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Nonphysical Sampling Distributions in Monte Carlo Free-Energy Estimation: Umbrella Sampling

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The free energy difference between a model system and some reference system can easily be written as an ensemble average, but the conventional Monte Carlo methods of obtaining such averages are inadequate for the free-energy case. That is because the Boltzmann-weighted sampling distribution ordinarily used is extremely inefficient for the purpose. This paper describes the use of arbitrary sampling distributions chosen to facilitate such estimates. The methods have been tested successfully on the Lennard–Jones system over a wide range of temperature and density, including the gas–liquid coexistence region, and are found to be extremely powerful and economical.

1. INTRODUCTION

Use of the Monte Carlo method of Metropolis *et al.* [1] to estimate averages for model systems is nowadays a relatively routine matter. This is suitable for mechanical properties such as the pressure or internal energy. On the other hand, statistical properties such as the entropy and free energy, because they cannot be expressed as ensemble averages, have not been so easily accessible. The conventional technique has been numerical integration, following the Monte Carlo determination of some derivative of the free energy at a series of state points connecting the state or system of interest to one with a known free energy. This somewhat cumbersome method is least efficient or altogether unworkable when the system undergoes a phase transition, because of the difficulty of defining a path of integration on which the necessary ensemble averages can be reliably measured, though it is in precisely such cases that free-energy estimates would be most useful. Recently [2] we described a generalization of the method of Valleau and co-workers [3–5] for measuring free-energy differences which overcomes such difficulties for the case of the liquid–gas transition of a Lennard–Jones fluid. The free-energy difference between the Lennard–Jones fluid and a soft-sphere fluid was determined at a series of densities on an isotherm below the Lennard–Jones critical temperature by sampling on an arbitrary distribution designed to explore in a single Monte Carlo experiment the parts of configuration space relevant both to the Lennard–Jones fluid and to the reference soft-sphere fluid. In this paper we demonstrate the feasibility of extending such techniques to explore systematically large regions of a phase diagram, applying them to the Lennard–Jones system in a wide range of temperature and pressure including part of the gas–liquid coexistence region.

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2. OUTLINE OF THE METHOD

The free-energy difference between the "system of interest," with internal energy $U(\mathbf{q}^N)$ at temperature T, and a reference system, with internal energy $U_0(\mathbf{q}^N)$ at temperature T_0, is easily expressed as an ensemble average

$$\begin{aligned}\frac{A}{kT}-\frac{A_0}{kT_0} &= -\ln\frac{\int \exp[(-U/kT)+(U_0/kT_0)]\exp(-U_0/kT_0)\,d\mathbf{q}^N}{\int \exp(-U_0/kT_0)\,d\mathbf{q}^N} \\ &= -\ln\left\langle \exp\left(-\frac{U}{kT}+\frac{U_0}{kT_0}\right)\right\rangle_0 \\ &= -\ln\langle \exp(-\Delta U^*)\rangle_0, \qquad (1)\end{aligned}$$

where $\langle\ \rangle_0$ denotes an average over a canonical ensemble of reference systems and U^* is the reduced energy U/kT. Here we will briefly review the qualitative features of the Monte Carlo sampling schemes used to obtain an accurate estimate of the right-hand side of (1); a more complete and formal description may be found in [2].

In practice it is more useful to regard the average in (1) as a one-dimensional integral over ΔU^*, i.e.,

$$\frac{A}{kT}-\frac{A_0}{kT_0} = -\ln\int_{-\infty}^{\infty} f_0(\Delta U^*)\exp(-\Delta U^*)d\,\Delta U^*, \qquad (2)$$

where $f_0(\Delta U^*)$ is the probability density of ΔU^* in the reference fluid, and therefore in a conventional Monte Carlo experiment on that fluid.

