Accurate Measurements of the Chemical Potential of Polymeric Systems by Monte-Carlo Simulation

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Abstract

We present a new Monte-Carlo method for estimating the chemical potential of model polymer systems. The method is based upon the gradual insertion of a penetrable ‘ghost’ polymer into the system and is effective for large chain lengths and at high densities. Insertion of the ghost chain is facilitated by use of an expanded ensemble in which weighted transitions are permitted between states characterising the strength of the excluded volume and thermal interactions experienced by the ghost chain. We discuss the implementation and optimisation of the method within the framework of the bond fluctuation model, and demonstrate its precision by a calculation of the finite-size corrections to the chemical potential.

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1 Introduction

Measurements of chemical potential by computer simulation are an important tool for determining the phase behaviour of model systems. For many years the standard technique for achieving this in atomic and simple molecular systems, has been the Widom particle insertion method [1]. This method involves repeatedly sampling the potential $U_t$ experienced by a single particle when it is added at random to the system of interest. The excess chemical potential $\mu_{ex}$ is then given by

$$\beta \mu_{ex} = -\ln < \exp(-\beta U_t) >$$  \hspace{1cm} (1)

For polymeric systems, however, the basic Widom method cannot be employed for obtaining estimates of $\mu_{ex}$. The extended structure of polymers renders the method unsuitable for all but the shortest chains and lowest densities, there being a prohibitively small probability of inserting a polymer at random without violating excluded volume restrictions. Clearly therefore different approaches are called for, and indeed several new techniques for measuring the chemical potential of model polymer systems have recently been developed [2]. We describe them in turn.

A method that ameliorates some of the difficulties associated with random chain insertion is the so-called configurational bias Monte Carlo method, first proposed by Siepmann [3] and later generalised by Frenkel and coworkers [4], and de Pablo and coworkers [5]. This technique utilises a biased insertion technique to ‘grow’ a polymer of favourable energy into a frozen snapshot of the system, thereby extending the range over which the Widom insertion technique is viable. A book-keeping scheme maintains a record of the statistical bias associated with choosing energetically favourable chain conformations, and this bias is subsequently removed when the chemical potential is calculated. The method is also amenable for use with Gibbs ensemble simulations, facilitating direct study of polymer phase equilibria [6, 7]. However in practice, the utility of the configurational bias approach is limited since it tends to break down for longer chain lengths ($\geq 20$ monomers) and higher densities ($\rho \geq 0.6$).

Another technique for obtaining $\mu_{ex}$ is the Chain Increment method of Kumar and coworkers [2, 8, 9]. This method hinges on the observation that the chemical potential of a chain of length $N$ is equivalent to the sequential sum of the incremental chemical potentials of all successively shorter chains $N-1, N-2, \ldots$. Since the incremental chemical potential seems to become largely independent of chain length for longer chains ($N \geq 15$) [10], it is possible to estimate the total chemical potential for a chain of arbitrary length by calculating the incremental chemical potential associated with adding one monomer to a chain end, and multiplying by the chain length. Separate sets of simulations of short chains ($N < 15$) may then be performed to provide corrections associated with the small-$N$ dependence of the incremental chemical potential. This method thus allows estimates of the chemical potential for arbitrary chain lengths, and indeed has facilitated the calculation of the liquid-vapour phase diagram for a bead-spring polymer model [11].

Recently Müller and Paul have developed a novel approach to calculating the chemical potential of polymer chains [12]. Their method involves a thermodynamic integration over the excluded volume interaction of a penetrable ‘ghost’ chain immersed in a system of ‘real’ polymers. A control parameter $\lambda$ tunes the strength of this interaction such that for $\lambda = 1$ the ghost decouples from the normal polymers, while for $\lambda = 0$ it behaves as a normal polymer. Separate simulations are performed at each of several $\lambda$ values in the range (0,1),
and thermodynamic integration with respect to $\lambda$, aided by multi-histogram extrapolation techniques, are used to obtain the chemical potential. The method was successful in obtaining $\mu_{\text{ex}}$ for lattice polymers up to $N = 80$ monomers and at melt densities ($\rho = 0.5$).

