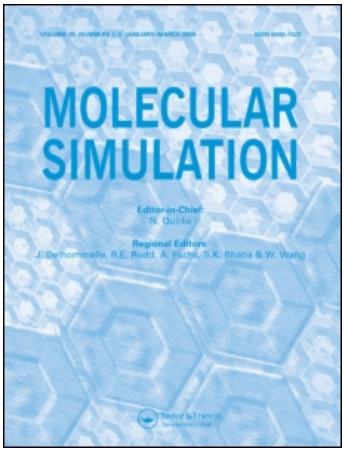

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THE CHEMICAL POTENTIAL OF DENSE LIQUIDS BY THE COUPLED TEST PARTICLE METHOD

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A new method for chemical potential estimation is proposed which is based on the coupled particle approach. The coupled particle method defines an attractive solution to the weighting function problem in *umbrella sampling*, bridging the gap between f and g distributions at high density. A way of eliminating the origin singularity is suggested, which is similar in spirit to the *restricted umbrella sampling* of Shing and Gubbins, but which is based on geometric rather than energetic criteria.

The method is illustrated on the Lennard-Jones system up to a reduced density $\rho^* = 1.1$ along the isotherm $T^* = 1.2$ and results are compared with the test particle insertion method and empirical equations of state. The new method is particularly useful at high liquid densities where it is superior to the other methods relying on the degree of overlap of f and g distributions. It gives reliable estimates of the chemical potential in the whole range of liquid densities.

Keywords: Monte Carlo; test particle; chemical potential; high density

1. INTRODUCTION

Although the general methods of chemical potential estimation (and more generally, the calculation of the free energy difference between two states) by means of computer simulations have been known for several decades [1, 2] and there are a number of excellent reviews [3–6], the subject continues to be intensively investigated [7–15]. The main problem concerned is the accuracy of sampling in the practical realization of numerical schemes.

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Most of the presently used methods are the variants of the 'ideal' test particle method of Widom [2] which is also known as the potential-distribution theorem (PDT). There is a complementary real test particle method, though it is rarely used and has been thoroughly criticized [16–19]. The chemical potential in PDT is related to the mean value of 'potential field' felt by the test particle, inserted randomly in the system, much like the test charge in electrostatics. As follows from [2], PDT provides a direct way of chemical potential estimation from conventional computational techniques such as Monte Carlo or molecular dynamics and works in practice surprisingly well at low to moderate densities. However, since the test particle samples uniformly configuration space and the method belongs to the general class of *crude* Monte Carlo methods, it becomes unreliable at higher densities.

Several methods have been suggested to overcome this difficulty (see, for example, [9]). The most significant are based on the use of so-called umbrella-sampling [20, 10, 13] and f and g energy distributions ratio for ideal and real test particles [18]. The latter method, which in the language of Bennett [21] belongs to the wide class of 'acceptance ratio' technique, extends the applicability of the method to higher densities, but since the magnitude of overlap of the f and g distributions decreases exponentially with density, it has an upper limit too. If two distributions are not far away, the optimized sampling procedure for the free energy difference has been suggested by Bennett [21], in which the Metropolis choice of transition probabilities is replaced by the Barker choice, the Fermi function (see, for example, [22]) and potentials are appropriately shifted by a constant, which unfortunately, but inevitably, includes the desired free energy value.

Umbrella-sampling, or the non-Boltzmann distribution method [3], is a generalization of the Metropolis method on the case of arbitrary weighting function $w(u)$ (for chemical potential u is the test particle potential). This method depends on the successful guess of the weighting function since the method itself does not contain an algorithm for constructing it [3]. Recently, Han [10] have used ideas of Bennett as a clue to this problem and estimated the chemical potential of dense fluid via umbrella-sampling in a single simulation. Subsequently, Ding and Valleau [13] used empirically derived energy-dependent weighting function to calculate the chemical potential of Lennard-Jones fluid up to high densities.

There is another way of sampling configurations relevant to chemical potential estimation. Under canonical conditions, introducing an arbitrary weighting factor $w(\boldsymbol{r}_n)$, $n \subseteq [1 \ldots N]$, is essentially equivalent to entering an additional term $V(\boldsymbol{r}_n)$ in the hamiltonian, which is related to the weighting

factor through the relation $w(\mathbf{r}_n) \equiv w(V(\mathbf{r}_n)) = \exp(-\beta V(\mathbf{r}_n))$. Thus, instead of sampling a non-Boltzmann distribution $w(u)$ for the test particle one can study Boltzmann distribution for the particle interacting with potential u. The way of the chemical potential estimation using such approach was originally suggested by Kirkwood [1]. He expressed the chemical potential of a fluid as a simple quadrature of the well defined mechanical quantity over the coupling parameter. In its general form, the coupling parameter approach is widely used in the determination of the free energy difference between two thermodynamic states [23] but seems seldom used to estimate the chemical potential, presumably for two reasons, because the direct test particle insertion method is more efficient, and because of its numerical instability in the limit of small coupling parameter values ($\lambda \to 0$) [7]. At high densities and/or at low temperatures, where the test particle insertion method is inefficient, the situation changes and a more cumbrous coupled particle method become superior. The latter problem, which sometimes is referred to as the 'origin singularity' and is a matter of a recent animated discussion [23–25], has however a simple but efficient solution, as we show in the following section.

Mon and Griffiths [7] studied different implementations of the coupled particle approach for 2D Lennard-Jones fluids and their general conclusion was not encouraging. The method has been reviewed by Haile [26] and successfully applied to the excess free energy estimation in fluid mixtures in the isothermal-isobaric ensemble.

The object of the present paper is to introduce a new technique for estimating the chemical potential that is reliable at high liquid densities. The method, like the thermodynamic integration method, is applicable at any density, but does not suffer from the origin singularity. It also requires fewer intermediate points than thermodynamic integration and is computationally more efficient since it is based on PDT. In the §2 the method of estimating the chemical potential through multi-stage g sampling for a gradually increasing coupling parameter is described. In §3 the method is demonstrated on the Lennard-Jones system for the highest possible liquid densities along the isotherm $T^* = 1.2$. The conclusions are presented in §4.

2. THEORY

2.1. The Coupled Test Particle Approach

Consider a closed system containing fluid mixture of $N - 1$, identical, classical particles and a solute particle (test particle) interacting with the rest

through a scaled potential $u_\lambda = u_0 + u'_\lambda$, where u_0 is a reference potential and u'_λ is in the general case a homogeneous function of some parameter λ, which measures a test particle coupling to the rest of the system. The system is confined in a volume V and immersed in a heat bath of temperature T. The potential part of the hamiltonian in pairwise approximation is written

$$U_\lambda = U_0 + u'_\lambda, \tag{1}$$

where U_0 is the interaction energy of N particles at the value of coupling parameter $\lambda = 0$. As pointed out by Kirkwood [1] the chemical potential of liquid can be expressed in a very simple manner in terms of canonical ensemble. Following his ideas, the chemical potential of the test particle in the coupled test particle insertion method (CTPI) is estimated from the free energy difference between two thermodynamic states in the process of continuous transformation of the hamiltonian when λ passes from 0 to its final value. The chemical potential of a fluid is then identified with the chemical potential of a fully coupled test particle.