In order to determine accurately the right-hand side of (2) such a Monte Carlo experiment would evidently have to produce good estimates of the values of $f_0(\Delta U^*)$ for that range of ΔU^* over which the product $f_0(\Delta U^*)\exp(-\Delta U^*)$ takes on its largest values. The corresponding region of configuration space is in fact that which would normally be sampled by a conventional Monte Carlo experiment *not* on the reference system but on the "system of interest" itself. This is easy to see for, if $f(\Delta U^*)$ is the probability density of ΔU^* in such an experiment,

$$f(\Delta U^*) = f_0(\Delta U^*)\exp(-\Delta U^*)\,Q_0/Q, \qquad (3)$$

where Q and Q_0 are the configurational integrals of the "system of interest" and the reference system, respectively. This is of limited usefulness since, without knowledge of the free-energy difference being sought, Q_0/Q is unknown, and the measurement of $f(\Delta U^*)$ (along with Eq. (3)) can give only *relative* values of $f_0(\Delta U^*)$ in the region where its *absolute* value is required. On the other hand, the range of ΔU^* over which a conventional *reference-system* experiment yields *absolute* values of $f_0(\Delta U^*)$ will not be adequate to evaluate the right-hand side of Eq. (2). Whether or not a reference system could be chosen so that the ranges of ΔU^* sampled by the two experiments overlapped, thus allowing a proper normalization of $f_0(\Delta U^*)$ throughout [3, 6], it is clear from the sharply peaked distributions of ΔU^* obtained in such experiments that conventional Boltzmann sampling is *not* an efficient way to explore the relevant part of configuration space.

Instead a Markov chain may be generated having a limiting distribution $\pi(\mathbf{q}'^N)$ which differs from the Boltzmann distribution for either system. We write it for convenience in the form

$$\pi(\mathbf{q}'^N) = \frac{w(\mathbf{q}'^N)\exp(-U_0(\mathbf{q}'^N)/kT_0)}{\int w(\mathbf{q}^N)\exp(-U_0(\mathbf{q}^N)/kT_0)\,d\mathbf{q}^N}, \tag{4}$$

where $w(\mathbf{q}^N) = W(\Delta U^*)$ is a weighting function chosen to favor those configurations with values of ΔU^* important to the integral in (2). Provided that $W(\Delta U^*)$ is such that the resulting Monte Carlo experiment continues as well to sample adequately those parts of configuration space that would be sampled by a Boltzmann-weighted experiment on the reference system, the unbiased ensemble average of any function $\theta(\mathbf{q}^N)$ can be recovered from the results of the π-sampling experiment according to

$$\begin{aligned}\langle\theta\rangle_0 &= \frac{\int(\theta/w)w\exp(-U_0/kT_0)\,d\mathbf{q}^N}{\int(1/w)w\exp(-U_0/kT_0)\,d\mathbf{q}^N}\\ &= \frac{\langle\theta/w\rangle_w}{\langle 1/w\rangle_w},\end{aligned} \tag{5}$$

where $\langle\ \rangle_w$ denotes an average over the distribution (4). Similarly $f_0(\Delta U^*)$ can be recovered from $f_w(\Delta U^*)$, the probability density of ΔU^* in the "biased" Monte Carlo experiment based on (4),

$$f_0(\Delta U^*) = \frac{f_w(\Delta U^*)/W(\Delta U^*)}{\langle 1/w\rangle_w}. \tag{6}$$

By trial and error $W(\Delta U^*)$ is adjusted until $f_w(\Delta U^*)$ is as wide and uniform as possible; the more rapidly varying $f_0(\Delta U^*)$ is then determined over this same wide range using (6).

Obviously it is required that the sampling distribution π specified by W should cover simultaneously the regions of configuration space relevant to two or more physical systems. We call this "umbrella sampling."

In the calculations described in the following sections weighting functions were used which brought about sampling of a range of ΔU^* up to three times that of a conventional Monte Carlo experiment, allowing accurate determination of values of $f_0(\Delta U^*)$ as small as 10^{-8}. Where this type of gain is still not sufficient to sample the entire range of ΔU^* values additional (equally powerful) "umbrella-sampling" experiments can be carried out with different weighting functions exploring successively overlapping ranges of ΔU^*. (Satisfactory weighting functions $W(\Delta U^*)$ are easy to find for such ranges of ΔU^*, and convergence of the runs was rapid. Evidently one could in principle always use only a *single* Monte Carlo run, choosing the sampling distribution to cover the *whole* of the relevant part of configuration space. However, for very wide-ranging distributions the choice of a successful $W(\Delta U^*)$ becomes tedious; we found it more convenient to use more modest overlapping umbrella distributions as described.)