In this paper we present a further method for calculating the chemical potential of polymer chains that is effective both at large chain lengths and high densities. The method is efficient, requiring only a single simulation, and exact in the sense that no approximations are involved. In the following sections we describe the method and discuss its implementation and optimisation.

## 2 Method

### 2.1 Background

The strategy of the present method is similar in spirit to that of Müller and Paul [12]. We consider a system of volume $V = L^d$ containing $n$ polymers of length $N$, plus a single penetrable ghost polymer. The monomers of the normal polymers experience an attractive short-range interaction $J(r)$ and are subject to strict excluded volume restrictions. An intra-molecular bond potential $U(r)$ controls the bond lengths and angles between neighbouring monomers of the chain.

The ghost polymer is subject to the same intra-molecular bond potential as the normal polymers and its monomers must not overlap with one another. However, the excluded volume restriction between ghost monomers and normal monomers is now replaced by an athermal effective repulsive potential $K = -\frac{1}{\beta}ln\lambda$, where $\lambda$ is a parameter, variable in the range $(0, 1)$, that controls the strength of the repulsion. The magnitude of the attractive thermal interaction between ghost monomers and normal monomers is also modified by a factor $(1 - \lambda)$.

For a given choice of $\lambda$, the canonical partition function of the system is given by

$$Z(n, N, V, \lambda) = \prod_{i=1}^{(n+1)N} \left\{ \int dr_i \right\} e^{-\beta\left[ E_t(\{r\}) + E_a(\{r\}) \right]}$$

where the integration is over all configurations of the monomers $i$, subject to excluded volume restrictions.

The thermal part of the configurational energy $E_t(\{r\})$ is defined by

$$E_t(\{r\}) = \sum_{(j,k)} J(|r_j - r_k|)\delta_{\alpha_j\alpha_k} + (1 - \lambda) \sum_{(j,k)} J(|r_j - r_k|)(1 - \delta_{\alpha_j\alpha_k}) + \sum_{(l,m)} U(r_l - r_m)$$

where $j$ and $k$ run over all monomers, while $l$ and $m$ run over all neighbouring pairs of monomers on the same chain. We assign $\alpha_j = 1$ for a normal monomer and $\alpha_j = 0$ for a ghost monomer.

The athermal part of the configurational energy $E_a(\{r\})$ is given by

$$E_a(\{r\}) = -\frac{1}{\beta} N_o(\{r\})ln\lambda$$

where $N_o(\{r\})$ is the total number of overlaps between the ‘excluded volume’ shell of ghost monomers and those of normal monomers.

Clearly, by tuning $\lambda$ one is able to interpolate smoothly between two special cases:
\[ \lambda = 0, \text{ for which the ghost behaves as a normal polymer} \]
\[ \lambda = 1, \text{ for which the ghost decouples from the polymer system}. \]

The ratio of the partition function at these limits defines the excess chemical potential:
\[ \exp(\mu_{ex}) = \frac{Z(n, N, V, 1)}{Z(n, N, V, 0)} \tag{5} \]

Following the recently proposed method of expanded ensembles [13, 14], we now consider an ensemble that facilitates direct measurement of the ratio of the partition functions appearing in equation 5. The ensemble is defined by the partition function:
\[ \Omega = \sum_{m=0}^{M-1} Z_m(n, N, V, \lambda_m) \exp(\eta_m) \tag{6} \]

where \( 0 \leq m \leq (M - 1) \) indexes a set of \( M \) \( \lambda \)-states spanning the range \((0, 1)\), with \( \lambda_0 = 0 \) and \( \lambda_{M-1} = 1 \). The \( Z_m \) are the canonical partition functions defined in equation 2 with \( \lambda = \lambda_m \), while the \( \eta_m \) are positive pre-weighting factors the significance of which will be described.

