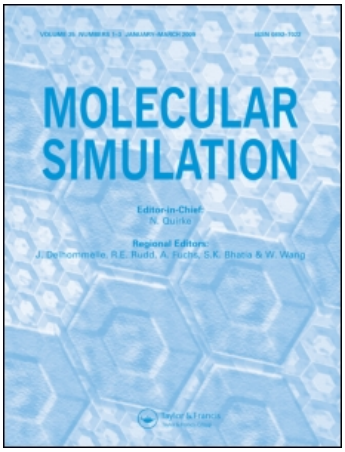

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Direct Calculation of the Excess Free Energy of the Dense Lennard-Jones Fluid

Mihaly Mezei[a]
[a] Department of Chemistry and Center for Study in Gene Structure and Function, Hunter College of the CUNY, New York, NY, USA

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DIRECT CALCULATION OF THE EXCESS FREE ENERGY OF THE DENSE LENNARD-JONES FLUID

MIHALY MEZEI

Department of Chemistry and Center for Study in Gene Structure and Function, Hunter College of the CUNY, New York, NY 10021, USA

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The excess free energy of the Lennard-Jones fluid near its triple point was calculated with a nonlinear thermodynamic integration method directly from an ideal gas reference state and is found to be in good agreement with earlier calculations. The effect of the truncation of the inner core on the computed free energy was also examined.

KEY WORDS: Free energy, Monte Carlo computer simulation, Lennard-Jones fluid, nonlinear thermodynamic integration.

INTRODUCTION

The calculation of free energy from computer simulation is of current interest [1–3]. Two major issues have arisen: the search for an adequate representation of the intermolecular energy (i.e. choice of potential form and its parameters) and the choice of the numerical technique that gives reliable results with the minimum computational effort. It is important to stress that the two issues are essentially independent of each other. The aim of this paper is to deal with the second issue only, using the Lennard-Jones fluid near its triple point as a model system. Since the representation of the non-bonded interactions in most potentials includes a Lennard-Jones term, the results of the study should be relevant to most other systems. Furthermore, the excess free energy of the Lennard-Jones fluid at selected states has already been determined by different workers using different numerical techniques to a precision of 1% or better.

The calculation of free energy differences are particularly ill-conditioned when the transition between two systems involves the creation or annihilation of particles. It has been argued earlier [1, 4] that such cases would be handled most effectively by nonlinear thermodynamic integration. This paper presents calculations of the excess free energy of the Lennard-Jones fluid at $\varrho^* = 0.8$, $T^* = 0.75$ using a nonlinear thermodynamic integration method on a path that goes directly from the ideal gas state to the fluid state. It will be also shown that the change of the r^{-12} repulsion to a function finite in the range [0–0.8 σ] has practically no effect on the excess free energy of the liquid but that this change does not seem to improve the efficiency of the calculation.

BACKGROUND

The state $\varrho^* = 0.8$, $T^* = 0.75$ was chosen because several earlier studies calculated its excess free energy. Reduced units (starred) are defined by $\varrho^* = N\sigma^3/V$, $T^* = kT/\varepsilon$ with N, V and T the number of particles, volume and temperature, respectively and ε and σ are the parameters of the Lennard-Jones potential:

$$E_{LJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{1}$$

(With some abuse of notation the symbol $E_{LJ}(X^N)$ will later be used to denote the sum of $E_{LJ}(r)$ over all pairs of particles.) For this system, pressure integration by Hansen and Verlet [5] gave the excess free energy $A' = -3.35$ (in units of ε). Torrie and Valleau obtained $A' = -3.345$ using umbrella sampling to calculate the free energy difference between the soft-sphere fluid and the Lennard-Jones fluid [6]. Recently, Mezei calculated A' for the same system using various grand canonical ensemble simulation techniques [7] and obtained values ranging from -3.30 to -3.35. In another calculation, described in the Appendix, the particle insertion method of Widom was used, giving $A' = -3.34$.

