calculated from single GEMC simulations using Clapeyron-like equations and fluctuation formulas. A Padè approximant is used to widen the range where the extrapolation is accurate. These methods are demonstrated on atomic Lennard-Jones fluid. The procedure is found to be an accurate and useful tool to calculate wide sections of the VLE curves. With this procedure the saturation heat capacity can be directly determined using the calculated derivatives.

Keywords: Taylor series expansion; NpH ensemble; μVL ensemble; Vapour–liquid equilibria

INTRODUCTION

The Gibbs ensemble Monte Carlo (GEMC) simulation [1] is one of the most popular simulation methods used to study the fluid phase equilibria. In a Gibbs ensemble (GE), the system is divided into two distinct simulation boxes (or into more boxes, if more than two coexisting phases are simulated [2]). Each box represents a region deep inside one of the coexisting phases. In the original form of GEMC, the total volume (V), the total number of species (N) and the temperature (T) are constrained to be constant. In this GEMC version the basic ensemble is the canonical (NVT) ensemble. In addition to the particle displacements within each box, the simulation steps consist of particle and volume exchanges between the boxes. The canonical Monte Carlo acceptance criteria are used to keep the temperature fixed independently in the two boxes. The adjustment of the relative volumes and the particle exchange step ensure that both subsystems are at the same pressure (mechanical equilibrium) and at the same chemical potential (chemical equilibrium). If the total volume is chosen so that the average density lies between the densities of the two phases examined, the system will settle down to a point, where one simulation box contains one of the phases (e.g. a liquid phase) and the other box contains the other phases (e.g. a vapor phase).

For one component systems, the phase rule enables us to specify one intensive variable, the temperature, the pressure (p) or the chemical potential (μ), when two phases coexist. This fact gave the idea to implement two alternative GEMC simulation methods [3]. In the NpH basic ensemble the pressure, the total number of particles and the total enthalpy ($H = E + pV$, where E is the total energy) and in the μVL basic ensemble the chemical potential, the total volume and the total Hill energy ($L = E - \mu N$) are kept constant. Unlike the conventional NVT-GEMC method, the GEMC simulations based on these basic ensembles allow the exchange of heat between the correlated subsystems. It was shown that in the determination of the vapour–liquid equilibrium (VLE) the capability of these algorithms is similar to that of the original (NVT) method; however, in the determination of the vapor

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pressure curves, the NpH version has some advantages over the others [4]. The NpH version is particularly beneficial when the pressure calculation via the virial becomes problematic (e.g. hard core potential or complex intermolecular potential functions).

In other methods developed to determine phase coexistence, the simulation of the separate bulk phases is performed independently and phase equilibria are determined from one-phase relations. The conventional techniques require many simulations along an isotherm [5] to locate a coexistence point. In the NpT plus test particle (NpT + TP) method [6,7] the chemical potential is expressed as a function of the pressure at a fixed temperature in both phases. The $\mu(p)$ relations are written in the form of Taylor series, where the coefficient of the Taylor series (i.e. the pressure derivatives of the chemical potential) can be determined from fluctuation formulas. The intersection of the two chemical potential branches defines the phase equilibrium point. Similar series expansion procedures were applied to the NpT [8,9], NVT [10], Rpμ [11] (where $R = E + pV - \mu N$ is the Ray energy) and μVT [12,13] ensembles. It is important to emphasize that these methods have the capability to yield phase equilibrium results not only in one point, but in a certain phase space interval.

The original NVT-, as well as the NpH- and μVL-GEMC methods give results only for one equilibrium point in the VLE curve. Useful generalization of the isothermal GEMC calculation was proposed recently for one- [14] and multi-component [15] systems, which applies the Taylor series expansion method for the coexistence quantities. These algorithms predict the VLE curves by Taylor series near the simulated equilibrium point. The coefficients of the Taylor series, which are in this case the derivatives of different quantities along the VLE curve, are determined in a straightforward way using special fluctuation formulas [16]. Furthermore, the coefficients for the equilibrium chemical potential and pressure can be calculated using Clapeyron-like equations resembling the Gibbs-Duhem integration method proposed by Kofke [17,18]. It was shown that the application of a Padè approximant considerably widens the temperature range where the extrapolation is accurate. The extrapolation scheme requires only minor modifications in the original GEMC computer code to get the Taylor series coefficients.

To complete these earlier studies, we have considered two further schemes for extrapolating in the GE. We present the implementations of the Taylor series based VLE extrapolation method for the one component NpH and μVL variants of the GEMC simulation. In the case of the NpH variant, the non-independent equilibrium variables are expressed as a function of the pressure, while in the case of the μVL variant, as a function of the chemical potential. To test the methods, GEMC simulations were performed on the Lennard-Jones (LJ) fluid and the first and second order Taylor series coefficients were determined in the phase equilibrium points for both the NpH and μVL versions.

METHOD

Derivatives from Fluctuation Formulas

Our goal is to express the different equilibrium quantities as a function of the pressure in the NpH-GE, and as a function of the chemical potential in the μVL-GE. For the general form of the relations, we represent the independent intensive variables with x, and the non-independent configurational intensive variables with y. In the NpH version x is to be replaced by p, in the μVL version, by μ. We express the $y(x)$ relation with Taylor series. For y any of the calculated intensive equilibrium variables can be chosen, such as the number density ($\rho = N/V$), the one-particle potential energy (u), the temperature, the pressure (only in the μVL, version) or the chemical potential (only in the NpH version).

