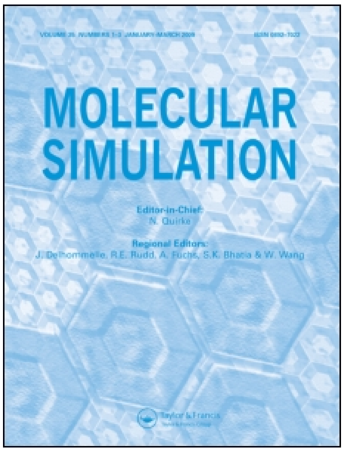

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# Scaled Particle Theory and the Efficient Calculation of the Chemical Potential of Hard Spheres in the NVT Ensemble

S. Labík[a]; W. R. Smith[b]
[a] Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic [b] Department of Mathematics and Statistics, University of Guelph, Guelph, Ontario, Canada

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# SCALED PARTICLE THEORY AND THE EFFICIENT CALCULATION OF THE CHEMICAL POTENTIAL OF HARD SPHERES IN THE NVT ENSEMBLE[1]

S. LABÍK

*Department of Physical Chemistry, Institute of Chemical Technology,*
*Prague 166 28, Czech Republic*

and

W.R. SMITH

*Department of Mathematics and Statistics, University of Guelph, Guelph,*
*Ontario N1G 2W1, Canada*

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We propose and test a new method for calculating the chemical potential of a hard-sphere fluid using Monte Carlo calculations in the NVT ensemble, which we call the SP-MC method. The method employs ideas from scaled particle theory (SPT), including a recent new SPT result of Smith and Labík for hard-sphere mixtures. The method is based on the calculation of the chemical potential at infinite dilution of a series of hard spheres of smaller diameter than that of the system of interest. Using this easily obtained data in conjunction with theoretical considerations, the chemical potential of the hard-sphere system may be accurately obtained. The SP-MC method is more precise than any other currently available method, and it can be used up to extremely high densities, including into the metastable region.

KEY WORDS: Hard spheres, scaled particle theory, chemical potential

## 1 INTRODUCTION

The development of efficient computer simulation techniques for the direct calculation of the chemical potential is a problem of continuing interest (*e.g.* [1–9]). A number of variants of Widom's test-particle-insertion (TPI) method in the NVT ensemble [1] have been proposed, including umbrella sampling [5, 6], excluded volume map sampling [7], a method [8] based on some ideas of scaled-particle theory [10], and a recent method that uses a force-balance Monte Carlo technique [9]. At low and moderate densities, all available methods give reasonably accurate and precise results, but they become increasingly imprecise at high densities. At such conditions, grand canonical ($\mu VT$) ensemble simulations [2], also fail to produce precise results without very long computer runs, since the number of molecules in the system becomes invariant at high densities.

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The basic form of the TPI method for calculating the chemical potential of a hard-sphere system (of unit sphere diameter) involves generating the usual Markov chain of particle moves and simultaneously measuring the probability $P(1)$ that an additional particle can be inserted into the system at a randomly selected location. The chemical potential is the given in terms of this quantity by [1]

$$\beta\mu = -\ln P(1) \tag{1}$$

$\mu$ is the excess chemical potential and $\beta = 1/kT$, where $k$ is Boltzmann's constant and $T$ is the absolute temperature. The insertion probability is related to $V_s$, the "spare volume" available to the inserted sphere centre, by [11, 12]

$$P(1) = V_s/V \tag{2}$$

where $V$ is the overall system volume. Combining Equations (1) and (2) gives

$$\beta\mu = -\ln[V_s/V] = -\ln[P(1)] \tag{3}$$

The above equations show that the basic TPI method is intrinsically inefficient at high densities, where $V_s/V$, and hence $P(1)$, are very small and difficult to measure precisely in a simulation. Direct use of Equation (1) gives a highly imprecise value of $\mu$ at high densities without the use of very long computer runs, since the probability of successfully inserting an additional particle into the system is very small. For example, when $\beta\mu \approx 15$ (a typical value observed in subsequent results), a single successful insertion occurs on average only once in every $\exp(15) \approx 3 \times 10^6$ attempts.

In this paper, we propose and test a new method for calculating the chemical potential that combines conventional Monte Carlo simulation in the NVT ensemble with a recently obtained new result based on scaled particle theory ideas [13], which relates the derivative of the chemical potential with respect to the size of the inserted solute particle and the properties of the fluid solvent into which it is inserted. We call our approach the SP-MC method. We illustrate its use for calculating the chemical potential of a hard-sphere fluid system and demonstrate its accuracy and excellent precision up to extremely high densities, even into the metastable region. We also discuss possible extensions of the approach to other fluids.