The calculations presented in this paper used a nonlinear thermodynamic integration technique described in [1], that is formally equivalent to a linear thermodynamic integration with an integral transform, as suggested by Mruzik *et al.* [8]. As usual for free energy simulations a coupling parameter λ is introduced such that the function $E(\lambda, X^N)$ gives zero for $\lambda = 0$ the reference system) and $E_{LJ}(X^N)$ for $\lambda = 1$. The work described here used

$$E(\lambda, X^N) = \lambda^k E_{LJ}(X^N) \tag{2}$$

It can be related to the choice proposed by Cross [4]:

$$E(\lambda, X^N) = 4(\lambda\varepsilon)[(\lambda\sigma/r)^{12} - (\lambda\sigma/r)^6] \tag{3}$$

Rearranging Equation (3) gives

$$E(\lambda, X^N) = \lambda^{13}4\varepsilon(\sigma/r)^{12} - \lambda^7 4\varepsilon(\sigma/r)^6 \tag{4}$$

showing that the linear scaling of both Lennard-Jones parameters (e.g. Equation (3)) corresponds to a λ exponent between 7 and 13 in Equation (2). It is to be stressed however that the coupling of Equation (2) always define a transcritical path and thus it is ensured that no complications would arise from possible phase transition along the path.

Following the general ideas of Kirkwood [9] it was shown that using Eq. (2) one obtains [1]

$$A' = \int_0^1 k\lambda^{k-1}\langle E(\lambda, X^N)\rangle\lambda \, d\lambda \tag{5}$$

Here the symbol $\langle \ldots \rangle\lambda$ stands for the Boltzmann average of the quantity enclosed using $E(\lambda, X^N)$ as the energy in the Boltzmann factor. The integrand of Equation (5) has to be evaluated with a numerical quadrature. Equations (2) and (5) generalize easily for the case when the reference system is not the ideal gas.

For the choice of the exponent k, three points are to be made. First, it has been shown previously [10] that $\langle E(\lambda, X^N)\rangle\lambda$ is monotonous in λ, thus for $k = 1$ (linear coupling) the whole integrand would be monotonous, thereby increasing the con-

fidence in the interpolation implicit in any numerical quadrature. Second, it has been noted that for the creation of a new particle the integrand may diverge at $\lambda = 0$, making the integral of Equation. (5) an improper one — this can have serious effect on the precision of any numerical quadrature. The nature of this divergence is known [1, 8, 11]: its limiting behaviour is $\lambda^{(kd/n)-1}$ for a potential with r^{-n} repulsion in the d-dimensional space [1]. Thus, choosing $k \geq 4$ for the Lennard-Jones fluid ensures a singularity free integrand. Third, too large a value for k would underemphasize too much the λ region near 1.

A different proposal to deal with the singularity issue by Wilson and coworkers [12] suggests the truncation of the inner core of the Lennard Jones term, arguing that the energy values at distances not sampled during a normal simulation can be modified without affecting a calculated free energy value. In principle, such a truncation should lower the calculated excess free energy value since if

$$E^{t}_{LJ}(X^N) \leq E_{LJ}(X^N) \tag{6}$$

then

$$\exp[-E^{t}_{LJ}(X^N)/kT] \geq \exp[-E_{LJ}(X^N)/kT] \tag{7}$$

and therefore

$$-kT\ln\int\exp[-E^{t}_{LJ}(X^N)/kT]\,dX^N \leq -kT\ln\int\exp[-E_{LJ}(X^N)/kT]\,dX^N \tag{8}$$

A calculation, using $k = 1$ with a truncated Lennard-Jones interaction showed that the difference is indeed very small.

CALCULATION AND RESULTS

The excess free energy of the Lennard-Jones fluid at $\varrho^* = 0.8$, $T^* = 0.75$ has been calculated with a 5-point Gauss-Legendre quadruture using $k = 4$, 5, 6 and 7 in Equation (5), giving $A' = -3.363 \pm 0.007$, -3.356 ± 0.014, -3.353 ± 0.005 and -3.358 ± 0.008, respectively, in excellent agreement with the previously computed values. The calculations used 160 particles in a simple cubic simulation cell under periodic boundary conditions. A 2.5 σ cutoff was applied to the potential and its effect has been corrected with the assumption that the density is constant for $r \geq 2.5\ \sigma$. Boltzmann averages were calculated over a sample of 2×10^6 configurations, generated by the Metropolis Monte Carlo method [13]. Figure 1 displays the calculated integrand values and the fitting polynomials used in the quadrature.