The GEMC calculation directly yields the equilibrium quantities as an ensemble average at the state point, where the simulation is performed. The variables taken in the simulation basic point have a zero subscript in this paper ($y_0 = y(x_0) = \langle y(x_0)\rangle$, brackets denote the ensemble average). The second order Taylor series for the equilibrium value of y along the y_0 point can be written in the form of

$$y^{\mathrm{T}}(x) = y_0 + \left(\frac{\mathrm{d}\langle y\rangle}{\mathrm{d}x}\right)_0 (x - x_0) + \frac{1}{2}\left(\frac{\mathrm{d}^2\langle y\rangle}{\mathrm{d}x^2}\right)_0 (x - x_0)^2. \quad (1)$$

Here we omit to indicate the phase equilibrium variables with a special character, as all variables are phase equilibrium quantities. The "T" superscript is used for Taylor series functions.

The x derivatives of $\langle y\rangle$ at x_0 are taken along the VLE curve. We can write the first derivative of the $\langle y\rangle$ as the following general formula in all versions of the GEs:

$$\left(\frac{\mathrm{d}\langle y\rangle}{\mathrm{d}x}\right)_0 = \langle y\rangle\langle\varphi\rangle - \langle y\varphi\rangle, \quad (2)$$

where

$$\langle\varphi\rangle = \frac{\mathrm{d}Q^{\mathrm{Gibbs}}/\mathrm{d}x}{Q^{\mathrm{Gibbs}}}. \quad (3)$$

In this equation, Q^{Gibbs} is the partition function for the GE. In the case of the NVT basic ensemble,

$\phi = U$, as the reciprocal temperature, $\beta = 1/kT$, is chosen as the independent x variable [16] (k is the Boltzmann constant and U is the total configurational energy, $U = U_1 + U_2$; in the following subscripts 1 and 2 are used for the two coexisting phases). The dimensionless partition functions for NpH-GE and μVL-GE are [3]:

$$Q_{\mathrm{NpH}}^{\mathrm{Gibbs}} = \frac{b^{Nf/2}}{N!\Gamma(Nf/2)} \sum_{N_1=0}^{N} \frac{N!\Gamma(Nf/2)}{N_1!\Gamma(N_1 f/2) N_2!\Gamma(N_2 f/2)} \times \int_0^H \mathrm{d}H_1 \int V_1^{N_1} K_1^{N_1 f/2-1}\, \mathrm{d}r_1^{3N_1}\, \mathrm{d}V_1 \times \int_2 V_2^{N_2} K_2^{N_2 f/2-1}\, \mathrm{d}r_2^{3N_2}\, \mathrm{d}V_2, \tag{4}$$

$$Q_{\mu\mathrm{VL}}^{\mathrm{Gibbs}} = \int_0^L \mathrm{d}L_1 \int_0^V \mathrm{d}V_1 \times \left(\sum_{N_1=0}^{\infty} \frac{b^{N_1 f/2}}{N_1!\Gamma(N_1 f/2)} \int_1 V_1^{N_1} K_1^{N_1 f/2-1}\, \mathrm{d}r_1^{3N_1} \right) \times \left(\sum_{N_2=0}^{\infty} \frac{b^{N_2 f/2}}{N_2!\Gamma(N_2 f/2)} \int_2 V_2^{N_2} K_2^{N_2 f/2-1}\, \mathrm{d}r_2^{3N_2} \right), \tag{5}$$

where $b = 2\pi m/\hbar^2$, with m being the particle mass, and $\hbar$ the Planck constant. Furthermore, Γ is the Gamma-function, f is the molecular degree of freedom, r is the spatial coordinate of particles including all possible orientations and K_i is the total kinetic energy of the subsystem i (here it is assumed that the kinetic energy depends quadratically on the particle momenta). Considering that $K = H - pV - U$ in the NpH version, and $K = L + \mu N - U$ in the μVL version of the GE, we obtain:

$$\varphi = (V_1/K_1)n_1 + (V_2/K_2)n_2 \tag{6}$$

for the NpH version, and

$$\varphi = (N_1/K_1)n_1 + (N_2/K_2)n_2 \tag{7}$$

for the μVL version, where $n_i = N_i f/2 - 1$.

The second derivative of $\langle y \rangle$ can be obtained by differentiating the RHS of Eq. (2) once more:

$$\left(\frac{\mathrm{d}^2\langle y\rangle}{\mathrm{d}x^2}\right)_0 = 2\langle y\rangle\langle\varphi\rangle^2 + \langle y\rangle\langle\varphi^2\rangle - 2\langle y\varphi\rangle\langle\varphi\rangle + \langle y\varphi^2\rangle. \tag{8}$$

The fluctuation formulas in Eqs. (2) and (8) contain the ensemble averages of y and ϕ as well as their double and triple products that can be easily yielded from the GEMC simulation.

Note that theoretically it is possible to use higher order Taylor series terms to express $y(x)$, but the efficiency of the prediction is not expected to increase because of the necessary inclusion of higher order fluctuation formulas having large statistical uncertainties. Meanwhile, as was shown in previous papers [14,15], it is useful to apply a 0:1 Padè approximant [19] for the second order Taylor series. The Padè approximants were designed to improve the convergence of the Taylor series, whose terms are known up to order n. The Padè approximants reproduce the expansion to order n, and provide an estimate of the remainder of the series. The Padè approximant used for the second-order Taylor series expansion for the VLE curve can be written as

$$y^{\mathrm{P}}(x) = y_0 + t'/(1 - t''/t'), \tag{9}$$

where the "P" superscript represents the 0:1 Padè approximant function (to make distinction from the Taylor series indicated by superscript "T"). t' and t'' are the first and second order terms of the Taylor series in Eq. (1):

$$t' = \left(\frac{\mathrm{d}\langle y\rangle}{\mathrm{d}x}\right)_0 (x - x_0), \tag{10}$$

and

$$t'' = \frac{1}{2}\left(\frac{\mathrm{d}^2\langle y\rangle}{\mathrm{d}x^2}\right)_0 (x - x_0)^2. \tag{11}$$

Derivatives from Clapeyron-like Equations

Using the reciprocal temperature β, and the βp and $\beta\mu$ products instead of T, p and μ as the intensive variables to describe phase equilibria is legitimate, since their equality in the two phases is also fulfilled. We introduce these variables to get a more compact form of the equilibrium formulas.