To realise a Monte-Carlo simulation within this expanded ensemble, it is necessary to allow for two types of MC steps. Firstly there are the usual trial monomer displacements at constant \( \lambda \). Secondly there are trial transitions between neighbouring \( \lambda \)-states, the spatial coordinates of all polymers remaining fixed. These \( \lambda \)-transitions are accepted or rejected according to some criterion satisfying detailed balance, such as metropolis:
\[ P_a(n \rightarrow m) = \min(1, \exp[N_o(\ln \lambda_m - \ln \lambda_n) + \beta(\lambda_n - \lambda_m)E_G + \eta_m - \eta_n]) \tag{7} \]

where \( E_G = \sum_{j,k} J(|\mathbf{r}_j - \mathbf{r}_k|)(1 - \delta_{\alpha_j \alpha_k}) \) is the interaction energy of the ghost polymer with the other polymers. It should be stressed, however, that these \( \lambda \)-transitions do not drive the system out of equilibrium as they would if we were considering a simple canonical ensemble. Within the expanded ensemble framework, both types of moves—monomer displacements and \( \lambda \)-transitions—are necessary to bring the system into equilibrium.

In the course of the expanded ensemble simulation a histogram \( p(\lambda_m) \) can be accumulated describing the probability with which each of the \( M \) \( \lambda \)-states is visited. Formally this probability distribution takes the form:
\[ p(\lambda_m) = \frac{Z_m}{\Omega} \exp(\eta_m) \tag{8} \]

From which it follows that
\[ \frac{p(\lambda_{M-1})}{p(\lambda_0)} = \frac{Z_{M-1} \exp(\eta_{M-1})}{Z_0 \exp(\eta_0)} \tag{9} \]

The excess chemical potential is then calculable as:
\[ \mu_{ex} = \ln \left[ \frac{\tilde{p}(\lambda_{M-1})}{\tilde{p}(\lambda_0)} \right] \tag{10} \]

where
\[ \tilde{p}(\lambda_m) \equiv p(\lambda_m) \exp(-\eta_m) \tag{11} \]
Now, the principal difficulty in implementing such a scheme, is that the ratio of the partition functions $Z_{M-1}/Z_0$ appearing in equation 9 can (even for short chains) span very many orders of magnitude. In order to obtain a histogram $p(\lambda_m)$ having counts for all $m$, it is therefore necessary to employ a pre-weighting scheme that will encourage the simulation to sample $\lambda$-states that would otherwise be highly unfavourable. This is achievable by suitable choices of the pre-weighting factors $\eta_m$ featuring in equations 6–11. Unfortunately however, the choice of suitable $\eta_m$ cannot be determined directly \textit{a-priori}. For example, the weights that would yield a perfectly flat sampled distribution (i.e. $p(\lambda_m) = \text{constant}$), are given by

$$\eta_m = \int_{\lambda_m}^{1} d\lambda \ln Z(n, N, V, \lambda) d\lambda$$

in which $Z(n, N, V, \lambda)$ is, of course, unknown. Nevertheless, it turns out that it is possible to implement a straightforward iterative scheme for obtaining suitable $\eta_m$.

### 2.2 Determining the pre-weighting factors

The goal is to determine values for the pre-weighting factors $\eta_m$ that allow the system to visit each $\lambda$-state with probabilities of similar magnitude. This may be accomplished by the following procedure.

1. Choose a set of $M$ $\lambda$ values at which states are to be placed. The exact value of $M$ is not too important at this stage, although it should not be too small. A discussion of the optimal choice for $M$ is given in section 3.1. For most purposes, however, between 5 and 15 states will suffice. For reasons that will also be described later, these states should be distributed such that their density increases with increasing $\lambda$.

2. Starting with all pre-weighting factors $\eta_m = 0$, conduct a relatively short simulation ($10^4$–$10^5$ Monte-Carlo sweeps), accumulating the histogram $p(\lambda_m)$. As a rule, the vast majority of counts will be confined to the end state $m = M - 1$. Provided, however, that the adjacent state ($m = M - 2$) is placed close to $\lambda = 1.0$, the system will also (albeit rarely) make some excursions to this state too.

3. Suppose now that counts were obtained for $p(\lambda_m)$ in the $i$ states $M-i, M-i+1, \ldots, M-1$. New estimates for $\eta_m$ are obtained by linear extrapolation using the iterative formula:

$$\eta'_m = \eta_m - \ln p(\lambda_m) \quad M-i \leq m \leq M-1 \quad \text{(13)}$$

$$\eta'_m = \eta_{M-i} + \frac{\lambda_{M-i+1} - \lambda_{M-i}}{(\lambda_{M-i} - \lambda_{M-i+1})}(\eta'_{M-i} - \eta'_{M-i+1}) \quad 0 \leq m < M-i$$

4. Next perform another short simulation with the new pre-weighting factors $\eta'_m$. In this second simulation, $p(\lambda_m)$ will receive counts in at least $i+1$ $\lambda$-states.