The particular choice of the final value of λ and a functional dependence of u'_λ on λ is unimportant here since the target value, the potential of the fully coupled particle, is invariant to the transformation path, and without loss of generality a linear dependence is assumed in the following *i.e.* $u'_\lambda \propto \lambda u$ for $\lambda \in [0, 1]$. It is essential, however, that the fully coupled particle is indistinguishable from the solvent particles, and that the presence of u_0 does not change the final state.

The chemical potential can be written as a sum of two terms,

$$\mu = \mu_0 + \mu_\lambda|_0^1 \equiv \mu_0 + \mu', \tag{2}$$

where μ_0 is the chemical potential of the reference particle ($\lambda = 0$), for which the chemical potential is either known analytically or can be easily determined in the course of simulation. It includes also a term $\beta^{-1} \ln N$, which takes care of the indistinguishability of the test particle at $\lambda = 1$. The second term, μ', accounts for the chemical potential difference between fully charged test particle and the reference particle. This is realized in the simulation in several discrete steps with increments in the coupling parameter at each step. The chemical potential difference for each pair of successive λ-points is estimated from the PDT [2], and the chemical potential of a liquid is defined by the relation

$$\exp(-\beta\mu) = \exp(-\beta\mu_0) \prod_{k=1}^{n} \langle \exp(-\beta(u_{\lambda_k} - u_{\lambda_{k-1}})) \rangle_{\lambda_{k-1}}, \tag{3}$$

where $\lambda_0 = 0$, $\lambda_n = 1$, the angle brackets denote canonical ensemble average for the coupling parameter indicated by the subscript, and the formal expression for the chemical potential have been used,

$$\mu = \mu_0 + \sum_{k=1}^{n} \Delta\mu_{\lambda_k} \equiv \mu_0 + \sum_{k=1}^{n} (\mu_{\lambda_k} - \mu_{\lambda_{k-1}}). \tag{4}$$

Equation (3), which is a multistage version of the test particle insertion method, has been previously used in the chemical potential estimation [7] and was thought to be unreliable. We shall demonstrate that this can be accurately applied at all liquid densities. Initial simulation are performed on a system containing a reference test particle, and a set of Boltzmann factors $\langle \exp(-\beta\mu_\lambda)\rangle_0$ are collected for progressively larger values of coupling parameter and used to determine λ_1, which serves as a reference system in the next calculation. The procedure has been repeated for $\lambda_2, \ldots, \lambda_{n-1}$, until eventually a converged value $\langle \exp(-\beta u)\rangle_{\lambda_{n-1}}$ is obtained. The convergence criterion at each step is the relative (fractional) standard error in the block means [5] of the averaged Boltzmann factor less than some fixed value, which eventually defines the accuracy of the chemical potential estimation. This is discussed in more details in the next section. We note here that even for the highest calculated density a value of n equal to 5 seems to be appropriate (recall, $n = 1$ corresponds to the Widom's insertion method).

It is interesting to note that such an approach can be considered as a finite-difference version of Kirkwood's method, which defines an alternative way of evaluation of the chemical potential, by simple integration over the potential energy transformation path of a solute particle. Thus, substituting excess chemical potential from PDT into the identity

$$\beta\mu'_\lambda = \int_0^\lambda d\lambda' \frac{\partial \beta\mu'_{\lambda'}}{\partial \lambda'}, \tag{5}$$

immediately yields

$$\beta\mu'_\lambda = \int_0^\lambda d\lambda' \left\langle \frac{\partial \beta u_{\lambda'}}{\partial \lambda'} \right\rangle_{\lambda'} = \int_0^\lambda d\lambda' \langle \beta u \rangle_{\lambda'}, \tag{6}$$

where the last equality is valid for linear coupling. This result can be also obtained directly from the fundamental relation between the energy and reversible work in the canonical ensemble.

2.2. Choice of the Reference System

Since the efficiency of the numerical procedure critically depends on the degree of the overlap of the energy distributions for the final and initial hamiltonian, it can be perceptibly improved by the appropriate choice of the reference system. The idea to enrich sampling with configurations giving the main contribution in (3) has been exploited in the 'restricted umbrella sampling' method [18] by using energy-dependent weighting function. However, this procedure requires an additional simulation with an ideal test particle in order to exclude the influence of the weighting function. We adopt another approach which has an advantage that the corrections can be readily made analytically. This method is based on the simple observation that at short distances the dominant interaction is the repulsion, independently of the potential model or type of molecules. Following Parsonage and co-workers [27], we express the interaction energy of the test particle with solvent particles as a sum of hard-core part and a soft interactions,

$$u_\lambda = \lambda u + u_{\mathrm{HS}}. \tag{7}$$

The reference particle ($\lambda = 0$) is represented by a hard sphere particle, and this approach avoids any insertion singularity. The diameter of the single HS particle is chosen so that it has no effect in the fully coupled system.

The chemical potential of the reference hard-sphere particle can be calculated straightforwardly from the PDT, *i.e.* from the probability that the randomly placed test particle does not overlap. This is valid in principle for a hard-sphere particle of any size, and by varying the hard-sphere diameter σ_{HS} one can adjust the rate of non-overlapped configurations to any desired value, *e.g.* 50%. There is however a catch. Rigorously, the above procedure requires an additional run for a pure solvent system. To avoid this, one can estimate μ_{HS} for a system with $\lambda = 0$ from the acceptance rate of the test particle displacements with a maximum displacement parameter set equal to half of the box length. The advantage of this approach is that the μ_{HS} is estimated as a by-product in the run aimed at estimation of $\Delta\mu_{\lambda_1}$; the shortcoming is that it gives an approximate value since it is defined for the system in which the test particle is already present.

The chemical potential of the test particle in the reference system can also be estimated from the scaled-particle theory [28]. To see this, one can imagine that the hard sphere potential is 'transfered' to solvent molecules and thus the reference system can be considered as a solution of an ideal particle in the modified solvent. The original and modified systems would

have the same statistical properties if the presence of hard core in solvent interactions does not affect the generated configurations; more precisely, if the closest approach of two solvent molecules in particular simulation is $\geqslant \sigma_{HS}$. The chemical potential of the solute particle μ_{HS} in this case is known exactly (see (31) in [28]), and the corresponding first term in (2) is

$$\beta\mu_0 \equiv \ln N + \beta\mu_{HS} = \ln \Lambda^3\rho - \ln(1 - \pi\rho\sigma_{HS}^3/6), \tag{8}$$

where Λ is the thermal de Broglie wavelength, and $\rho = NV^{-1}$ is the number density.