To express the Taylor series for the $\beta(p)$, $\beta\mu(p)$, $\beta(\mu)$ and $\beta p(\mu)$ functions, it is important to realise that, as opposed to the other configurational quantities, the first-order term can be determined from simple ensemble averages through Clapeyron-like equations, and the fluctuation formulas appear only in the second-order term. Starting with the standard thermodynamic relation

$$\mathrm{d}(\beta\mu) = u\,\mathrm{d}\beta + v\,\mathrm{d}(\beta p), \tag{12}$$

(where v is the one-particle volume) we can write the first derivatives for the above quantities along the VLE curves. The first derivatives in the NpH version are:

$$\frac{\mathrm{d}\beta}{\mathrm{d}p} = -\beta_0 \frac{\Delta v_0}{\Delta h_0}, \tag{13}$$

$$\frac{\mathrm{d}(\beta\mu)}{\mathrm{d}p} = \beta_0 \frac{\Delta(v/h)_0}{\Delta(1/h)_0}, \tag{14}$$

where h is the one-particle enthalpy and Δ represents the change of the given one-particle property upon phase transition at x_0 (for example: $\Delta v_0 = \langle v_1 \rangle - \langle v_2 \rangle$, where the liquid and vapour phases are labeled by 1 and 2, respectively).

The first derivatives in the μVL version are

$$\frac{\mathrm{d}\beta}{\mathrm{d}\mu} = \beta_0 \frac{\Delta\rho_0}{\Delta(l/v)_0}, \tag{15}$$

$$\frac{\mathrm{d}(\beta p)}{\mathrm{d}\mu} = \beta_0 \frac{\Delta(1/l)_0}{\Delta(v/l)_0}, \tag{16}$$

where l is the one-particle Hill energy. The derivatives of the conventional T, p and μ variables can also be deducted from these equations. For example:

$$\frac{\mathrm{d}T}{\mathrm{d}p} = T_0 \frac{\Delta v_0}{\Delta h_0}, \tag{17}$$

or

$$\frac{\mathrm{d}p}{\mathrm{d}\mu} = \frac{\Delta(1/l)_0}{\Delta(v/l)_0} - p_0 \frac{\Delta\rho_0}{\Delta(l/v)_0}. \tag{18}$$

The second derivatives include fluctuation formulas through the use of regular first derivatives, e.g.:

$$\frac{\mathrm{d}^2\beta}{\mathrm{d}\mu^2} = \beta_0 \frac{\Delta\rho_0}{\Delta(l/v)_0}\left(\frac{\Delta\rho_0}{\Delta(l/v)_0} + \frac{(\mathrm{d}\Delta\rho_0/\mathrm{d}\mu)}{\Delta\rho_0} - \frac{(\mathrm{d}\Delta(l/v)_0/\mathrm{d}\mu)}{\Delta(l/v)_0}\right). \tag{19}$$

Saturation Heat Capacity

Knowing the p and μ derivatives of the various quantities along the VLE curve it is possible to directly calculate the saturation heat capacity (c_s). The definition of the saturation heat capacity referred to one particle is the following:

$$c_\mathrm{s} = T\left(\frac{\partial(S/N)}{\partial T}\right) = -\beta\left(\frac{\partial(S/N)}{\partial \beta}\right), \tag{20}$$

where S/N is the one-particle entropy, and the derivatives, like all other derivatives in this paper, are taken along the VLE curve. Deduced from basic thermodynamic relations, c_s can be expressed using the quantities yielded by the proposed methods. See Eqs. (21) and (22) for the formulas of the NpH and μVL versions, respectively

$$\frac{c_\mathrm{s}}{k} = -\beta h - \beta\left(\frac{\mathrm{d}\beta}{\mathrm{d}p}\right)^{-1}\left(\beta\frac{\mathrm{d}h}{\mathrm{d}p} - \frac{\mathrm{d}(\beta\mu)}{\mathrm{d}p}\right), \tag{21}$$

$$\frac{c_\mathrm{s}}{k} = -\beta l - \beta\left(\frac{\mathrm{d}\beta}{\mathrm{d}\mu}\right)^{-1}\left(\beta\frac{\mathrm{d}l}{\mathrm{d}\mu} + \beta p\frac{\mathrm{d}v}{\mathrm{d}\mu} + v\frac{\mathrm{d}(\beta p)}{\mathrm{d}\mu}\right). \tag{22}$$

The values of h, $(\mathrm{d}h/\mathrm{d}p)$, l, $(\mathrm{d}l/\mathrm{d}\mu)$ and $(\mathrm{d}v/\mathrm{d}\mu)$ can be taken either in liquid or in vapor phases. The capability of calculating the saturation heat capacities in this direct way, similarly as in the extrapolation method developed for the NVT-GEMC calculation [14], is an advantageous feature of our technique, since the calculation methods for the saturation heat capacities on the basis of the conventional one-phase simulation techniques require a foreknowledge of the VLE curves [20].