To make maximum use of the information thus gained on $f_0(\Delta U^*)$ over a wide range of ΔU^*, it often proves useful to consider scaling the reduced energy difference between the two systems by a strength parameter α. The information obtained on $f_0(\Delta U^*)$ then suffices to estimate

$$\left(\frac{A}{kT}\right)_\alpha - \frac{A_0}{kT_0} = -\ln \int f_0(\Delta U^*) \exp(-\alpha\, \Delta U^*) d\, \Delta U^* \tag{7}$$

for all α between 0 and 1 simultaneously. The physical interpretation of these "intermediate" systems depends on the particular systems and energy difference under consideration and is more conveniently discussed in the context of the various types of calculations described in the following section.

3. APPLICATION TO A MODEL SYSTEM

In order to test the effectiveness of these methods we have applied them to the Lennard–Jones fluid. We were especially interested in using the techniques to investigate a phase transition region, since this is notoriously difficult using conventional methods. At the same time there are some reliable earlier results for this system, using the more cumbersome conventional techniques, and these afford direct tests of the method.

The investigations were carried out in two stages.

(a) *Altering the Force Law*

We first determined the free-energy difference between a Lennard–Jones fluid, with internal energy

$$U = 4\epsilon \sum_{i<j} [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6], \tag{8}$$

and an inverse-twelve "soft-sphere" fluid [7] at the same temperature, with internal energy

$$U_0 = 4\epsilon \sum_{i<j} (\sigma/r_{ij})^{12}. \tag{9}$$

This was done at seven densities on the supercritical isotherm $kT/\epsilon = 2.74$. The relevant energy difference is then simply

$$\Delta U^* = (U_6/kT) = (-4\epsilon/kT) \sum_{i<j} (\sigma/r_{ij})^6 \tag{10}$$

so that

$$(\Delta A/NkT) = -(1/N) \ln\langle \exp(-U_\sigma/kT)\rangle_0 , \tag{11}$$

and the umbrella sampling (4) is carried out using a weighting function which favors soft-sphere configurations with large negative values of U_6. These calculations are similar in all respects to those previously reported [2] for a subcritical isotherm and will not be described in more detail here. We note, however, that at the higher densities on the supercritical isotherm the "soft-sphere" reference system and the Lennard–

Jones system have sufficiently similar configurations that a *single* umbrella-sampling experiment is powerful enough to determine ΔA. This is illustrated in Fig. 1 for the highest density studied. The solid line is $f_w(U_6)$, the probability density of U_6 that resulted from the umbrella sampling; the dotted line is $f_0(U_6)$, the unbiased probability of U_6 for a soft-sphere fluid as obtained by reweighting $f_w(U_6)$ according to Eq. (6); the broken line is the function $f_0(U_6)\exp(-U_6/kT)$ normalized to unity, also obtained by reweighting $f_w(U_6)$. The weighting function used to carry out this particular experi-

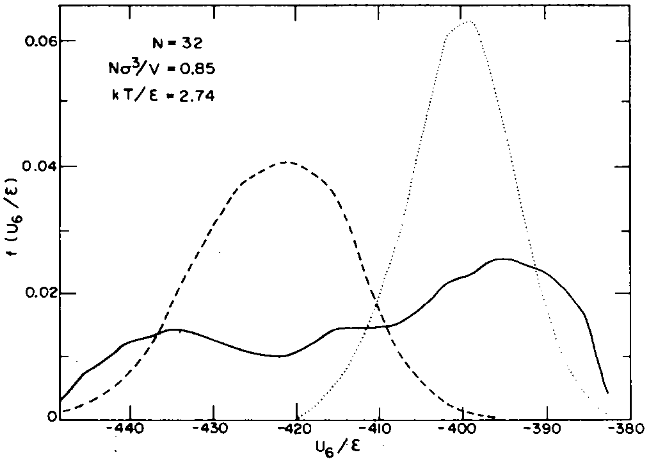

FIG. 1. Probability density functions for U_6 in a 32-particle soft-sphere fluid at $kT/\epsilon = 2.74$, $N\sigma^3/V = 0.85$. Solid line, f_w, the biased probability density. Dotted line, f_0, the unbiased probability density obtained by reweighting f_w. Broken line, relative values of $f_0(U_6/\epsilon)\exp(-U_6/kT)$ normalized to unity.