In practice, when choosing σ_{HS} it is sufficient if $\exp(-\beta u(\sigma_{HS})) \ll 1/M$, where M is the sample size. For example, in the particular case of Lennard-Jones potential, the choice $\sigma_{HS} = 0.8\sigma$ is suitable.

2.3. Energy Distributions for the Test Particle

Detailed information about the test particle can be obtained from its canonical potential distribution function [29]

$$g_\lambda(\theta) = \langle \delta(\theta - u(\mathbf{r})) \rangle_\lambda, \tag{9}$$

where $\delta(x)$ is the Dirac delta function and $u(\mathbf{r})$ is the value of potential at $\mathbf{r}$. This function is connected with ϕ_q function of Gibbs (see (272) in [29]) by simple relation $g(u) = \exp(\phi_q(u)/k)$, where k is the Boltzmann's constant. Similar functions have been used by McDonald and Singer in their evaluation of the configurational integral [30] and by Shing and Gubbins [18] in the chemical potential estimation. $g_\lambda(u)$ defines the probability density that the potential of the field, felt by the test particle is equal u. Equivalently, $g_\lambda(u)du$ for all $\lambda > 0$ is the probability of finding the test particle in an unspecified state with potential energy in du around u_λ.

As follows from PDT, the chemical potential of a fluid can be expressed in terms of potential distribution function for the real and ideal test particle (9),

$$\exp(\beta\mu'_\lambda) = \int_{-\infty}^{\infty} du\, g_\lambda(u) \exp(\beta\mu'_\lambda), \tag{10}$$

and

$$\exp(-\beta\mu'_\lambda) = \int_{-\infty}^{\infty} du\, g_0(u) \exp(-\beta\mu'_\lambda), \tag{11}$$

recall, $u \equiv u(r)$ is the value of a field at the point r, or the potential energy of the fully coupled test particle. The function g_λ in the limiting case $g_{\lambda=1} \equiv g_1$ coincide with the function g_N, used by Shing and Gubbins [18], but is different from the function defined by (2.15) in [7].

From the definition of $g_\lambda(u)$, (9) we have [3, 18]

$$g_\lambda(u) = g_0(u) \exp(\beta(\mu_\lambda - u_\lambda)), \tag{12}$$

and the chemical potential can be estimated from

$$\exp(\beta\mu) = \exp(\beta u) \prod_{k=1}^{n} (g_{\lambda_k}(u)/g_{\lambda_{k-1}}(u)) \tag{13}$$

where each quotient is a well-defined ensemble average. This gives another way of calculating the chemical potential. The price for this method is that it requires two distributions and hence two independent runs for each value of k.

We note that the so-called origin singularity problem which may arise in the free energy calculations using thermodynamic integration can be solved by the appropriate choice of the reference system. The problem [24, 25] is the divergence of the partial derivative of the free energy with respect to the coupling parameter at small values of coupling parameter ($\lambda \to 0$) and it may appear when the reference particle is the perfect gas particle, or when the systems with initial ($\lambda = 0$) and the final ($\lambda = 1$) hamiltonians have different numbers of particles. A simple but efficient solution is to redefine the path of the transformation of the hamiltonian to single out the term with singularity

$$\beta\Delta F = -\ln \langle \exp(-\beta u_\lambda) \rangle_0 + \int_\lambda^1 \left\langle \frac{\partial \beta U_{\lambda'}}{\partial \lambda'} \right\rangle_{\lambda'} d\lambda', \tag{14}$$

where ΔF is the free energy difference and λ in this case correspond to a small hard-sphere particle (or another appropriate hard body). The thermodynamic integration is performed over a path which does not include the singular point. Other methods of avoiding singularities can be found elsewhere [24, 25].

3. RESULTS AND DISCUSSION

When a new technique is introduced, its advantages (and disadvantages) can only be revealed by comparing with existent methods. Since the chemical potential estimated from the PDT converges asymptotically to the correct

value, the efficiency of the new method can be judged by comparing the convergence rates. The problems of estimation of the variance in the Monte Carlo estimates are well known [22,9] and the usual way is to compare uncertainties of two methods using the method of block means obtained on uncorrelated configurations. When comparing results of different methods, some care should be taken to ensure that the errors are estimated on the same amount of data, and to account for the other factors, like programming efforts and required computing resources.

To test the usefulness of this new approach, a system of Lennard-Jones particles has been chosen. This system has been thoroughly studied both analytically and by computer simulation methods and extensive data are available for a broad range of densities [9–11, 13, 18, 31] and summarized in two empirical equations of state (EOS) [32, 33].

3.1. Details of the Simulation

The interaction potential between i and j particles, as used in the simulation, is given by

$$u(r_{ij}) = \begin{cases} u_{LJ}(r_{ij}), & r_{ij} \leqslant r_{cut} \\ 0, & r_{ij} > r_{cut} \end{cases} \tag{15}$$

where r_{cut} is the potential cut-off radius, and $u_{LJ}(r_{ij})$ is the Lennard-Jones potential,

$$u_{LJ}(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}], \tag{16}$$

where parameters ε and σ are the normal energy and length parameters.

Calculations were performed using Metropolis Monte Carlo [5] technique in the canonical ensemble with the usual cubic periodic boundary conditions for densities ($\rho^* = \rho\sigma^3$) from $\rho^* = 0.4$ to $\rho^* = 1.1$ for the systems with particle number N from 80 at low density to $N = 125$ at high density along the isotherm $T = 1.2\varepsilon/k$. Interaction of one of the particles in the system was scaled by a factor λ, *i.e.* the particle displacements are performed taking into account this factor, but in the accumulated energy distribution the potential is taken that of a fully coupled particle. In addition, a hard-sphere term (7) has been included in the test particle interactions.

Intermolecular interactions were truncated at $r_{cut} = 2.5\sigma$ (unless specified otherwise), and in order to recover the properties of the full LJ system, the usual long-range correction [5] was added to the calculated quantities. For all quantities except the probability energy distributions, g_λ, energy corrections

were made after the run. In the Markov chain realization at every step an attempt was made to move either the test particle or one of the solvent particles with equal probability. In the trial displacements, the value of the maximum allowed displacement was chosen to give an acceptance probability of approximately 50%. In the test particle displacements for $\lambda = 0$ the new positions were chosen uniformly in the system and the hard sphere diameter of the test particle was set to $\sigma_{HS} = 0.8\sigma$. With this size, about 70% of attempted test particle moves have been accepted at the highest reported density. Inspection of the collected radial distribution function shows that in all runs not a single pair of solvent molecules was observed at separations below 0.8σ. The residual chemical potential of the reference hard-sphere particle was estimated from PDT using the procedure outlined in Section 2.2. Even at the highest simulated density $\rho^* = 1.1$ its value is very close to that obtained from the SPT (8) ($\mu'_{HS} = 0.3482(5)$ and 0.3494, respectively). The difference between two numbers is indeed much smaller than the total standard deviation, and for practical purposes can be neglected. No attempt to optimize the value of σ_{HS} has been made, however.