To summarize, we can calculate the derivatives of any intensive variables (even the saturation heat capacity) of the phase coexistence from fluctuation formulas. In addition, the Taylor series coefficients for β, βp and $\beta\mu$ (but also for T, p and μ) can be determined from Clapeyron-like equations. The first derivatives written in Clapeyron-like form contain only simple ensemble averages, while the second derivatives contain fluctuation formulas as well.

RESULTS AND DISCUSSION

GEMC calculations together with the extrapolation schemes described in the previous section have been applied and tested on the widely studied LJ model system. The LJ system is usually used for testing new simulation methods, as the VLE data of the LJ fluid are well known and are available in the literature obtained by different methods.

The parameters ε and σ characterizing the LJ potential were used to specify the reduced quantities: $T^* = kT/\varepsilon$ is the reduced temperature, $\beta^* = 1/T^* = \varepsilon/kT$ is the reduced reciprocal temperature, $U^* = U/\varepsilon$ is the reduced configurational energy, $u^* = U^*/N$ is the reduced one-particle configurational energy, $V^* = V/\sigma^3$ is the reduced volume, $\rho^* = N/V^*$ is the reduced number density, $p^* = p\sigma^3/\varepsilon$ is the reduced pressure and $\mu^* = \mu/\varepsilon$ is the reduced chemical potential. For pure atomic fluids, the chemical potential reads:

$$\mu = \mu_\mathrm{res} + kT\ln\rho - (3/2)kT\ln(kT) - (3/2)kT\ln b, \tag{23}$$

where "*res*" indicates residual property. The last term can be omitted here, as b can be set to one in our cases. The remaining part is called configurational chemical potential (see the temperature is a configurational property in the NpH and μVL ensembles), which can be written in the following dimensionless form:

$$\beta\mu = \beta\mu_\mathrm{res} + \ln\rho^* + (3/2)\ln\beta^*. \tag{24}$$

The NpH-GEMC calculations were performed using $N = 512$ particles, while the μVL simulation parameters were set to do the calculation with

particle numbers around $N = 512$. We used the minimum image convention, periodic boundary conditions and a spherical cut-off. The usual long-tail corrections were applied to energy, pressure, chemical potential, etc. In the individual molecule displacement the particles were chosen randomly.

In the NpH version a cycle consisted of N attempted displacements of molecules and one uncoupled volume change of the two subsystems, a coupled change in the enthalpies (heat exchange step) and n attempted exchanges of particles between the two subsystems. n was chosen to get 2–3 particle transfers per cycle. In the μVL version a cycle consisted of $3N$ particle displacements, creation and annihilations of molecules attempted with equal probabilities in subsystem 1 and 2, and a coupled change of Hill energy (heat exchange step) as well as of simulation volume. The total system enthalpies and Hill energies were chosen so that the one-particle energy lies between the energy of the pure liquid and pure vapor phases. Simulations were started either from face-centered cubic lattice configurations or from output configurations of previous runs. Equilibration runs with 20,000 cycles were followed by production periods of about 400,000 cycles. The maximum molecular displacement, volume, enthalpy and Hill energy changes were adjusted previously to obtain, where possible, a 40–50% acceptance rate for the attempted move. Estimates of the standard deviations were made by dividing the runs into about 50 blocks and calculating block averages. During the simulations all the quantities necessary to build up the fluctuation formulas were also accumulated.

In the NpH version the configurational chemical potentials were calculated according to Widom's particle insertion method [21], while in the μVL version the pressure is determined from virial sums.

In both versions of the GE, the calculations were performed at three different equilibrium points, which correspond to the $T^* = 1.05$, 1.15 and 1.25 reduced equilibrium temperatures.

The equilibrium variables were calculated as simple ensemble averages, while their first and second derivatives along the VLE curves were calculated by adapting the equations presented above. The VLE curves were constructed using the first and second order Taylor series and the Padè approximants of the second order Taylor series.

In the earlier work on the Taylor series extrapolation method [14] a procedure was proposed to estimate the range, where the extrapolation is probably accurate. However, if one has the equilibrium quantities from ensemble averages at different basic simulation points, then the extrapolated VLE curves can be verified by simple visual comparison. If all of the calculated equilibrium points are put on the VLE graphs, one can observe whether or not a given extrapolation curve starting from one point coincides with the other points. To our experience, instead of checking the inner consistency by using complicated formulas [14], it is more straightforward to estimate the extrapolation range in this visual way. In our special case of the LJ fluids we also have the accurate NpT + TP results [7] as reference data, which are used to check the basic simulation points and the extrapolation curves. For systems whose VLE was not previously studied, we suggest choosing the number of simulation points in such a way that the extrapolation starting from one point accurately reproduces the phase equilibrium results at the adjacent point.

Figure 1 shows the $p^*(T^*)$ curves obtained from the NpH version of the GEMC calculation for all three of the p_0^* simulation points. Even though the NpH version gives a $T^*(p^*)$ relationship, we constructed the $p^*(T^*)$ plots by inverting the original curves to let the reader easily compare our result with literature data. We note here that, indicating the thermodynamic consistency of our results, all the T, p, and μ extrapolations in the test system gave practically the same curves for both the vapor and liquid phases (this is the reason why we show only one set of curves for these relationships in this work).