The adherence to the limiting behaviour was examined by calculating the ratio R,

$$R = (\langle E(\lambda, X^N)\rangle_{\lambda'}/\langle E(\lambda, X^N)\rangle_{\lambda})/(\lambda'/\lambda)^{0.25} \tag{9}$$

where λ' is the lowest λ value used, 4.998×10^{-10}. R should be one as long as the limiting behaviour is strictly valid. The calculated values of R are given in Table I, showing that the limiting behaviour is observed within ca. 15% for $\lambda < 0.016$. The truncated core Lennard-Jones used

$$E_{LJ}(r) = \begin{cases} \text{for } r < 0.8\sigma: & [2 - (r/0.8)^2] * E_{LJ}(0.8) \\ \text{for } r \geq 0.8\sigma: & E_{LJ}(r) \end{cases} \tag{10}$$

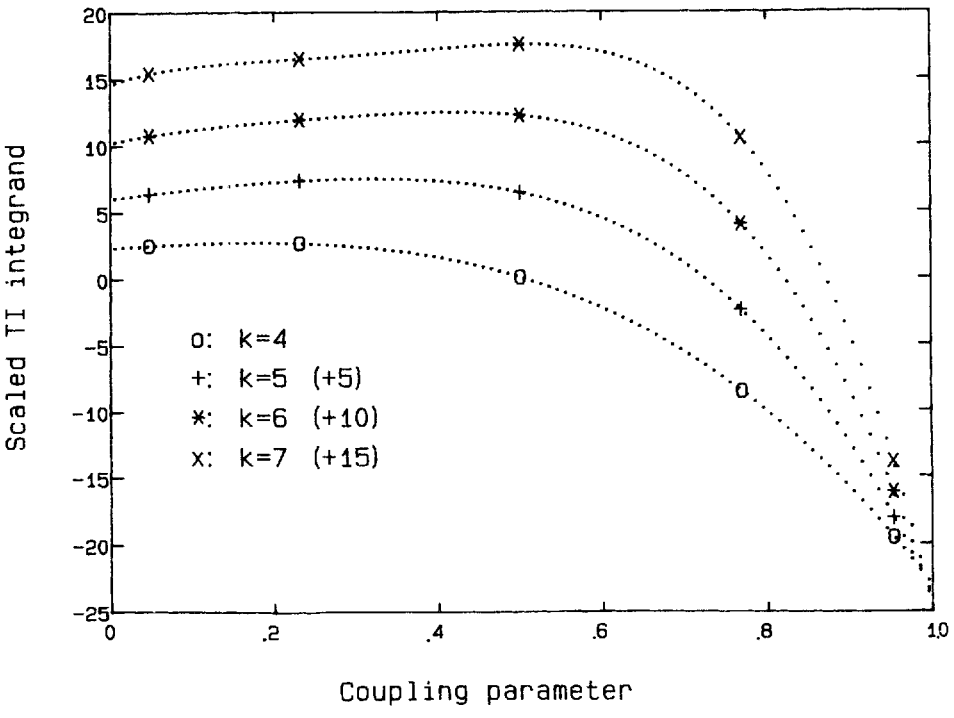

Figure 1 Integrand of the nonlinear thermodynamic integration and the approximating polynomial computed from the quadrature. The symbols 0, +, * and × stand for the calculated integrand values at $k = 4, 5, 6$ and 7, respectively. The dotted lines give the fitting polynomials. The curves for the successive k values are shifted upwards by 5 units for clarity.

Since this potential has no singularity at $r = 0.0$, $k = 1$ was used to take advantage of the monotonicity of the integrand. A 5-point Gauss-Legendre quadrature gave $A' = -3.71$ and showed that $\langle E(\lambda, X^N)\rangle_\lambda$ is nearly constant for $0.1 < \lambda \leq 1$ and is increasing steeply for $0 \leq \lambda \leq 0.1$. The fitting polynomial, shown in Figure 2, is

Table I. Test of the limiting behaviour of the thermodynamic integration integrand. R is the factor given by Equation (9) of the text quantifying the deviation from the limiting behaviour.

λ	$\langle E(\lambda, X^N)\rangle_\lambda$	R
4.999×10^{-10}	5.553×10^{6}	1.00
1.066×10^{-8}	5.658×10^{5}	0.99
2.272×10^{-7}	5.735×10^{4}	0.98
4.842×10^{-6}	6.081×10^{3}	0.93
3.485×10^{-5}	1.430×10^{3}	0.90
1.510×10^{-4}	4.946×10^{2}	0.87
6.544×10^{-4}	1.687×10^{2}	0.85
2.836×10^{-3}	5.488×10^{1}	0.87
7.913×10^{-3}	2.352×10^{1}	0.95
1.563×10^{-2}	1.173×10^{1}	1.13
3.125×10^{-2}	4.653	1.69