TABLE I

Numerical Weights Used for an Umbrella-Sampling Experiment for 32 Soft Spheres at $N\sigma^3/V = 0.85$, $kT/\epsilon = 2.74$[a]

U_6/ϵ	$W(U_6/\epsilon)$	U_6/ϵ	$W(U_6/\epsilon)$
≤ -444.3	1,500,000	−411.5	2.60
−441.6	400,000	−408.7	1.75
−438.9	100,000	−406.0	1.25
−436.1	25,000	−403.3	1.15
−433.4	6,600	−400.5	1.00
−430.7	1,700	−397.8	1.24
−427.9	470	−395.0	1.70
−425.2	150	−392.3	2.50
−422.4	50	−389.9	4.30
−419.7	22	−386.8	8.50
−417.0	10	≥ -384.1	16.00
−414.2	5		

[a] Linear interpolation was used to determine W for energies lying between table entries.

ment is shown in Table I. The free-energy differences and the resulting configurational free energy

$$A_c = -kT \ln(Q/N!\,\sigma^{3N}) \tag{12}$$

obtained by adding to ΔA the soft-sphere free energies of Hoover *et al.* [7] are shown in Table II.

TABLE II

Configurational Helmholtz Free Energy for the Lennard–Jones Fluid on the Isotherm $kT/\epsilon = 2.74$, Obtained from Eq. (11)

N	$N\sigma^3/V$	$(\Delta A/N\epsilon)$	$(A_c/N\epsilon)$
32	0.500	-5.90 ± 0.015	-4.45
108	0.500	-5.95 ± 0.01	-4.50
32	0.600	-7.62 ± 0.015	-3.64
32	0.700	-9.51 ± 0.015	-2.68
32	0.750	-10.54 ± 0.015	-2.11_5
32	0.800	-11.69 ± 0.015	-1.56_5
108	0.800	-11.68 ± 0.01	-1.557
32	0.835	-12.49 ± 0.015	-1.124
32	0.850	-12.85 ± 0.015	-0.890

For these calculations the "intermediate" systems of Eq. (7) would be ones in which the attractive part of the energy is scaled by the parameter α:

$$U_\alpha = 4\epsilon \sum_{i<j} \{(\sigma/r_{ij})^{12} - \alpha(\sigma/r_{ij})^6\}. \tag{13}$$

We have not reweighted the Monte Carlo data to derive any results for this somewhat unusual model, though such an approach could be used to obtain information on terms in a perturbation theory expansion of the Lennard–Jones free energy about that of the inverse-twelve soft-sphere system. A much more useful interpretation of this type of reweighting to intermediate systems can be made for the kind of calculations described in the following section.

(b) *Scaling the Temperature*

Whenever the reference system has the same internal energy function as the system of interest, Eq. (1) takes the simple form

$$\frac{A(T)}{kT} = \frac{A(T_0)}{kT_0} - \ln\left\langle \exp\left[-U\left(\frac{1}{kT} - \frac{1}{kT_0}\right)\right]\right\rangle_0, \tag{14}$$

and the most convenient way to write (2) is

$$\frac{A(T)}{kT} = \frac{A(T_0)}{kT_0} - \ln \int f_0(U) \exp\left[-U\left(\frac{1}{kT} - \frac{1}{kT_0}\right)\right] dU. \tag{15}$$

This is very powerful, because the "intermediate" systems that result from multiplying $-U$ in the exponent by a smaller number (cf. $\alpha < 1$ in (7)) can now be interpreted as those with temperatures *between* T and T_0. A single sampling of $f_0(U)$ can therefore give the free energy over a whole range of temperatures.