It should be noted that the two approximations made in the numerical calculation of the chemical potential may serve as a source of significant error at high densities. The first has been made in identifying the chemical potential with the Helmholtz free energy difference ΔF due to added particle [2]. In order to estimate the error due to this approximation, we can assume that the particle number N is a continuous variable. Expanding $\Delta F/\Delta N$ in a power series over ΔN about $\Delta N = 0$, after rearranging and setting $\Delta N = 1$ we obtain an expression for the error, $\Delta\mu$,

$$\Delta\mu \equiv \mu - \left.\frac{\Delta F}{\Delta N}\right|_{\Delta N = 1} = -\frac{1}{2}\frac{\partial\mu}{\partial N} - \frac{1}{6}\frac{\partial^2\mu}{\partial N^2} - \cdots . \tag{17}$$

Retaining the leading term we obtain the desired dependence of the chemical potential corrections on the particle number

$$\Delta\mu = -\frac{1}{N}(2\rho\chi_T)^{-1}, \tag{18}$$

where χ_T is the isothermal compressibility. Similar result has been obtained recently by Frenkel [31] using somewhat different approach. Physically, this result means that for the system of N particles, the insertion of an additional particle results in a change of density and therefore in the chemical potential $\mu[\rho, T]$, which is of $\mathcal{O}(N^{-1})$. For low density this causes no problem, but as the density increases, the error in chemical potential which is, as it is seen

from (17), to the leading order $\propto \delta\mu/\partial\rho$, also increases, and at high liquid density it can be significant. In fact, the reported data is contradictory, some authors observed appreciable N-dependence of the chemical potential [8, 9], while the others [13] found it surprisingly small.

Another potential source of systematic errors in the chemical potential at high density is the truncation of the interaction potential. The usual long-range correction is based on assumption that the liquid beyond the r_{cut} is uniformly disordered, *i.e.* the radial distribution function is unity. As a further check some of the calculations at high and low densities were repeated with larger particle numbers, 500 and 512, and with different values of r_{cut}.

For each of the calculated states, the system was first allowed to equilibrate. In order to ensure that the system has been sufficiently equilibrated, from $2-5\times10^6$ initial configurations at medium densities and up to 2×10^7 steps for $\rho^*=1.1$ has been discarded. We make no claim that this is a minimum equilibration period required, however. The statistics then have been collected for runs from 2 to 4×10^7 steps.

For each density, a set of the intermediate λ-points has been constructed using the observation that for a given sample $M(M=\Sigma_i^n M_i)$, the variance of the chemical potential has its smallest value when the relative uncertainties of all factors in the product in (3) are of the same magnitude. Particular values of λ_i has been defined as follows. For initial system with the reference test particle, a set of Boltzmann factors $\exp(-\beta\Delta\lambda_0^k u)$ has been collected in a short run, and the averages $\alpha_0^k=\langle\exp(-\beta\Delta\lambda_0^k u)\rangle_{\lambda_0}$ have been estimated in the usual way. The first value $\Delta\lambda_0^1$ was taken as an arbitrary small number (for the lack of better choice, a value of 0.01 can be taken, the convergence for small λ is rapid and the more appropriate value can easily be determined in a short run). Subsequent values, $\Delta\lambda_0^k$, were chosen as multiples of $\Delta\lambda_0^1$. The whole procedure thus involves only a single exponential estimation and several multiplications. For each k, the relative standard errors in α_0^k have been estimated using the block average method [5]. Using the fact that the standard error is $\propto M^{-1/2}$, errors were extrapolated for the expected M and from the desired accuracy ϵ in the estimation of $\exp(-\beta\mu)$, we find the maximum $\Delta\lambda_0^j$, for which the standard error is $\leqslant\epsilon/\sqrt{n}$, where n is the number of suggested λ-points. This gives the value of $\lambda_1=\lambda_0+\Delta\lambda_0^j$. The procedure then has been repeated for $\lambda_2,\ldots,\lambda_{n-1}$. Despite its apparent intricacy, it is straightforward in practical implementation. For reduced densities up to 0.9 a single intermediate point of $\lambda=0.4$ have been used and the chemical potential have been estimated from the results of a 2×10^7 MC steps run. At higher densities, more points is required for the accurate estimation of the chemical potential and the generated chains of configurations are longer. Table I summarizes details of the performed

simulations at high densities and presents values of intermediate λ-points as well as the values of the fractional standard errors in $\alpha = \exp(-\beta\mu')$.

For example, for the system of $N = 512$ particles at the density $\rho^* = 1.0$ we chose the following values, $n = 4$, $M = 3 \times 10^7$, and $\epsilon = 10\%$. From the desired accuracy, in a short trial runs the three intermediate λ-points have been defined as 0.1, 0.24 and 0.5. The four production runs were performed for $\lambda = 0$ and these three values. Figure 1 illustrates the dependence of the variation in α_i^j as a function of coupling parameter difference for two densities,

TABLE I Summary of the simulation parameters for high densities, intermediate values of the coupling parameter and fractional standard errors in the exponential of the chemical potential differences

$\rho\sigma^3$	N	$M/10^6$	λ_i				$\delta\alpha_{\text{CTPI}}$	$\delta\alpha_{\text{Widom}}$
0.8	100	20	0.4				0.03	0.04
	512[a]	20	0.4				0.03	0.03
0.9	125	30	0.3				0.12	0.06
	512[b]	30	0.3				0.07	0.12
1.0	125	30	0.1	0.24	0.5		0.09	0.5
	512	30	0.1	0.24	0.5		0.1	0.54
	512[b]	30	0.1	0.24	0.5		0.17	0.56
1.1	512	40	0.03	0.06	0.1	0.3	0.16	0.93

[a] $r_{\text{cut}} = 4.2$
[b] $r_{\text{cut}} = 4.0$

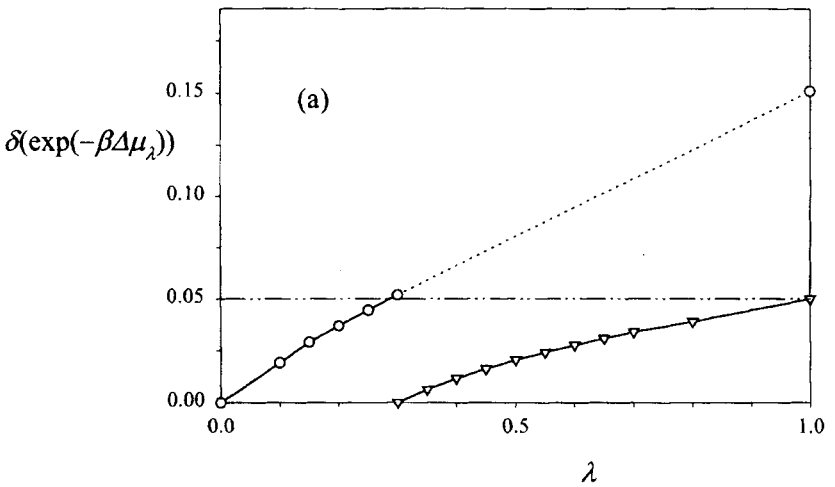

FIGURE 1 The relative standard errors of the Boltzmann factor of the chemical potential difference between two λ-points as a function of coupling parameter difference: (a) for density $\rho^* = 0.9$; (b) for density $\rho^* = 1.0$. Errors are calculated using block means from 150 blocks (a) and 200 blocks (b).