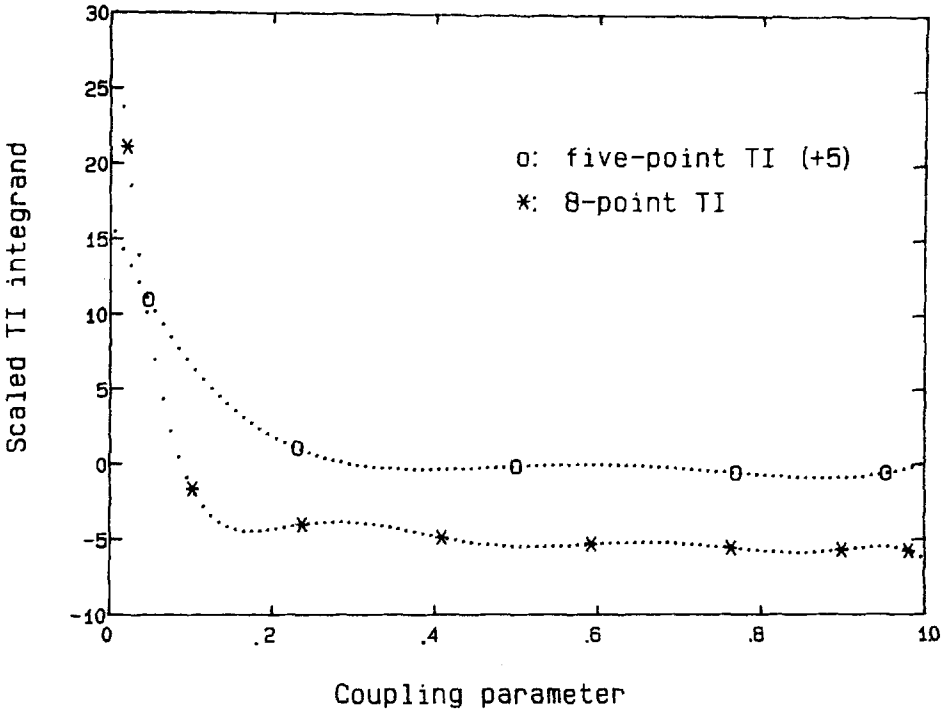

Figure 2 Integrand of the nonlinear thermodynamic integration and the approximating polynomial computed from the quadrature using the truncated Lennard-Jones potential. The symbols 0 and * stand for the calculated integrand values using a 5 and 8 point quadrature, respectively. The dotted lines give the fitting polynomials. The curve for the 5-point quadrature is shifted upwards by 5 units for clarity.

clearly inadequate to fit the integrand. Repeating the calculation with an 8-point quadrature gave $A' = -3.39$ but the fitting polynomial still suggested that the quadrature error would be rather large. To get a "definitive" answer, two 5-point quadratures were performed on the intervals [0, 0.1] and [0.1, 1] separately, giving $A' = 1.05 - 4.42 = -3.37$, very close to the untruncated value but slightly below it, as predicted by Equations (7–9).

DISCUSSION

The calculations described above demonstrate that nonlinear thermodynamic integration can be used reliably even when large scale particle creation is involved. This sets the method apart from most other techniques (perturbation method [6, 14], probability ratio method [15], overlap ratio method [16], acceptance ratio method [14]) where such a large scale particle creation would require a considerable number of intermediate states and thus illustrates the superiority of nonlinear thermodynamic integration for the calculation of free energy changes involving the creation (or annihilation) of several particles. (The only class of methods that are able to handle creation and annihilation with similar ease are the methods that involve insertion or

deletion of particles, see for example the Appendix, these methods fail however at liquid densities for complex solvents or solutes [7]). It has also been found that the result is largely insensitive to the choice of the exponent k. The fitting polynomial of the Gauss-Legendre quadrature, displayed on Figure 1, shows that the smoothest fit is obtained for $k = 4$ or 5. Combining this information with the requirement that the higher coupling parameter regions should also be sampled as much as possible, the recommended value is $k = 4$.

The truncation of the inner core of the potential was found less effective than expected. While the calculations have verified that the effect of truncation on the calculated A' is negligible, the resulting integrand, in spite of being monotonic in λ, was ill suited for the Gauss-Legendre quadrature and required significantly more quadrature points to calcualte A' with precision comparable to that of the untruncated calculations. While this might improve with the use of $k > 1$, the higher exponent would mean the loss of monotonicity of the integrand and thus most of the incentive for using the truncated potential is lost.