## 2 THE SP-MC METHOD

The essence of the method is to measure the probability of successful insertion of a solute particle with a range of diameter values, $x$, smaller than that of the solute hard-sphere diameter. Provided $x$ is not too large, such measurements are quite precise, even at very high densities. We combine these measurements with previously known SPT results and a new theoretical result to accurately extrapolate these values to $x = 1$, giving the chemical potential of the hard-sphere solvent.

$P(x)$, the probability of successful insertion of a cavity (or particle) of diameter $x$ into the system may be expressed as

$$P(x) = \exp[-\beta\mu^{\infty}(x)] \tag{4}$$

where $\infty$ denotes the fact that the added particle can be considered to be an additional system component at infinite dilution. Recently, Smith and Labík [13] derived an exact result relating $\beta\mu^{\infty}(x)$ to the properties of the mixture. The special form of this result relevant to the efficient computer simulation of the chemical potential of a pure hard-sphere fluid is

$$\left.\frac{\partial \ln P(x)}{\partial x}\right|_{x=1} = -12\eta\, g(1) = -3(z-1) \tag{5}$$

where $\eta = \pi\rho/6$ is the fluid packing fraction, and $g(1)$ and $z$ are, respectively, the contact value of the pair distribution function and the compressibility factor of the hard-sphere fluid.

Precise measurements of $P(x)$ may be made in the course of an NVT simulation by inserting points at random and calculating the distance to the nearest sphere centre. This yields statistics to obtain precise values of $P(x)$ up to some convenient value $x_{\max}$ (which decreases as the density increases, and at high densities is much less than 1). The goal is to extrapolate these precise results to obtain an accurate value of $P(1)$. Equation (5) is additional information that may be used to this end. (We note that values of $g(1)$ can be simultaneously obtained from the simulation to use in Equation (5)). Further additional information concerning $P(x)$ is available on the basis of known SPT results, exact in the limits of either low $x$ or low densities, where $P(x)$ is given by [10]

$$P(x) = 1 - \eta(1+x)^3 \tag{6}$$

Our method postulates a cubic interpolation form for ln $P(x)$ versus $x$ in the range $0 \le x \le 1$. The reasonableness of this assumption will be borne out by our results, but such a simple dependence is consistent with the recent data of Nezbeda and Kolafa [8]. Then, obtaining the first two coefficients of this polynomial from the Taylor expansion of Equation (6) and using the constraint of Equation (5) at $x = 1$, the following expression results for $x \in [0, 1]$:

$$\beta\mu^{\infty}(x) = -\ln P(x) = -\ln(1-\eta) + \frac{3\eta}{1-\eta}x + cx^2 + \left[4\eta g(1) - \frac{\eta}{1-\eta} - \frac{2}{3}c\right]x^3 \tag{7}$$

We fitted our simulation results for ln $P(x)$ to Equation (7) over a suitable range of $x$ (see subsequent discussion) to obtain $c$, and thence the chemical potential from $P(1)$, given by

$$\beta\mu^{\infty}(1) \equiv \beta\mu = -\ln(1-\eta) + \frac{2\eta}{1-\eta} + 4\eta g(1) + \frac{1}{3}c \tag{8}$$

## 3 SIMULATION DETAILS

We implemented the conventional NVT Monte Carlo method using periodic boundary conditions in a cubic box with $N = 2048$ spheres, employing a linked-list procedure. For each density, after the system was equilibrated by generating a sufficient number of configurations, we collected data according to the following procedures over each of 25 sub-experiments. We attempted to move each sphere