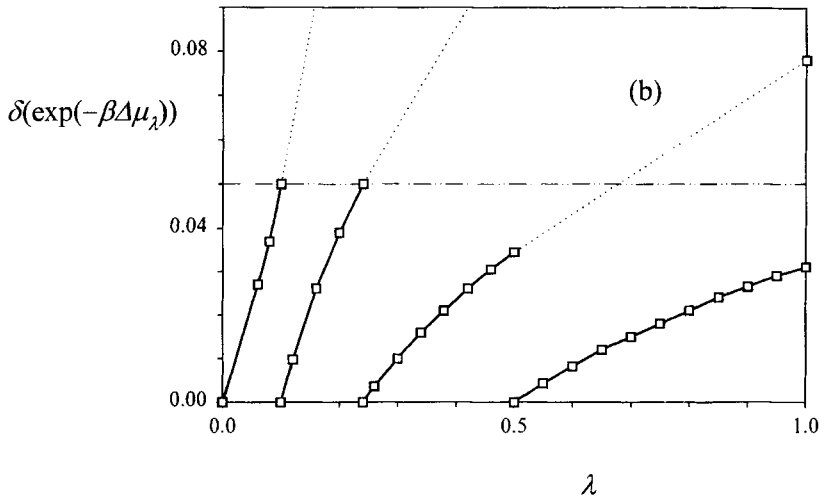

FIGURE 1 (*Continued*).

$\rho^* = 0.9$ (a), and $\rho^* = 1.0$ (b). From the test runs it is difficult to define exactly the positions of the optimal intermediate λ-points, and in the production runs the standard errors on the different λ-intervals might be slightly different from the predicted values. However, the final accuracy is only weakly affected by these deviations and it can be slightly improved by extending simulations on the intervals where the uncertainty is large.

3.2. Energy Distribution Functions Analysis

The g_λ distributions were calculated for densities from $\rho^* = 0.4$ to $\rho^* = 1.1$ in step of $\Delta\rho^* = 0.1$. Results, shown in the Figures 2–4, illustrate changes in the character of the probability distributions for the potential for values of the coupling parameter at three selected densities. A log scale is used for the energy axis in two last figures and the origin of the energy scale is shifted by $\beta\phi_0 = 15$. In these figures the distributions for g_0 are obtained for hard-sphere particles with $\sigma_{HS} = 0.5\sigma$ and corrected further by the μ'_{HS} to reproduce the distributions for the Widom test particle. At low density the configurations with low potential dominate, as one can see from g_0 for $\rho^* = 0.5$. Starting from approximately $\rho^* = 0.7$, the situation changes, and the distributions for ideal and real test particles are diverged. This is illustrated for two densities, $\rho^* = 0.9$ and $\rho^* = 1.0$, where the maximum for g_0 is shifted to the value of $\beta u = 247$ and $\beta u = 660$, respectively. Figures 2–4 illustrate also the differences in the direct and inverse test particle methods.

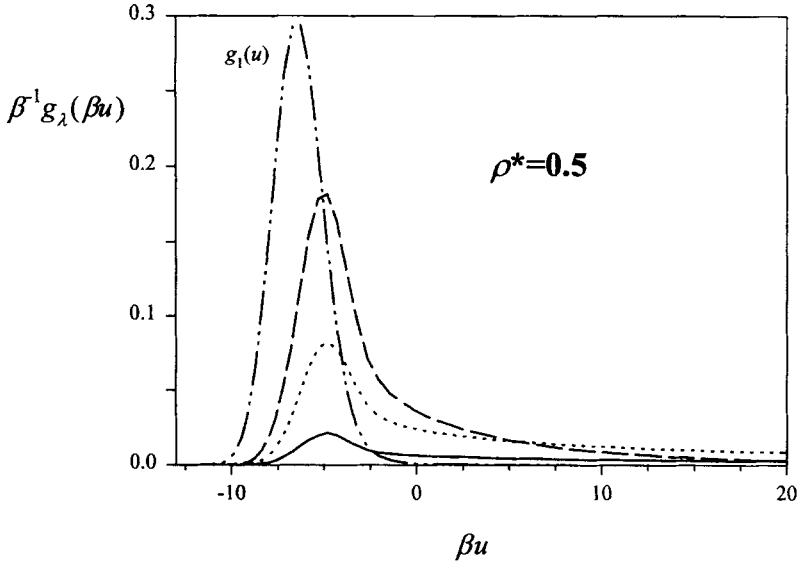

FIGURE 2 The probability density distributions of the potential of the canonically distributed coupled particle for a reduced density of $\rho^* = 0.5$ for different values of the coupling parameter: solid line, $\lambda = 0$; dotted line, $\lambda = 0.01$; dashed line, $\lambda = 0.1$; dash-dotted line, $\lambda = 1$.

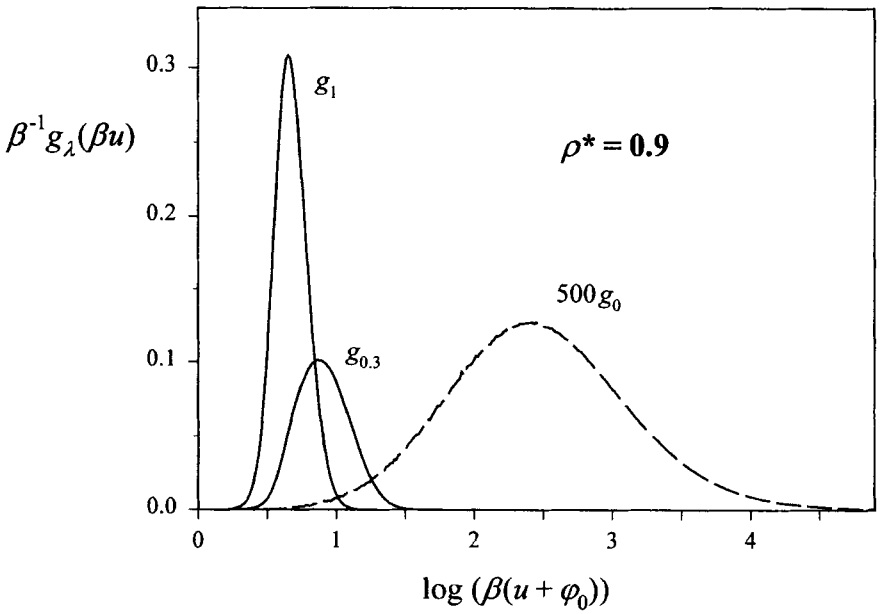

FIGURE 3 The probability density distributions of the potential of the canonically distributed coupled particle for a reduced density of $\rho^* = 0.9$ for values of the coupling parameter used in chemical potential calculation by CTPI method. Note that the distribution for $\lambda = 0$ (dashed line) is multiplied by 500.