The basic conclusions we make about this figure are more or less valid in all other figures of our test systems. The basic simulation points fit well with the reference curve. Small mismatches are only seen at the points corresponding to the highest temperature ($T^* = 1.25$). This is caused by the higher uncertainties observed close to the critical point. The first order series suitably reproduce the tangents of the reference curves (therefore the first derivatives are accurate). Nevertheless, the linear extrapolation can follow the curves only in a shorter range. The second order Taylor series curves are able to extrapolate for a wider pressure range; however, in several cases they diverge at higher distances from the basic point, such as in the $p_0^* = 0.034$ case. In most cases the Padè approximants give the best results. Analyzing the figures one can conclude that using only two simulation points (the lower and the upper), the Padè approximant can describe practically the whole range of the VLE curve. Meanwhile, one should consider that the curves starting from a simulation point that is close to the critical point can produce a slightly worse prediction even in the upper region.

We have compared our coexistence vapor pressure curves with the ones obtained earlier from the NVT version [14]. The Padè curves have nearly the same accuracy in the two cases, but we have observed a remarkable improvement in the accuracy of the second order Taylor series in the NpH case. Moreover, the NVT version was not able to produce a proper pressure curve starting from the calculated

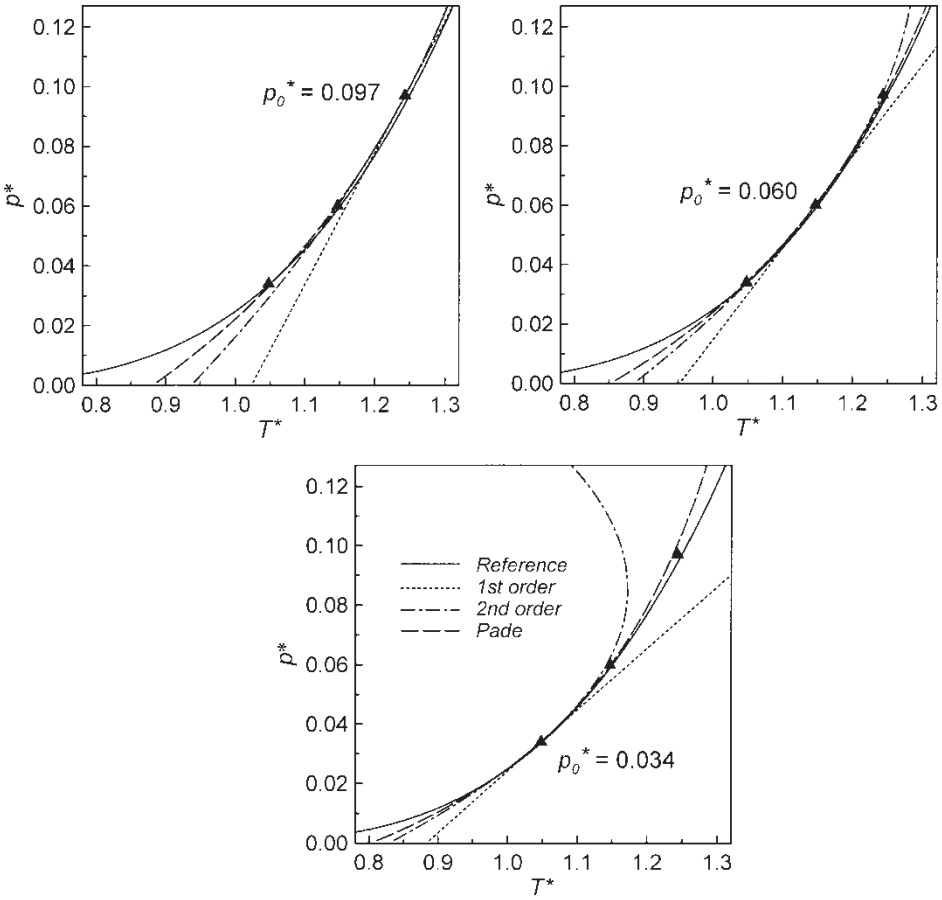

FIGURE 1 Extrapolating $p^*(T^*)$ curves of the LJ fluid obtained from the NpH version of the GEMC simulation. The first order Taylor series are indicated by dotted lines, the second order Taylor series by dashed-dotted lines, the Padè approximant of the second order Taylor series by dashed lines. A reference curve is constructed according to the NpT + TP reference data [7] and is shown as a solid line. Triangles represent the three basic simulation points at $p_0^* = 0.034$, 0.060 and 0,097. Different insets are used for extrapolation results at the three p_0^* points.

liquid phase basic pressure as opposed to the NpH version, where the curves constructed either from the liquid or vapor phase basic temperature are almost the same. The improvements can be explained by the advantages of the NpH version over the NVT version. One such benefit is derived from the difference in the calculation of the non-independent intensive variables. In the NpH case the pressure is chosen by the user, and the temperature is easily and reliably calculated from the kinetic energy; while in the isothermal NVT case the pressure is determined from virial sums, which fail to produce appropriate pressures (and of course, the Taylor series of the pressure) in the liquid phase at higher densities.

Other difficulties encountered in the NVT-GEMC method arise at low temperatures when the volume of the vapor phase cell is too large compared to the liquid phase cell. Because the total volume is fixed, the magnitude of the volume change has to be equal for the two cells. Since the liquid phase cell volume is small, the volume change should also be small making the sampling of the volume fluctuations of the large vapor phase cell inefficient. In the NpH version of the GEMC simulation the total volume is not fixed, and consequently the volume fluctuation of the two cells is independent from each other.