As reference systems we used the high-temperature Lennard–Jones systems at each of the seven densities in Table II. Umbrella sampling was used to measure $f_0(U)$ over a range extending to progressively lower energies, using additional sampling stages if necessary. For each density, the lowest energies so sampled will determine the lowest value of the temperature for which A can be reliably determined using (15). In addition to A, the average energy and specific heat can be calculated for any intermediate temperature, e.g.,

$$\langle U\rangle_T = \frac{\int U f_0(U) \exp\{-U[(1/kT) - (1/kT_0)]\}\, dU}{\int f_0(U) \exp\{-U[(1/kT) - (1/kT_0)]\}\, dU} \tag{16}$$

Mean values of quantities which are *not* functions of U can also be obtained in a similar way provided that $\bar{\theta}(U)$, the average value of θ for a fixed value of the energy is recorded for all U during the Monte Carlo run; then

$$\langle\theta\rangle_T = \frac{\int_{-\infty}^{\infty} f_0(U)\, \bar{\theta}(U) \exp\{-U[(1/kT) - (1/kT_0)]\}\, dU}{\int_{-\infty}^{\infty} f_0(U) \exp\{-U[(1/kT) - (1/kT_0)]\}\, dU}. \tag{17}$$

Such ideas were first proposed and successfully carried out by McDonald and Singer [8, 9] who attempted relatively small temperature changes ($\leqslant 15\ \%$) in the data from a single Boltzmann-weighted experiment. They become powerful in the present context because of the much larger energy ranges that can be spanned by the nonphysical umbrella samples. The results of a typical two-stage experiment for 32 Lennard–Jones particles near the triple-point density are shown in Fig. 2. The solid lines show

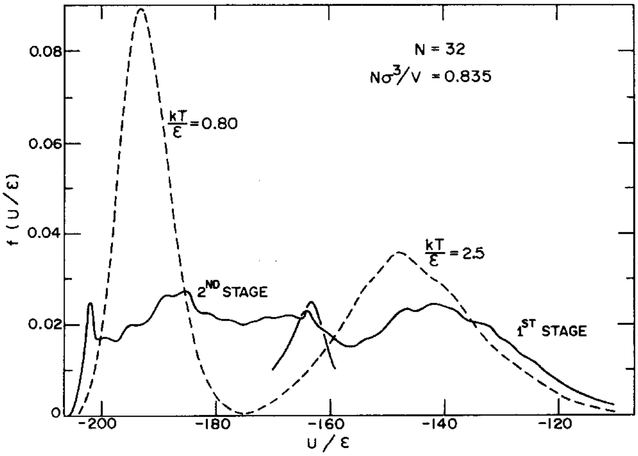

FIG. 2. Probability density functions of the total energy for 32 Lennard–Jones particles from umbrella sampling.

the energy distributions resulting from the two umbrella-sampling experiments while the broken lines are two examples of the reweighting of these data to obtain the energy distribution at various temperatures. This is typical of the possible gain—the energy and free energy of the system at fixed density in the temperature range $0.7 \leqslant kT/\epsilon \leqslant 2.8$, i.e., from the triple-point temperature to twice the critical temperature, are determined from only *two* umbrella-sampling experiments. For a system of 108 particles, where the Boltzmann distributions are much narrower relative to the total energy range, the same information can still be obtained with four umbrella experiments.

(c) *Corroboration of the Results*

In Table III some values of the free energy calculated from umbrella sampling are compared with previous Monte Carlo measurements by Hansen [10, 11] and by Levesque and Verlet [12], based on integration of pressures calculated for an 864-

TABLE III

Configurational Free Energy of the Lennard–Jones Fluid Obtained by Umbrella Sampling[a]

kT/ϵ	$N\sigma^3/V$	N	$A_c/N\epsilon$	Method[b]	Previous Monte Carlo results
2.74	0.80	32	−1.565	I	−1.56[c]
		108	−1.556		
1.35	0.50	32	−3.791	II	−3.85[d]
1.35	0.80	32	−3.236	II	−3.25[d]
		108	−3.229		
1.15	0.75	32	−3.633	I	−3.65[d]
			−3.638	II	
0.75	0.50	32	−3.657	II	−3.69[e]
0.75	0.60	32	−3.913	II	−3.93[e]
0.75	0.80	32	−4.265	II	−4.27[e]
		108	−4.265		
1.16	0.835	32	−3.444	II	−3.83[f]
0.902	0.835	32	−3.966	II	−3.92[f]
0.81	0.835	32	−4.168	II	−4.10[f]