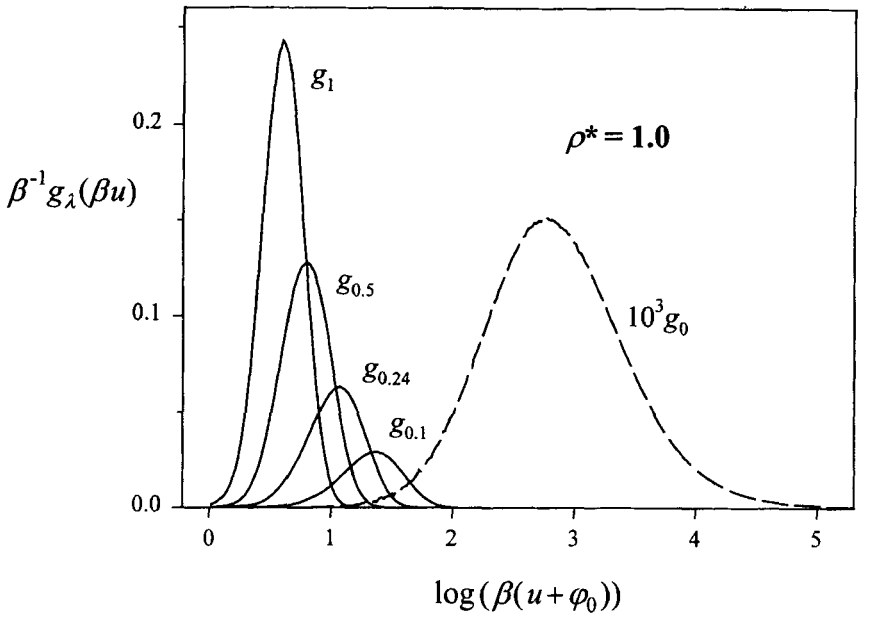

FIGURE 4 The same as in Figure 3, but for a reduced density $\rho^* = 1.0$. The distribution for $\lambda = 0$ (dashed line) is multiplied by 1000.

The main contribution to the chemical potential using the real particle method, as one can see from (10) comes not from the domains where g_λ is high, but from the domains, where the integrand itself, *i.e.*, $g_\lambda \exp(\beta u_\lambda)$ is high. This expression, by virtue of (12) is proportional to the g_0, which even at relatively low density, $\rho^* = 0.5$, is much broader than the g_λ, and substantial contributions come from the areas lying beyond the scope of usual computer simulation sampling. Therefore, the real particle method most frequently underestimate the chemical potential value, as was in fact observed by Powles [16] and by Guillot and Guissani [17]. However, in a long simulation it should converge to the correct value due to contribution from infrequent visits to the high-potential domains.

On the other hand, from (11) it is clear that the test particle method samples configurations with g_0, whereas the integrand is proportional to g_1. There is, however, an important difference from the real particle method. For the same sample size, the span of g_0 is much wider than g_1, and for low densities (for up to approximately $\rho^* = 0.8$ at this particular temperature) g_1 is entirely within g_0. This explains the success of Widom's method, (3), for low densities. At higher densities the g_0 and g_1 distributions diverge, and

the test particle method should tend to overestimate chemical potential for the same reason as the real particle underestimates it.

In summary, both methods are inefficient at high densities, but the reasons of inefficiency are different. While the ideal test particle method is unsuccessful for the same reason as any other crude Monte Carlo method (*i.e.* a Monte Carlo method with independent samples, see [22]), the efficiency of the real test particle method is even worse, since it designed to sample *preferentially* configurations, giving vanishingly small contribution to the integral value, and to avoid configurations, giving the major contribution to the result. Thus, assuming that the efficiency of the real particle method is proportional to entropy difference due to real test particle, *i.e.* is $\propto \exp s/k = \exp(-\beta(\mu' - u))$, where $u = 2\langle U_1 \rangle_1/(N-1)$ is the mean interaction energy of the particle, then the efficiency of the real particle method for the system considered at $\rho^* = 1$ is less than 4×10^{-5} of the efficiency at $\rho^* = 0.5$.

A partially coupled particle, for which g_λ goes continuously from that of a real particle to the ideal particle distribution as the coupling parameter λ changes from 1 to 0, defines therefore an attractive way of bridging two distributions. This can be seen in particular in the Figure 4. At this density, g_0 is vanishingly low in the region where g_1 is a maximum (note the scaling factor in g_0 distribution). Introducing three intermediate points with $\lambda = 0.1$, 0.24 and 0.5 dramatically improves accuracy of the method. Distribution for each intermediate value of the coupling parameter is a 'real' particle distribution for all smaller values of λ, and a 'ghost' particle distribution for all bigger values of λ, and any two distributions can be related via the transformation (12).

3.3. Results for the Chemical Potential

The chemical potential has been calculated using two methods, the CTPI (Eqn. (3)) and using Widom's PDT, over the same density range. In order to facilitate the comparison, both results for each density and system size are based on the same amount of data, *i.e.* the sample in the PDT method is nM_{CTPI}, where n is the number of multipliers in (3). The obtained values of the excess chemical potential using both methods and the corresponding errors are reported in Table II and are shown in Figure 5 there they are compared with the results of two empirical EOS given by Nicolas and co-workers [32], which is very successful at this temperature [34], and its recent refinement [33]. Note that both parameterizations give the same results to within 5% accuracy in the desired density range 0.9–1.1.

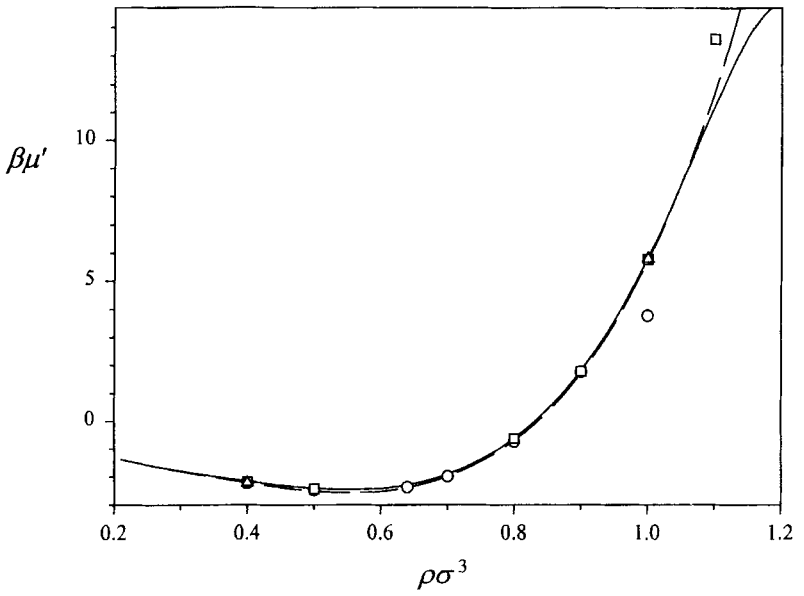

FIGURE 5 The density dependence of the chemical potential calculated by the CTPI method for $N \sim 10^2$ (circles), $N \sim 5 \times 10^2$ with $r_{cut} = 2.5\sigma$ (triangles), and $r_{cut} = 4.0\sigma$ (squares). The dashed and solid lines are calculated from the equations of state [32] and [34], respectively.