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APPENDIX

Widom has shown that the chemical potential of a fluid can be related to the following Boltzmann average:

$$\mu' = \langle \exp(-E(X_{N+1}, X^N)/kT) \rangle \tag{A1}$$

where $E(X_{N+1}, X^N)$ is the energy of interaction of a randomly inserted particle at X_{N+1}. For the efficient application of this formula, the fluid has to contain sufficient number of particle-size cavities and thus it is expected that the method would break down at high densities and/or low temperatures. Powles, Evans and Quirke [18] have shown, however, that for the Lennard-Jones fluid near its triple point, using molecular dynamics to generate configurational averages, the method is still able to give the chemical potential with adequate precision.

The calculation described in this Appendix performed a (T, V, N) ensemble simulation on 100 Lennanrd-Jones particles at $T^* = 0.75$ and $\varrho^* = 0.8$ under face-centered cubic periodic boundary conditions, using the Metropolis Monte Carlo method with force-biased displacements [19] for convergence acceleration. A 2.5 σ spherical cutoff was imposed on the interactions and contributions beyond 2.5 σ were estimated with the assumption that no density fluctuations exist beyond the cutoff. 2×10^6 Monte Carlo steps were run and at every 200 steps the program generated 200 random points and accumulated the average of Equation (A1). The excess free

energy was obtained as -3.34, in excellent agreement with the previously obtained values.

References

[1] M. Mezei and D.L. Beveridge, "Free Energy Simulations," *Ann. Acad. Sci. N.Y.*, **482,** 1 (1986).
[2] A. Pohorille and L.R. Pratt, "Theoretical methods for obtaining free energies of biomolecular equilibria in aqueous solution," in *Methods in Enzymology, Biomembranes,* **127,** (1986).
[3] D. Frenkel, "Free energy computation and first-order phase transitions," in *Molecular Dynamics Simulation of Statistical Mechanical Systems,* XCVII (1986), Soc. Italiana di Fisica, Bologna, Italy.
[4] A.J. Cross, "Influence of hamiltonian parametrization on convergence of Kirkwood free energy calculations, *Chem. Phys. Letters,* **128,** 198 (1986).
[5] J.P. Hansen and L. Verlet, "Phase transition of the Lennard-Jones system," *Phys. Rev.*, **184,** 151 (1969).
[6] G.M. Torrie and J.P. Valleau, "Nonphysical sampling distributions in Monto Carlo free energy estimation: umbrella sampling." *J. Comp. Phys.*, **23,** 187 (1977).
[7] M. Mezei, "Grand canonical ensemble study of dense liquid Lennard-Jones, soft spheres and water," *Mol. Phys.*, **61,** 565 (1987).
[8] M.R. Mruzik, F.F. Farid, F. Abraham, D.E. Screiber and G.M. Pound, "Monte Carlo study of ion-water clusters," *J. Chem. Phys.*, **64,** 481 (1976).
[9] J.G. Kirkwood, in "Theory of Liquids", B.J. Alder, ed., Gordon and Breach, New York (1968).
[10] M. Mezei, "Excess free energy of different water models computed by Monte Carlo methods," *Mol. Phys.*, **47,** 1307 (1982).
[11] W.C. Swope, H.C. Andersen, P.H. Berens and K.R. Wilson, "A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: application to small water clusters," *J. Chem. Phys.*, **76,** 637 (1982).
[12] K.R. Wilson, private communication.
[13] N.A. Metropolis, A.W. Rosenblut, M.N. Rosenbluth, A.H. Teller and E. Teller, "Equation of state calculation by fast computing machines," *J. Chem. Phys.*, **21,** 1087 (1953).
[14] C.H. Bennet, "Efficient estimation of free energy differences from Monte Carlo data." *J. Comp. Phys.*, **22,** 245 (1976).
[15] M. Mezei, P.K. Mehrotra and D.L. Beveridge, "Monte Carlo determination of the free energy and internal energy of hydration for the Ala Dipeptide," *J. Am. Chem. Soc.*, **107,** 2239 (1985).
[16] Jacucci and N. Quirke, "Monte Carlo calculation of the free energy difference between hard and soft core diatomic liquids," *Mol. Phys.*, **40,** 1005 (1980).
[17] B. Widom, "Some topics in the theory of fluids," *J. Chem. Phys.*, **39,** 2808 (1963).
[18] J.G. Powles, W.A. Evans and N. Quirke, "Non-Destructive molecular dynamics simulation of the chemical potential of a fluid," *Mol. Phys.*, **46,** 1347 (1982).
[19] M. Rao, C. Pangali and B.J. Berne, "On the force-bias Monte Carlo simulation of water: methodology, optimization and comparison with molecular dynamics," *Mol. Phys.*, **37,** 1773 (1979).