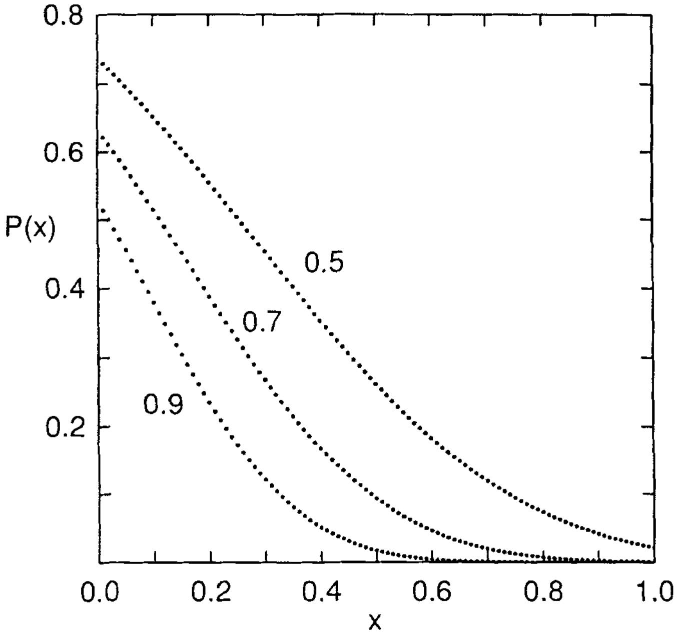

Figure 1

10 times, and then analyzed the resulting configuration to obtain data for $g(r)$, $r \in (1, 1.1)$ (which was subsequently analyzed to obtain $g(1)$). Using this configuration, we also obtained data for $P(x)$ by inserting 10,000 points at randomly selected locations in the configuration. This procedure (attempting to move each sphere 10 times, followed by the collection of $P(x)$ data) was performed 100 times. Each sub-experiment thus corresponds to a total of $\approx 2.5 \times 10^6$ particle insertions and $\approx 5 \times 10^6$ Monte Carlo steps.

We analyzed each sub-experiment by calculating the constant $c$ in Equation (7) from a least-squares fit of the data obtained over $x \in (0, x_{\mathrm{max}})$, where $x_{\mathrm{max}}$ corresponds to $P(x_{\mathrm{max}}) \approx 0.001$. This allowed us to obtain $\beta\mu$ from Equation (8). The final value of $\beta\mu$ was obtained as the average over the 25 sub-experiments, and we estimated its precision by calculating the standard deviation over the sub-experiments.

In the process of the simulation, the raw value of $P(1)$ in each sub-experiment was also used to obtain the value of $\beta\mu$ according to the direct Widom TPI method [1].

We used the Fortran compiler on an HP-Apollo 730 (Cobra) computer. A typical sub-experiment consumed about 2 minutes of computer CPU time.

## 4 RESULTS AND DISCUSSION

In Figure 1 are shown our simulation results for $P(x)$ at three densities. The chemical potential is given by $\ln P(x)$ at $x = 1$. It is seen that $P(x)$ itself is vanishingly small near $x = 1$ at the higher two densities shown.

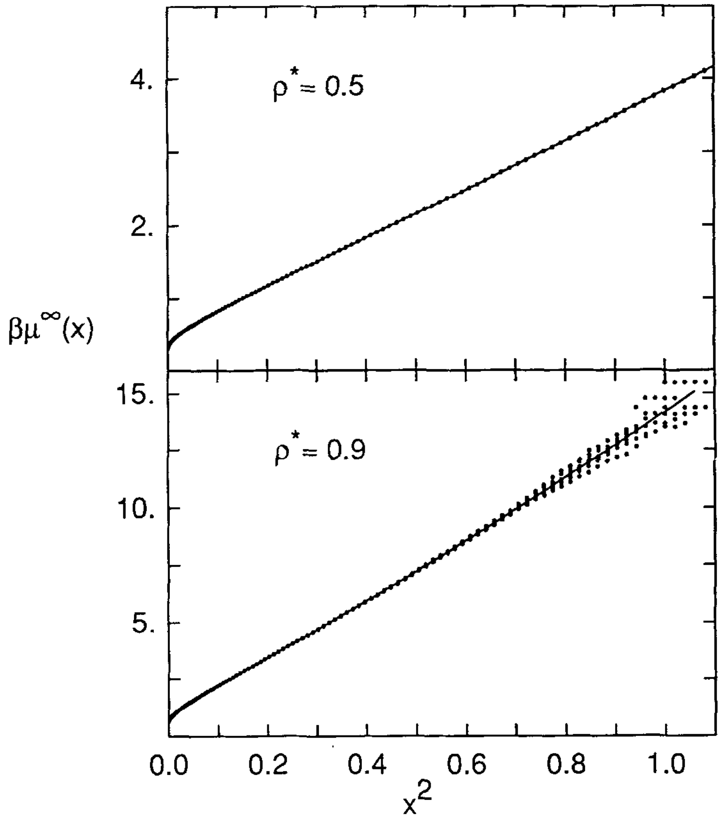

Figure 2

In Figure 2, we show our results for $\beta\mu^{\infty}(x)$ corresponding to the lowest and highest densities in Figure 1. Each curve shown is the result of the least-squares fit of Equation (7) using data over the range (0, ≈ 0.6), where the data show negligible scatter. Beyond 0.6 the curve is thus an extrapolation, whose derivative at $x = 1$ is constrained via Equation (5). It is seen that the curves agree very well with the data, even though this has considerable scatter for the high density at large $x$. We remark that for this density the data points yielding $\beta\mu \approx 15$ correspond to a single successful particle insertion in $\exp(15) \approx 3 \times 10^6$ attempts, *i.e.* about once in each sub-block of our simulations. Also, we note in passing that Figure 1 of Nezbeda and Kolafa [8] indicates that $\beta\mu^{\infty}(0) = 0$, which, from Equation (6) is incorrect.