TABLE II Comparison of the excess chemical potential, calculated from the PDT and by the CTPI method along the $T^* = 1.2$ isotherm

	EOS [32]	EOS [34]		Widom TP	CTPI
$\rho\sigma^3$	$\beta\mu'$	$\beta\mu'$	N	$\beta\mu'$	$\beta\mu'$
0.4	−2.209	−2.154	80	-2.202 ± 0.005	-2.221 ± 0.008
			246	-2.214 ± 0.005	-2.204 ± 0.008
			246[a]	-2.177 ± 0.006	-2.185 ± 0.005
0.5	−2.510	−2.404	80	-2.476 ± 0.003	-2.469 ± 0.007
			500[a]	-2.424 ± 0.005	-2.434 ± 0.005
0.64	−2.385	−2.411	80	-2.386 ± 0.009	-2.372 ± 0.007
0.7	−1.987	−1.908	80	-2.064 ± 0.012	-1.986 ± 0.009
0.8	−0.692	−0.608	100	-0.75 ± 0.04	-0.74 ± 0.03
			512[b]	-0.636 ± 0.03	-0.625 ± 0.03
0.9	1.723	1.821	125	2.10 ± 0.12	1.69 ± 0.06
			512[b]	1.89 ± 0.12	1.78 ± 0.07
1.0	5.730	5.828	125	4.0 ± 0.6	3.78 ± 0.09
			512	6.0 ± 0.7	5.8 ± 0.1
			512[b]	5.2 ± 0.8	5.78 ± 0.09
1.1	11.73	11.22	512	–	13.6 ± 0.2

[a] $r_{cut} = 4.2$
[b] $r_{cut} = 4.0$

For densities up to reduced density 0.8, both methods have approximately the equal convergence, and provide reliable estimation of the chemical potential. At higher densities, the CTPI method become superior. The uncertainties in α have been estimated using block averages of sufficient length, which has been confirmed by the independence of the standard error, estimated on the same amount of data, on the block length. A single value of 2×10^5 configurations has been used for the whole range of densities, from which the standard errors in the chemical potential, reported in Table II, have been calculated by the error propagation. The difference between two methods is clear at high densities. Thus, comparing at $\rho^* = 1.0$ the standard relative errors in α, estimated for the ideal test particle method from $M = 1.2 \times 10^8$ MC steps and the CTPI method shows that in order to obtain the same accuracy, the former method requires approximately 40 times longer simulation than the total length of the four CTPI runs. For the upper density $\rho^* = 1.1$, the independent block averages of α, calculated using PDT, spawned over 40 orders of magnitude and the relative standard error estimated from $M = 2 \times 10^8$ configurations, was yet close to 100%. The general agreement between the CTPI and the results from both equations of state is excellent up to the highest simulated density. At the density $\rho^* = 1.1$ however the CTPI method gives the chemical potential value which is 15% higher than those obtained from EOS, which can be considered as a good agreement taking into account the empirical nature of EOS and the fact that they have been derived from the data set at lower densities. The difference can be also a manifestation of the size effect, which means that a larger system is required at this density.

The chemical potential for density $\rho^* = 1.0$ and the system of 125 particles appears to be somewhat lower than predicted from EOS. Repeated calculations with 512 particles and for two different truncation distances, $r_{cut} = 2.5\sigma$ and 4.0σ give results which agree within the statistical errors, whereas for the smaller system result differs significantly. In all cases the calculated radial distribution function exhibited similar liquid structure. The difference therefore has been attributed to the errors, mentioned in §3.1 and its relative magnitude indicates that 125 particles at this density is not sufficient for reliable estimation of the chemical potential.

One general feature was observed for the extremely dense liquid systems from the analysis of g_λ distributions of the coupled particle. The distributions rapidly converge to smooth curves, but this is a fake convergence. Averaging over the next block of configurations gives a different distribution, usually slightly translated from the previous. This was observed at high densities only, where g_1 and g_0 are separated, and as a result much

longer simulations have been made to obtain the desired accuracy. A possibility of this difficulty and possible ways of its overcoming have been discussed by Hastings [22].

Note, that the two upper density points, 1.0 and 1.1, are in fact in the metastable transition region between liquid and solid phases [32]. Initial configurations for these two state points were generated from the final equilibrated liquid configurations for lower density by uniform compression. To monitor structural changes the radial distribution function was periodically collected. No transitions to solid state, however, was observed in a long test run of 2×10^8 MC steps from which we concluded that for the chosen system size and potential cut-off both densities are in the liquid phase. Equilibration processes at this density become very slow and the potential energy has been stabilized only after 2×10^7 steps.

Finally, an attempt was made to simulate a system at density 1.2. However, during the equilibration phase, after 3×10^7 steps, the system underwent a phase transition to a fcc solid. The value of the chemical potential for the solid appears to be $\beta\mu' = 5.4 \pm 1.0$, which is far below the expected value for the liquid branch. This result will be checked by calculating the solid chemical potential by other methods, *e.g.* thermodynamic integration [35] however, this is beyond the scope of the present paper.

It should be noted that configurations generated for all intermediate values of λ can be used in the calculation of the canonical average of any mechanical quantity after appropriate reweighting [22, 13]. If, for example, the generated configurations are from $p_i \propto \exp(-\beta(u_i + w_i))$ where w_i is some weighting function, to sample from the canonical distribution, $\exp(-\beta u_i)$ one need to assume a weight $\exp(\beta w_i)$ to each configuration. Thus, in the *crude* Monte Carlo, which corresponds to $w_i = -u_i$ each configuration should be weighted by a factor $\exp(-\beta u_i)$. In our case, when one of the particles in the system is partially coupled to the rest, to calculate, for example, the radial distribution function for canonically distributed ensemble, corresponding accumulators for the coupled particle should be incremented by $\exp(-\beta(1-\lambda)u)$ instead of 1. A similar procedure can be applied to any other mechanical quantity.