[a] The error usually quoted for the free energies of the final column obtained by thermodynamic integration is 0.01–$0.03N\epsilon$. The uncertainty in the present free energies includes this error for the reference system plus an uncertainty of $0.01N\epsilon$ in ΔA.

[b] Method I, calculated using Eq. (11); method II, calculated using Eq. (15).

[c] = [10].

[d] = [12].

[e] = [11].

[f] = [13].

particle system. The table also compares our results with estimates by Gosling and Singer [13] based on an intuitive "free-volume" interpretation of acceptance ratios in Monte Carlo runs. The quoted results of the umbrella-sampling methods are only a few values selected for these comparisons: data are of course available for the densities studied at *all* temperatures in the range $0.7 \leqslant kT/\epsilon \leqslant 2.8$.

Over the whole range of temperature and density the present results agree with those of the pressure integrations to within the combined statistical uncertainties. This is so whether A_c is determined by relating it directly to a soft-sphere reference system or by temperature reweighting to relate it to a high-temperature Lennard–Jones fluid using (15). At $kT/\epsilon = 1.15$, $N\sigma^3/V = 0.75$, both of these umbrella-sampling methods have been used independently, and agree excellently with each other and with Hansen's results.

Most of the calculations reported here are for a relatively small system of 32 particles. Consequently the overall agreement with the thermodynamic integration results for 864 particles seems to confirm our earlier conjecture [2] that the N-dependence of free-energy *differences* between dense systems is very mild. For example, calculations by the present methods for 32 and 108 particles at $N\sigma^3/V = 0.8$ (cf. Table III) show no statistically significant N-dependence. This is very pleasing since it means that good free-energy estimates can be made very economically, where there exist good data for a suitable reference system.

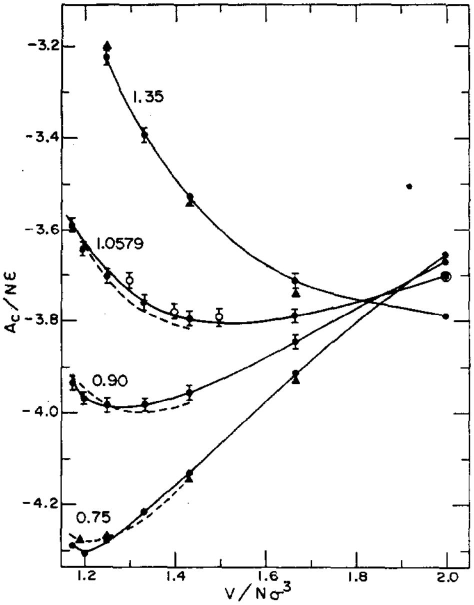

FIG. 3. Configurational Helmholtz free energy of the Lennard–Jones fluid in the vicinity of the liquid–gas coexistence curve. The open circles are free-energy estimates based on Eq. (11), the closed circles are based on Eq. (15). The triangles are the results of Verlet and co-workers [10–12], the broken curves the fitted equation of McDonald and Singer [14].

Figure 3 shows further comparisons between some free-energy results obtained by umbrella-sampling and those of thermodynamic integration results of the Orsay group [10–12] (triangles) and of McDonald and Singer [14] (broken lines [15]) in the vicinity of the gas–liquid coexistence curve. The open circles are the present results for direct soft-sphere to Lennard–Jones free-energy estimates using (11), and include some of the results we reported earlier [2], the closed circles are results of the temperature-reweighting procedure, Eq. (15). The solid lines are simply visual aids connecting isothermal free-energy estimates of this work, and the error bars show one standard deviation of the mean of ΔA. The agreement of the two umbrella-sampling routes to A_c on the isotherm $kT/\epsilon = 1.0579$ is particularly gratifying, as the original starting points were two quite different soft-sphere systems, one at $kT/\epsilon = 2.74$, the other at $kT/\epsilon = 1.0579$.