In Fig. 2 we present the $p^*(\rho^*)$ curves for the vapor side. The visual comparison of these results with the corresponding $T^*(\rho^*)$ curves in Ref. [14] gave us further indication that the NpH version is superior to the NVT one. However, we have to note that the real $p^*(\rho^*)$ curve has more linear characteristic in the studied sections than the $T^*(\rho^*)$ curve, and consequently, the former is better suited for extrapolation. This is also the reason why the first order Taylor series gives the best results in certain regions of these plots. The fact that the first order Taylor series should have a precedence over the others appears more significantly in the $p^*(\rho^*)$ curves of the liquid side (see Fig. 3). In the case of the calculated $\beta\mu(p^*)$ relations the Padè curves give particularly good results. This is shown in Fig. 4, where the three Padè curves starting from the three basic points are put on one

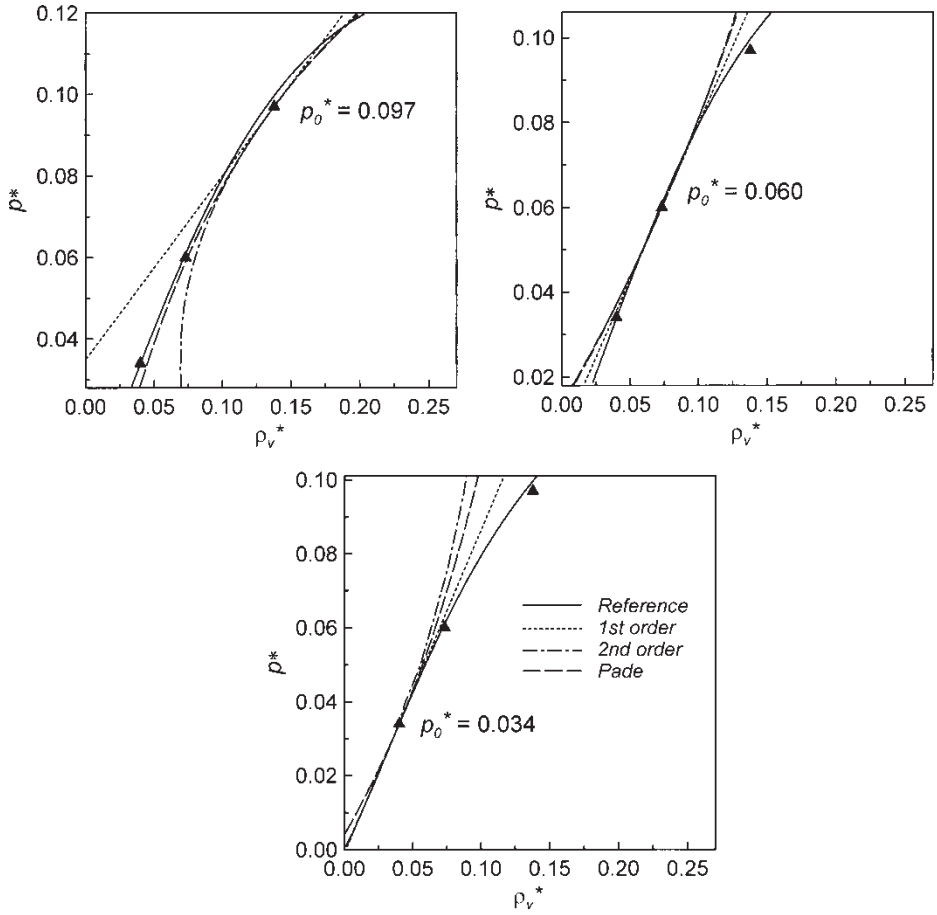

FIGURE 2 Extrapolating $p^*(\rho^*)$ curves for the vapor phase of the LJ fluid obtained from the NpH version of the GEMC simulation. Parts, lines and symbols as for Fig. 1.

diagram. All the three Padè curves reproduce the reference line in the intermediate range of pressure. They slightly deviate from each other only at low and high pressures.

Figure 5 shows the $T^*(\mu^*)$ curves obtained from the μVL simulation. Note that the VLE curves, where the different equilibrium variables are drawn against the configurational chemical potential used in the μVL ensemble, have a point near $T^* = 0.95$, where the direction of the curves turns back. Consequently, one chemical potential value should result in two values of the dependent variable, one above and one below this point. In Fig. 5, the upper parts of the curves belong to the coexistence points above $T^* \approx 0.95$. The simulation point at $\mu_0^* = -3.847$ (corresponding to $T^* \approx 1.05$) is near this turning point and the extrapolation curves are not able to make a prediction for the lower part of the plot, and give mostly improper results in the other direction. The other two simulation points are in a smoother regions of the VLE curve, and work better. The Padè curves give the best results here as well. The $p^*(\mu^*)$ curves (which are not presented in this paper) show similar characteristics with the exception of the calculated p_0 points of the liquid phase which exhibit some deviation from the reference data. This is caused by the less accurate pressure calculation from virials, like in the case of the NVT-GE. The $\rho^*(\mu^*)$ curves for the vapor phase reproduce the literature data with somewhat less accuracy.

Note that the application of the Padè approximant needs some special care because, although it can significantly increase the accuracy of the prediction in many cases, it can give much worse results for certain sections of the extrapolation curve than the second or the first order Taylor series. The Padè approximation has a special characteristic, and a general rule applicable to all cases cannot be given to determine the ranges where it enhances or worsens the extrapolation. A special rule was successfully applied in an earlier paper [15] using the following criterion: if the t''/t' quotient is less than a predefined value a (where a is close to zero), then the Padè approximant is used, otherwise the second order Taylor series is chosen for extrapolation. In our case there was no need to apply this rule because the above criterion was always fulfilled.