The typical convergence of the coupled particle method and the Widom's test particle insertion method for the system with 512 particles are illustrated in Figures 6 and 7 for densities $\rho^* = 0.9$ and 1.0, respectively. At lower density, during the first 15×10^6 MC steps the CTPI method converged to the value which is within 2% of its final value, estimated from the two times longer run. At this density the test particle insertion method exhibits stronger random deviations due to infrequent but dominant contributions from the

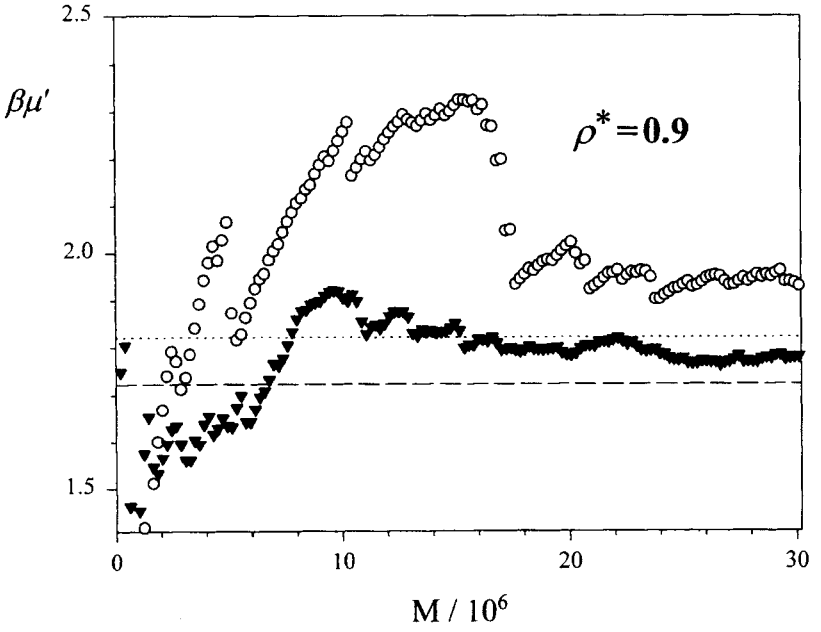

FIGURE 6 The convergence of the chemical potential calculated by different methods for $\rho^* = 0.9$: filled triangles, the CTPI method; open circles, Widom's test particle insertion method. The dashed and dotted lines are the chemical potentials obtained using EOS [32] and [34].

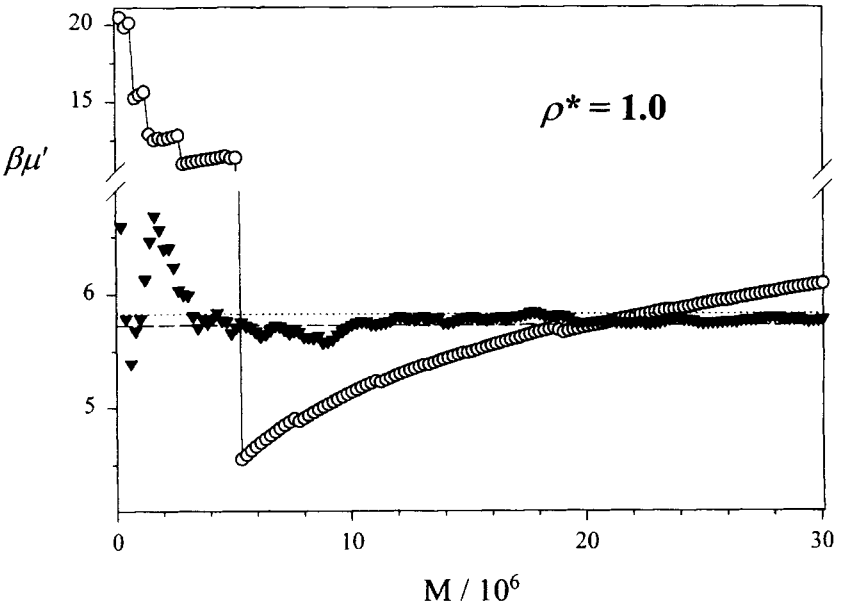

FIGURE 7 The convergence of the chemical potential for $\rho^* = 1.0$: and the system containing 512 particles: filled triangles, CTPI method; open circles, Widom's test particle insertion method. The dashed and dotted lines correspond to EOS [32] and [34], respectively.

low-energy part of spectrum with constant drift towards higher values between them. At the upper density, accuracy of the chemical potential in Widom's method is determined by extremely rare random hits, which is seen by strong dramatic jumps. The variation, estimated between them is deceptively low. The general tendency nevertheless is correct, and for a considerably longer run it is expected to converge to the correct value even at this extreme density.

4. CONCLUSION

We have demonstrated that the CTPI method gives accurate chemical potential of the Lennard-Jones liquid phase for the whole range of densities, including those typical for the solid phase. At low densities, the CTPI method is comparable in efficiency with the Widom's method, which is probably the most efficient and economic available method at these densities. At higher densities, (*e.g.* at the reduced densities between 0.8 and 0.9 for the particular case considered in this paper), where f and g distributions start to diverge, Widom's method and other direct methods, relying on the overlap ratio of the two distributions, like $f-g$ sampling of Shing and Gubbins or the 'cavity-biased' insertion method [5], become inefficient. At these densities the variation in the chemical potential estimated using CTPI method is comparable with 'umbrella-sampling' estimations of Han [10] and Ding [13] (the standard error at $\rho^* = 0.9$ is 0.07 in all three methods, after appropriate extrapolation on the Markov chain of the same length). The advantage of 'umbrella-sampling' is that the chemical potential (of free energy difference, in general) is estimated from the single simulation, the shortcoming however is familiar one [3], despite the method is known for more than two decades, there is no universal solution to the weight-function problem, which is determined by trial and error, like in [13] for the LJ system. When f and g distributions are not too far away from each other, the general solution is given in [10], which works presumably up to $\rho^* = 0.9$. At still higher densities however there is a danger of trapping with ergodicity problems due to infrequent transitions between two ensembles. The similar problem is likely to arise at high densities for the umbrella sample distribution in [13], where at $\rho^* = 0.9$ the two regions are separated by the low transition zone. The utility of the method in this case requires a further investigation. At these densities the CTPI method is a good alternative to the above methods and can be more economical.

For a single-component system, CTPI method can be used to estimate the free energy difference between two thermodynamic states more efficiently

than the usual thermodynamic integration methods, since only a single particle undergoes the transformation of the hamiltonian; the method is equally applicable to large and small systems and all data can be used in calculating averages after the suitable 'reweighting'. In addition, the algorithm can easily be implemented on the parallel computer with perfect balancing.

Recently, several methods have been developed aimed at the free energy calculation of solids using computer simulation [35–38]. The convergence problems using 'harmonic' [35,37] and 'direct' methods [36,38] are more acute in this case than for liquids. Since in the CTPI method the 'integration' path does not require the crossing of the phase boundary, the process is reversible in the solid phase. An interesting and challenging problem is to investigate the usefulness of the method in this case. The work is currently in progress.

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