Although portions of the three low-temperature isotherms of Fig. 3 are well within the liquid–gas coexistence region and, when taken together with the low-density virial series, would clearly violate the stability criterion $(\partial^2 A/\partial V^2) \geqslant 0$, no associated convergence problems were encountered in the umbrella-sampling experiments. Apparently the supercritical Lennard–Jones fluid is as suitable as the soft-sphere fluid proved to be [2] for use as a reference state from which umbrella-sampling is able to explore successfully the unstable regime.

This close agreement between the present free energies and those obtained by thermodynamic integration is to be contrasted with some rather large discrepancies in the case of the free energies [16] resulting from the method for estimating entropies proposed by Gosling and Singer [13] (cf. Table III). For example, the disagreement of $0.4N\epsilon$ at $kT/\epsilon = 1.16$ corresponds to an error of 20 % in the nonideal entropy (the quantity actually estimated by their technique) and is equivalent to an overestimation of the configurational integral of a 108-particle system by a factor of 10^{16}. It appears that that technique cannot be relied upon to give quantitative results for the entropy and free energy.

TABLE IV

Unbiased Mean Internal Energy for the Lennard–Jones Fluid

$N\sigma^3/V$	kT/ϵ	$\langle U_{LJ}/N\epsilon\rangle_0$	
		Umbrella[a]	Conventional[b]
0.50	1.35	−3.32	−3.37 (a)
0.70	1.35	−4.66	−4.68 (a)
0.75	0.827	−5.38	−5.38 (b)
0.75	0.977	−5.26	−5.244 (c)
0.75	1.304	−5.01	−5.02 (b)
0.80	0.092	−5.65	−5.656 (c)
0.80	1.06	−5.51	−5.507 (c)

[a] Umbrella sampling: Obtained by reweighting the results of umbrella sampling using Eq. (16).

[b] Conventional: (a) Monte Carlo [12]; (b) Molecular dynamics [17]; (c) Monte Carlo [14].

Finally, in Table IV, the mean internal energy U of the Lennard–Jones fluid as determined by reweighting the results of umbrella-sampling experiments according to Eq. (16) is compared with conventionally determined values [12, 14, 17]. The generally good agreement is best for the higher densities, for which neglect of the density fluctuations caused by use of the small 32-particle system would be expected to have the least effect. The standard deviation of the mean for the energies obtained by reweighting data from umbrella-sampling Monte Carlo experiments, such as those in Table IV, is about $0.02N\epsilon$ for a run of $3\text{–}5 \times 10^5$ configurations, somewhat higher than for a Boltzmann-weighted experiment of similar length. These standard deviations are estimated in the customary way [18] by treating averages over sequences of m steps within the entire Monte Carlo run of M steps as M/m independent estimates to which the appropriate statistical formulas may be applied. The determinations of the value of m constituting an independent sample must be treated with more than usual care when recovering unbiased averages from umbrella-sampling experiments. In Eq. (5), for example, the values of the numerator and denominator will be strongly correlated for short blocks of configurations. As a result the mean value calculated as

$$\langle \theta \rangle_0 = \sum_{i=1}^{M/m} \langle \theta/w \rangle_i / \langle 1/w \rangle_i \tag{18}$$

will in general depend on m, where $\langle\ \rangle_i$ is an average over the ith block of m configurations. In practice the appropriate block size has been determined in each case by increasing m until no systematic trends could be detected in either the average given by (18) or in the standard deviation of the mean. The free-energy difference (2) is itself the *logarithm* of the average calculated, and can therefore be obtained with great precision, usually to within about $0.005NkT$ for $N = 108$. This high precision makes the technique ideally suited to the study of mixtures, where it is exactly the relatively small free-energy *differences* that are the physically important but computationally elusive property. In fact the techniques described here have now been exploited to determine the free energy and phase diagram of a model binary mixture with an upper critical solution temperature [19, 20].