Stages 3 and 4 are then simply repeated until weights are obtained that allow the simulation to explore the entire $\lambda$ domain. This iteration procedure can of course be easily automated if desired. Once suitable weight factors are obtained, a longer simulation can be performed to obtain the desired statistical accuracy for $p(\lambda_m)$. The chemical potential is then obtained directly from equation 10.
In some circumstances shortcuts to obtaining suitable weight factors can also be exploited. For example, it is advantageous to carry out the above procedure for a small system. This entails little computational effort, and assuming that the finite-size dependence of $\mu_{ex}$ is not too great, the weights acquired should serve for long runs on larger systems. Additionally, if it is desired to obtain $\mu_{ex}$ for a variety of chain lengths at a single density, weights determined for a rather short chain can be extrapolated to longer chain lengths by exploiting the approximate linear dependence of $\mu_{ex}$ (and $\eta_m$) on the chain length $[10]$. Refinements to the extrapolation procedure outlined above can also be envisaged. For instance, a polynomial fit to all the weights already determined, might extend the range of the extrapolation procedure, allowing two or more weights to be determined per iterative cycle instead of just one. In practice, however, (and as is demonstrated in the following section), the above procedure yields the weight factors surprisingly rapidly.

3 Application to the Bond Fluctuation Model

In order to test our method for measuring $\mu_{ex}$, we have implemented an expanded ensemble simulation using the bond fluctuation model. This is a lattice model for polymers in which polymer chains are represented as $N$ monomer units, each occupying a unit-cell of a simple cubic lattice. Successive monomers are connected by bonds, the bond vector of which is allowed to assume one of 108 distinct values. The number of allowed bonds is dictated by prescribed restrictions on the bond lengths and the necessity to prevent chains from crossing one another. Aside from these restrictions however, no explicit intra-molecular potential is incorporated. Excluded volume effects are catered for by requiring mutual self avoidance of monomers: no lattice site can be occupied simultaneously by two monomers (unless, as is possible in the present case, one happens to be a ghost monomer). For simulations in the thermal regime, an attractive inter-molecular potential can be applied as required. Polymer moves are facilitated either by a local monomer displacement algorithm (as was the case in the present work), or alternatively by reptation type moves. Further details concerning the model can be found in references [15, 16].

Simulations were performed using a metropolis algorithm for both the local monomer displacement algorithm and the $\lambda$-transitions [17]. In the course of the simulations, a number of different chain lengths and densities were studied in both the thermal and athermal regimes. We begin, however, by describing how the weight factors $\eta_m$ were obtained for an athermal system of polymers of length $N = 40$ monomers in a volume $V = 40^3$ at volume fraction $\rho = 0.4$.

A total of eight $\lambda$-states were employed, these being placed at the $\lambda$ values shown in table 1. It is not possible to place a $\lambda$-state exactly at $\lambda = 0$ since this causes a computational error when the transition probabilities (equation 7) are calculated. Nevertheless, the value of $\lambda_0$ can be made extremely small, resulting in negligible error. For reasons made clear in subsection 3.1, the distribution of $\lambda$-states was chosen such that their density increased with increasing $\lambda$. The ratio of the number of displacement moves per monomer to the number of attempted $\lambda$-transitions was set at 4 : 1 respectively.

The evolution of the iterative procedure by which the weights were obtained, is also shown in table 1. Each run constitutes one iterative cycle, in which a further weight factor was determined. It is seen that for each run the extrapolated guess (equation 13) systematically overestimates the $\eta_m$ value to be determined, resulting in proportionally more weight for the
corresponding entry in $p(\lambda_m)$ on the ensuing run. However, this overestimate is subsequently corrected on the following cycle, when the weight factor is reduced with respect to the others. The final weights are presented in the last column of table [1]. Despite the need for several cycles to determine the weight factors, the whole procedure was surprisingly rapid, consuming only 30 minutes CPU time on an IBM RS/6000 workstation.