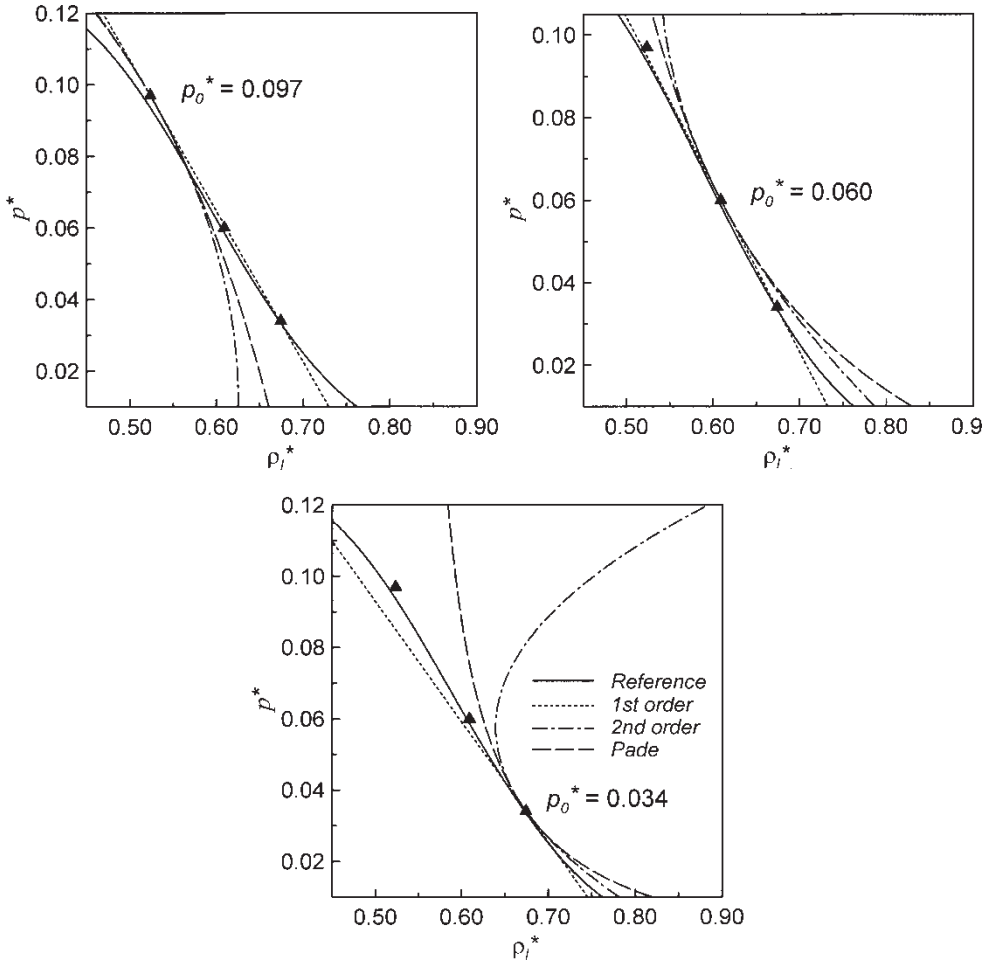

FIGURE 3 Extrapolating $p^*(\rho^*)$ curves for the liquid phase of the LJ fluid obtained from the NpH version of the GEMC simulation. Parts, lines and symbols as for Fig. 1.

In the previous section we gave the equations for the saturation heat capacity based on the NpH- and μVL-GEMC simulations, which contain only the averages and derivatives provided by the method (see Eqs. (21) and (22)). In Table I we present the results for c_s of the LJ system together with former data from NVT-GEMC calculation [14] and from one phase NVT and NpT simulations [22]. According to the different definitions of the configurational chemical potential, the expression $(\beta\mu)$ appearing in the heat capacity equations include an additional term of $(3/2)\ln\beta$ as compared to the corresponding expression in the NVT version. Consequently the calculated c_s/k values have to be decreased by the values derived from this additional term to obtain the same quantities as had been determined in the isothermal GEMC (namely the non-ideal part of the saturation heat capacity). It is seen from the table that the agreement between our present and earlier data is satisfactory, though the data for the higher $T^* \approx 1.25$ temperature have a larger deviation. The NpH version also has an advantage here: the corresponding equation contains only one derivative term that must be determined from fluctuation formula, while in the case of the two other versions, the equations contain two such derivative terms. The remaining terms can be calculated from the more precise simple averages.

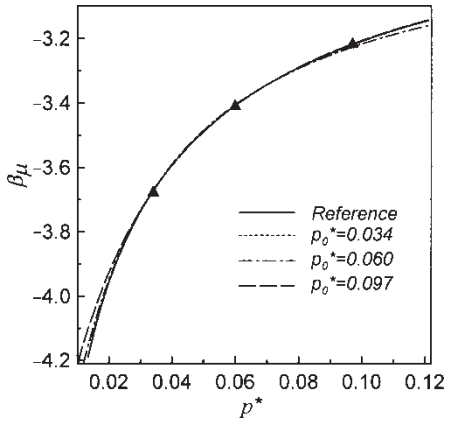

FIGURE 4 Extrapolating $\beta\mu(p^*)$ curves of the LJ fluid for the Padè approximant obtained from the NpH version of the GEMC simulation. Symbols and solid line as for Fig. 1. The three different curves starting from the three p_0^* points are put on one diagram. The dotted, dashed-dotted, dashed lines are used for $p_0^* = 0.034$, 0.060 and 0,097, respectively.