An indication of the robustness of our procedure is the dependence of the results on the choice of the data interval used to fit Equation (7). This is illustrated in Table 1, which compares results obtained using several data intervals for the (high) density $\eta = 0.45$ ($\rho = 0.86$). It is seen that almost any reasonable data set may be chosen, and that the value of $\beta\mu$ is insensitive to this choice.

In Table 2 our results for $\beta\mu$ are shown and compared with results obtained from several semi-empirical hard-sphere equations of state, the direct (TPI) method, and

**Table 1** Sensitivity of the chemical potentials at $\eta = 0.45$ calculated by the SP-MC method to the data set. The precisions indicated are one standard deviation over the 25 sub-experiments.

| *data interval* | $\beta\mu$ |
|---|---|
| 0.0–0.55 | 12.378 ± 0.013 |
| 0.1–0.55 | 12.376 ± 0.013 |
| 0.2–0.40 | 12.378 ± 0.013 |
| 0.3–0.60 | 12.372 ± 0.013 |
| 0.4–0.70 | 12.368 ± 0.012 |

**Table 2** Chemical potentials from MC simulations and from several equations of state.

| $\pi$ | $\eta$ | *CS[14]* | *B[15]* | *K[16]* | *TPI (this paper)* | *FB [9]* | *SP-MC (this paper)* |
|---|---|---|---|---|---|---|---|
| 0.5 | 0.2618 | 3.806 | 3.814 | 3.816 | 3.817 ± 0.002 | 3.84 ± 0.04 | 3.818 ± 0.005 |
| 0.7 | 0.3665 | 7.359 | 7.381 | 7.383 | 7.377 ± 0.015 | 7.36 ± 0.04 | 7.389 ± 0.010 |
| 0.8594 | 0.4500 | 12.326 | 12.359 | 12.355 | 12.449 ± 0.216 | - | 12.376 ± 0.013 |
| 0.9 | 0.4712 | 14.105 | 14.137 | 14.130 | 14.341 ± 0.571 | 14.1 ± 0.2 | 14.176 ± 0.018 |
| 0.925 | 0.4843 | 15.345 | 15.376 | 15.366 | - | - | 15.420 ± 0.026 |
| 0.94 | 0.4922 | 16.150 | 16.179 | 16.166 | - | - | 16.202 ± 0.055 |
| 1.00 | 0.5236 | 19.903 | 19.918 | 19.893 | - | - | 20.012 ± 0.067 |

**Table 3** Compressibility factors obtained from MC simulations and from several equations of state.

| $\pi$ | $\eta$ | *CS[14]* | *B[15]* | *K[16]* | *MC (this paper)* |
|---|---|---|---|---|---|
| 0.5 | 0.2618 | 3.262 | 3.268 | 3.270 | 3.270 ± 0.008 |
| 0.7 | 0.3665 | 5.710 | 5.727 | 5.728 | 5.731 ± 0.016 |
| 0.8594 | 0.4500 | 9.385 | 9.407 | 9.403 | 9.407 ± 0.017 |
| 0.9 | 0.4712 | 10.75 | 10.768 | 10.760 | 10.783 ± 0.021 |
| 0.925 | 0.4843 | 11.707 | 11.726 | 11.715 | 11.739 ± 0.027 |
| 0.94 | 0.4922 | 12.334 | 12.351 | 12.339 | 12.336 ± 0.071 |
| 1.0 | 0.5236 | 15.299 | 15.302 | 15.278 | 15.348 ± 0.084 |

the force-balance (FB) method of Attard [9]. It is seen that the predictions of the equations of state agree well with our results, except at the highest densities, where the former appear to be slightly low. The TPI results are in agreement with ours, although the method's precision has deteriorated considerably by $\rho = 0.9$. Similar remarks apply to the FB results, although its precision is better than that of the TPI method. Table 2 also shows that the precision of the SP-MC method is an order of magnitude better than that of the others shown, and that it produces precise values up to the extremely high density $\rho = 1.00$, which is in the metastable region and well beyond the freezing transition density of $\rho \approx 0.94$ [17].