Having obtained suitable weight factors, a longer run of $2 \times 10^6$ Monte Carlo sweeps (MCS) was performed. Figure 1(a) shows the pre-weighted distribution $p(\lambda_m)$ obtained from this run, while figure 1(b) shows the form of the reweighted distribution $\tilde{p}(\lambda_m) \equiv \exp(-\eta_m)p(\lambda_m)$. The associated chemical potential is $\mu_{ex} = 61.4(1)$, corresponding to a random insertion probability of $10^{-26}$.

With regard to figure 1(a), it should be pointed out that the apparent noise in $p(\lambda_m)$ is illustrous. The variations in $p(\lambda_m)$ represent not statistical uncertainty (which in this instance is much smaller than the variation), but rather deviations of the weights from their ‘ideal’ values as prescribed by equation 12. Provided though that these deviations are not so great as to hinder the random walk of the system between the $\lambda$-states, there will be practically no influence of the weight factors themselves on the statistical accuracy of $\mu_{ex}$, since their effect is simply removed when the reweighted distribution $\tilde{p}(\lambda_m)$ is formed.

To demonstrate that the method is effective for even longer chain lengths and higher densities, we have studied an athermal system of polymers of chain length $N = 80$ at a volume fraction $\rho = 0.5$, contained in a volume $L = 40^3$. The weight factors were determined exactly as before, although as discussed in subsection 3.1, more $\lambda$-states (14 in total) were required to prevent the acceptance rate falling too low. The ratio of displacement moves per monomer to attempted $\lambda$-transitions was set at 10 : 1 respectively. Having determined suitable weight factors, a production run of $4 \times 10^6$ MCS was carried out, resulting in the distributions shown in figure 2. The corresponding estimate for the chemical potential is $\mu_{ex} = 175.9(1)$, in good agreement with that obtained previously under the same conditions using thermodynamic integration [12].

Turning now to the thermal regime, we have employed a short-range square well potential to study a system of volume $L = 40^3$ and chain length $N = 40$ at a volume fraction $\rho = 0.2$ and temperature $T = 2.0$. The procedure for determining the $\eta_m$ is similar to before, although a complication arises in the fact that $\tilde{p}(\lambda_m)$ is no longer monotonic. The forms of $p(\lambda_m)$ and $\tilde{p}(\lambda_m)$ are shown in figure 3. The latter distribution displays a broad minimum, manifesting the competition between the positive athermal contribution to the chemical potential (which dominates as $\lambda \to 1$) and the negative thermal contribution (which dominates for small $\lambda$). To obtain the weight factors in this case it was necessary to start the extrapolation procedure at both ends of the $\lambda$ range, (i.e. $m = 0$ and $m = M - 1$) and work in towards the position of the minimum. The final complete set of weights was then obtained by requiring continuity at the $\lambda$ value where the two sets coincide (in effect by adding a constant to one set). The chemical potential estimated from a run of $2 \times 10^6$ MCS is $\mu_{ex} = -0.01(7)$. This very small value of $\mu_{ex}$ indicates the close proximity of the temperature to the $\Theta$-point of the model.

### 3.1 Optimisation of the method

In situations where very high statistical accuracy is required, long runs can be necessary and a little effort to optimise the method may pay dividends. Two interconnected factors influence the statistical accuracy that can be realised for a given expenditure of computational effort. Firstly there is the choice of the number of $\lambda$-states $M$, and secondly there is the acceptance
rate for \( \lambda \)-transitions. These factors jointly control the magnitude of the correlation time for the \( \lambda \)-transitions. To the extent that \( p(\lambda_m) \) can be regarded as flat, the system will execute a one-dimensional random walk between the \( \lambda \)-states and the correlation time will be given by:

\[
\tau(M) \simeq \frac{M^2}{P_a(M)} \tag{14}
\]

where \( \tau(M) \) is measured in units of transition attempts and \( P_a(M) \) is the acceptance rate for \( \lambda \) transitions, which we assume to be constant for each state. To appreciate how \( P_a(M) \) depends on the number of \( \lambda \)-states \( M \) (and their placing) it is instructive to consider the transition probabilities for an athermal system:

\[
P_a(n \rightarrow m) = \min(1, \exp[N_o(\ln \lambda_m - \ln \lambda_n) + \eta_m - \eta_n]) \tag{15}
\]