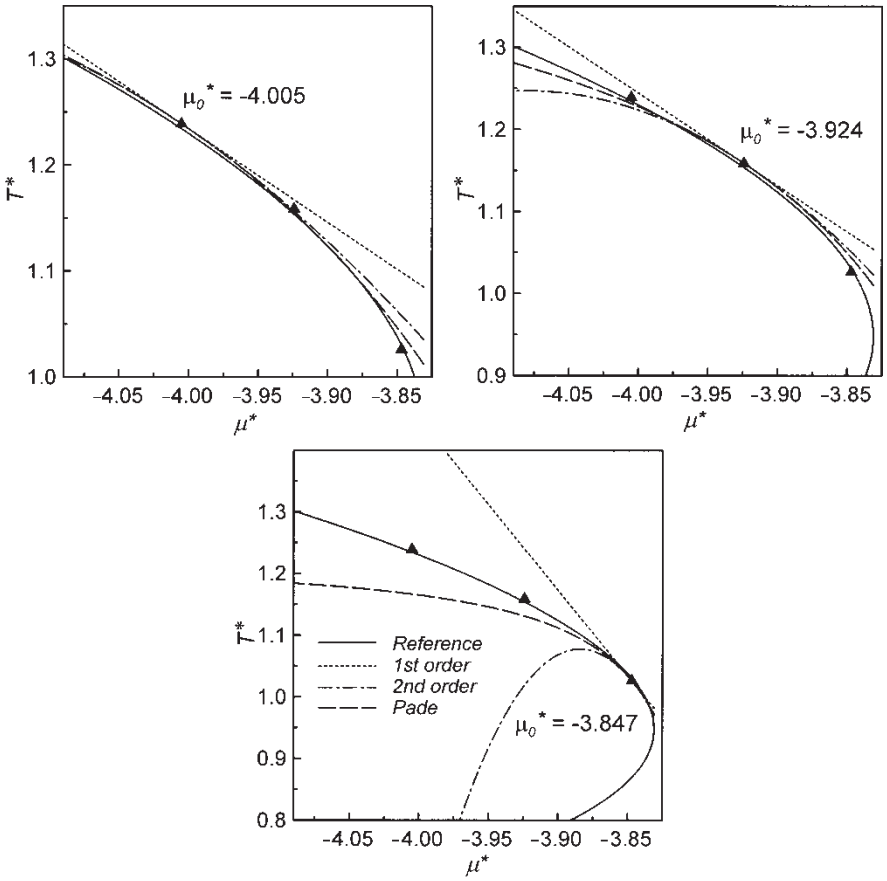

FIGURE 5 Extrapolating $T^*(\mu^*)$ curves of the LJ fluid obtained from the μVL version of the GEMC simulation. Parts and lines are as for Fig. 1. Triangles represent the three basic simulation points at $\mu_0^* = -3.847$, -3.924 and -4.005. Different insets are used for the extrapolation results at the three μ_0^* points.

CONCLUSION

We developed the Taylor series based extrapolation schemes for the one component NpH and μVL versions of the GEMC simulation. These methods are the implementations of the efficient and powerful extrapolation technique applied recently to the GEMC simulation based on the NVT-GE. The coefficients of the first and second order Taylor series can be calculated from the data yielded by the GEMC simulation using fluctuation formulas or Clapeyron-like equations without major modification of

TABLE I Saturation heat capacities calculated with Eqs. (21) and (22) from the results of the NpH and μVL versions of the GEMC simulation

p_0^*, μ_0^* or T_0^*	*Method*	c_s/k *(liquid)*	c_s/k *(vapour)*
$p_0^* = 0.034$, $T^* = 1.048(5)$	NpH-GEMC	4.73(19)	−7.00(25)
$T_0^* = 1.05$	NVT-GEMC [14]	4.76(14)	−7.11(36)
$T_0^* = 1.05$	NVT MC [22]	4.613(53)	−6.729(39)
$T_0^* = 1.05$	NpT MC [22]	4.84(15)	−7.42(14)
$p_0^* = 0.060$, $T^* = 1.147(7)$	NpH-GEMC	5.68(18)	−7.78(27)
$\mu_0^* = -3.924$, $T^* = 1.159(10)$	μVL-GEMC	5.57(20)	−8.15(52)
$T_0^* = 1.15$	NVT-GEMC [14]	5.43(10)	−8.29(36)
$T_0^* = 1.15$	NVT MC [22]	5.486(47)	−7.304(45)
$T_0^* = 1.15$	NpT MC [22]	5.80(23)	−8.17(19)
$p_0^* = 0.097$, $T^* = 1.244(9)$	NpH-GEMC	7.47(40)	−11.91(38)
$\mu_0^* = -4.005$, $T^* = 1.239(11)$	μVT-GEMC	7.94(51)	−9.97(55)
$T_0^* = 1.25$	NVT-GEMC [14]	9.35(39)	−9.10(42)
$T_0^* = 1.25$	NVT MC [22]	8.705(65)	−11.503(74)
$T_0^* = 1.25$	NpT MC [22]	8.24(47)	−11.50(63)

The reference data are taken from NVT-GEMC calculations [14] and one phase NVT and NpT simulations [22]. The numbers in parentheses denote the statistical uncertainties in the last digits.

the original computer code. The application of a Padè approximant considerably widens the range over which the extrapolation is satisfactory. The results presented for the LJ fluid demonstrate that from a few separate simulations in different phase equilibrium points the whole range of practical importance of the VLE curve for pure molecular fluids can be constructed. The results of the proposed calculation can be easily verified by checking the coincidences of curves starting from the adjacent points. We proposed formulas for the calculation of the saturation heat capacity from the NpH- and μVL-GEMC simulations. Comparing the capability of the Gibbs ensemble extrapolation schemes adapted for the different basic ensembles, the NpH version seems to have some advantages over the others.

Acknowledgements

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