4. DISCUSSION

The basic idea of designing Monte Carlo experiments to sample the configuration space of the system according to an arbitrary distribution of states can be useful in several ways. First, such sampling procedures render estimates of free-energy differences of the form $\langle \exp(-\Delta(U/kT)) \rangle_0$ practical and efficient. This in turn eliminates the need of the more roundabout and expensive thermodynamic integrations, and is particularly advantageous when the system undergoes a phase transition, since it appears that by applying umbrella-sampling which embraces a stable reference system, information can be collected in or near the unstable regions of the phase diagram of the complete system without the usual associated convergence problems. Secondly, because umbrella distributions of the type described here span a much larger region of configuration space than do Boltzmann-weighted Monte Carlo experiments on either the reference system or the system of interest, a correspondingly greater amount of information about the system can be obtained simply by collecting and later reweighting the appropriate data. For example, Levesque and Verlet [12] used data from five Monte Carlo runs to establish a path of integration between a soft-sphere fluid and the Lennard–Jones system whereas a single umbrella-sampling suffices for 32 particles at high temperature. For a fluid of 32 Lennard–Jones particles at fixed density only two umbrella-sampling experiments are needed to sample the regions of configuration space appropriate to all temperatures between that of the triple point and twice that of the critical point, whereas numerous runs (of similar length) would be required for conventional $1/T$ integrations. The cost efficiency of the method is therefore high. Such sampling gains could likewise be realized for the other commonly used ensembles (isothermal–isobaric and grand canonical) with relatively straightforward modifications of the techniques used here for the canonical case.

In fact, although the choice of ΔU as the single argument of the weighting function w defined in (4) was a natural one for the free-energy difference problem, the general case in which w is any arbitrary function of the coordinates can extend the usefulness of the biased sampling to a wider range of problems. For example, we have used such a sampling scheme to measure the communal entropy of a hard-sphere fluid [4], though the sampling distributions used did not turn out to be particularly efficient. The method has been quite successful, however, in Monte Carlo experiments designed to get particular microscopic information [21] (rather than merely macroscopic thermal averages) where the sampling problems are different in nature but similar in magnitude to those associated with measuring free-energy differences according to Eq. (1).

Superficially, the most serious limitation of the sampling techniques described here may appear to be the lack of a direct and straightforward way of determining the weighting function to use for a given problem. Instead, $w(\mathbf{q}^N)$ must be determined by a trial-and-error procedure for each case, often beginning with the information available from the distribution in a very short Boltzmann-weighted experiment which is then broadened in stages through subsequent short test runs with successively greater bias of the sampling. What this rather inelegant procedure lacks aesthetically is more than compensated by the efficiency of the ultimate umbrella-sampling experiment. The test runs require a small amount of time relative to the final production run and are necessary anyway, even in the absence of biasing weights, in order to age the system. One cannot expect to replace this trial-and-error procedure with a trustworthy a priori estimate of the correct value of $w(\mathbf{q}^N)$, not only because of the great variety of problems to which the technique might be applied, but because a guess sufficiently accurate to work would constitute prior knowledge of $f_0(\Delta U^*)$ and hence of ΔA itself. At present, the most efficient trial-and-error procedure involves an interaction between the trial computer results and human judgment. It is important to emphasize, however, that the necessary experience seems to be very readily obtained. A possible embellishment of the technique would be to program the computer to carry out itself the trial-and-error development of a good weighting function.

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15. These data are presented in the form of an equation for free-energy *differences* between states in the dense fluid region, designed to fit the ensemble averages of pressure and energy obtained by Monte Carlo experiments at a large number of state points. The absolute free energies plotted in Fig. 3 result from forcing agreement with the present results at the single point $N\sigma^3/V = 0.80$, $kT/\epsilon = 1.00$.
16. The total entropy values actually reported have first been converted back into excess entropies in reduced units and then to free energies using the internal energies of McDonald and Singer [14] for the corresponding state points. This introduces an additional uncertainty in $A_c/N\epsilon$ of less than 0.01 and is therefore not important for the comparison being made here.
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