In addition to ensuring that \( p(\lambda_m) \) is approximately flat, the rôle of the weights in this equation is to partially compensate for positive changes in the exponent associated with transitions to smaller \( \lambda \) values. The extent to which they are successful in this regard (and hence the size of the acceptance rate) depends on the degree of overlap between the distributions of \( N_o(\lambda_m) \) and \( N_o(\lambda_n) \). In order to ensure a sufficiently high acceptance rate, sufficient \( \lambda \)-states must be employed to guarantee an appreciable overlap between the distributions. Moreover, to maintain an approximately constant acceptance rate for all states it is necessary to increase their density at higher \( \lambda \) values. This is illustrated in figure 4 where the distribution function \( N_o(\lambda) \) is plotted for a variety of fixed \( \lambda \) values. The distributions shown have approximately equal overlap although the \( \lambda \)-states are placed closer together for larger \( \lambda \).

The above considerations illustrate the compromise to be struck in minimising the correlation time: if \( M \) is too large, \( \tau \) will be large and accordingly it will be difficult to accumulate uncorrelated statistics. Similarly, if \( M \) is too small, a low acceptance rate will ensue and consequently \( \tau \) will again be large. However, it should be stressed that the correlation time is not the sole factor governing the optimum choice of \( M \). For a given length of run, the statistical quality of \( p(\lambda_m) \) may be improved by choosing a smaller value of \( M \), even at the expense of a larger correlation time. If the sampling frequency is chosen commensurate with the correlation time (equation 13), a fraction \( 2/M \) of the total number of samples will fall into the two extrema states \( p(\lambda_0) \) and \( p(\lambda_{M-1}) \) used to calculate \( \mu_{ex} \). Now, since the statistical error on \( \mu_{ex} \) is dependent on the number of entries in these end states, it follows that the optimal choice of \( M \) is given, not by the minimum in \( \tau(M) \), but by the minimum in \( M^2/P_a(M) \). In figure 5 we plot this function for a system of athermal polymers with \( N = 40 \) and \( \rho = 0.2 \). A minimum obtains for \( M = 6 \), corresponding to an acceptance rate \( P_a \approx 20\% \). Thus it would appear that in the present method, the optimal acceptance rate can be considerably less than the value of 50\% or so used for normal particle displacements.

Finally we address briefly the question of the optimal choice of the ratio of local displacement moves to \( \lambda \)-transitions. Clearly the issue is again one of efficiency. If too few local moves are attempted between transition attempts, then the number of overlaps \( N_o \) will systematically deviate from the canonical average \( < N(\lambda) > \) and the acceptance rate may suffer. On the other hand, if the ratio of local moves to transition attempts is too high, a longer run will be necessary to obtain good statistics in \( p(\lambda_m) \). For the present model, we find that following a \( \lambda \) transition, between 4 (\( N = 40 \)) and 10 (\( N = 80 \)) local moves attempts per monomer are sufficient to decorrelate the number of overlaps. We note also in this context, that relatively few local moves are required to decorrelate the spatial position of the ghost polymer. This is
because the ghost polymer frequently samples $\lambda$-states in which it completely decouples from the normal polymers, thereby allowing it to diffuse around the system with relative ease. This latter feature of the method is in favourable contrast to the thermodynamic integration method [12], in which several hundred trial displacements are required for a ghost polymer with fixed small $\lambda$ to diffuse away from its starting point.

### 3.2 Finite-size corrections to the chemical potential

Measurements of the chemical potential in finite-size systems are known to be relatively strongly effected by finite-size effects. Indeed for a system of $n$ particles, the leading corrections vary like $n^{-1}$. Recently, Siepmann et al have derived an expression for the leading finite-size dependence of $\mu_{ex}$ in terms of density derivatives of the pressure [18]

$$\Delta \mu_{ex}(n) = \frac{1}{2n} \left( \frac{\partial P}{\partial \rho} \right) \left[ 1 - k_b T \left( \frac{\partial \rho}{\partial P} \right) - \rho k_b T \left( \frac{\partial^2 P}{\partial \rho^2} \right) \frac{2}{\left( \frac{\partial P}{\partial \rho} \right)^2} \right] + O(n^{-2}) \quad (16)$$

where $\rho = n/V$ is the polymer number density. Provided that the equation of state is known independently, this equation permits a calculation of the finite-size dependence of the chemical potential, thereby facilitating an extrapolation to the thermodynamic limit.