In Table 3 are shown our results for the compressibility factor $z$ obtained from our simulation results for $g(1)$. These results are compared with the results of the 3 indicated semi-empirical hard-sphere equations of state. In all cases the results agree with the predictions of our calculations within their estimated precision.

In Table 4 we consider the single (high) density $\rho = 0.86$ and compare the precision of the SP-MC results with that of the TPI method and of several improved approaches recently suggested by Nezbeda and Kolafa [8]. It is seen that our method is about 4 times more precise than that of the best method suggested in

**Table 4** Comparison of precision of chemical potential calculations at $\eta = 0.45$ using several methods.

| *Method* | $\beta\mu$ | *Precision* |
|---|---|---|
| TPI [8] | 12.355 | ±0.152 |
| TPI (this paper) | 12.450 | ±0.216 |
| [A] | 12.47 | ±0.083 |
| [B] | 12.32 | ±0.063 |
| [C] | 12.38 | ±0.048 |
| SP-MC (this paper) | 12.376 | ±0.013 |

[A] is the gradual insertion method from [8]
[B] is the semi-grand-canonical ensemble method from [8]
[C] is the scaled grand-canonical ensemble method from [8]

Reference [8], which is in turn about 4 times as precise than that obtained by the direct TPI method. Also, in contrast to other methods, the precision of our results does not deteriorate with increasing density.

We also tested our approach for the hard-sphere solid. In Figure 3 are shown the results obtained for both the solid state and the (metastable) liquid state at the extremely high density $\rho = 1$. (The "solid-state" simulations were intialized from a crystalline configuration.) The figure shows that the solid and fluid curves are distinct. The highest values of $\beta\mu$ shown in each case correspond to a single successful particle insertion in the entire simulation run (in $\approx \exp(14) \approx 10^6$ attempts). Although the fluid state results can be extrapolated reasonably, we

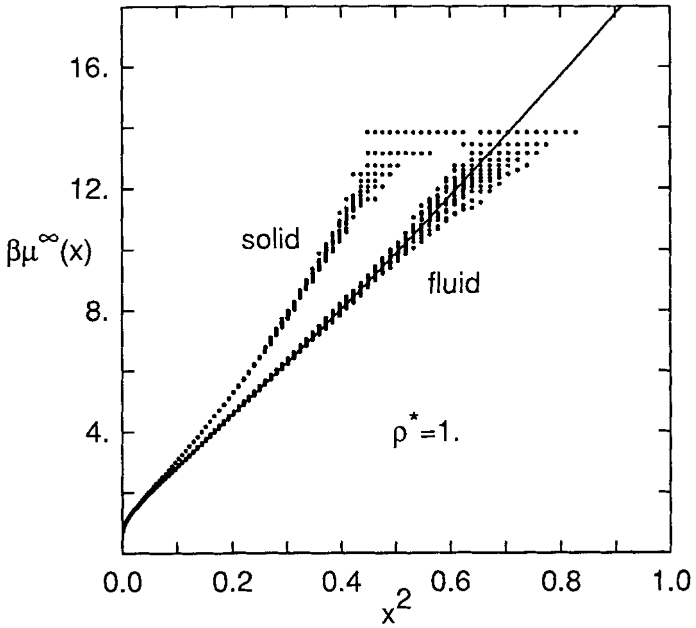

Figure 3

believe that this is not the case for the solid branch. The indicated data are actually measuring only the chemical potential of small-particle impurities of diameter $x$ which are not located at solid lattice sites. Thus, $\lim_{x \to 1} \ln P(x)$ does not correspond to the chemical potential of the hard-sphere solid, and Equation (5) does not hold. The solid state chemical potential thus cannot be obtained by the method proposed here.

## 5 CONCLUSIONS

We have proposed a new method for calculating the chemical potential of a hard-sphere fluid, which we call the SP-MC method. The SP-MC method requires only the collection of data for the probability of successful insertion of particles over a range of diameter values much smaller than that of the hard-sphere fluid itself. Our method utilizes a recently derived new theoretical result, based on scaled particle theory ideas, to accurately and precisely extrapolate this data to obtain values of the chemical potential. The method produces very precise results up to extremely high densities, including even into the metastable region. The method as proposed cannot be directly used to compute the chemical potential of the hard-sphere solid.

We are currently investigating the extension of our approach to calculating the chemical potential of general simple fluids such as the Lennard-Jones fluid, as well as nonspherically symmetric bulk fluids and inhomogenous fluids.

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