As a test of the precision and accuracy of our method, we have attempted to measure the finite-size dependence of $\mu_{ex}$ for our model and compare it with equation (16). To this end we have simulated systems of athermal polymer chains of length $N = 40$ at volume fraction $\rho = 0.2$ for system sizes $L = 40, 47$ and 60. In accord with the findings of the previous subsection, 6 $\lambda$-states were utilised. Runs comprising $10^7$ MCS were performed, and the $\lambda$ value was sampled every 180 transition attempts. For each system size studied, 16 independent runs were carried out in order to test the statistical independence of the data and assign errors to the results.

The resulting estimates for the excess chemical potential are $\mu_{ex}(40) = 19.78(2), \mu_{ex}(47) = 19.69(2), \mu_{ex}(60) = 19.59(2)$, where the value for $L = 47$ has been corrected for the fact that $\rho = 0.2$ does not correspond to a whole number of polymers. Figure 6 shows how these estimates compare with equation (16). The broken line represents the predicted finite-size shift in $\mu_{ex}$ obtained by feeding the equation of state data of Müller and Paul [12] into equation (16). Assuming an infinite-volume chemical potential of $\mu_{ex}(\infty) = 19.50$, the measured finite-size shift in $\mu_{ex}$ is consistent to within error with the prediction of equation (16).

### 4 Conclusions

In summary, we have presented an efficient method for measuring the chemical potential of polymeric systems that is effective at both large chain lengths and high densities. Although some preliminary effort is required to find suitable pre-weighting factors, this is not excessively time consuming and is generously rewarded by the very high accuracy that can subsequently be attained. In contrast to the Chain Increment method [8], the estimate of $\mu_{ex}$ derives from a single simulation and is in principle exact. The present method should therefore provide a more accurate alternative in applications such as determining the polymer-solvent coexistence curve of long chain molecules (where configurational bias Gibbs ensemble simulations are not feasible). Finally we remark that the present approach is not limited to homopolymer chains, and should also facilitate measurements of $\mu_{ex}$ for copolymers as well as more complex polymer architectures such as branched or ring structures.
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References

[1] B. Widom, J. Chem. Phys. 39, 2808 (1963).
[2] For a review see S. Kumar in Computer Simulation of Polymers, (E.A. Colbourn, Ed.), Longman, Harlow, U.K., (1994).
[3] J. I. Siepmann, Mol. Phys. 70, 1145 (1990).
[4] D. Frenkel and B. Smit, Mol. Phys., 75, 983 (1992); D. Frenkel, G.C.A.M. Mooij and B. Smit, J. Phys. Condens. Matter 4, 3053 (1992).
[5] J. J. de Pablo, M. Laso and U.W. Suter, J. Chem. Phys. 96, 6157 (1992).
[6] G.C.A.M. Mooij, D. Frenkel and B. Smit, J. Phys. Condens. Matter 4, L255 (1992).
[7] J. I. Siepmann, S. Karaborni and B. Smit, J. Am Chem. Soc. 115, 6454 (1993); J. I. Siepmann, S. Karaborni and B. Smit, Nature 365, 330 (1993).
[8] S.K. Kumar, I. Szleifer and A.Z. Panagiotopoulos, Phys. Rev. Lett. 66, 2935 (1991).
[9] S.K. Kumar, J. Chem. Phys. 97, 3550 (1992).
[10] I. Szleifer and A.Z. Panagiotopoulos, J. Chem. Phys. 97, 6666 (1992).
[11] Y-J Sheng, A.Z. Panagiotopoulos, S.K. Kumar and I. Szleifer, Macromolecules 27, 400 (1994)
[12] M. Müller and W. Paul, J. Chem. Phys. 100, 719 (1994).
[13] A.P. Lyubartsev, A.A. Martsinovski, S.V. Shevkunov and P.N. Vorontsov-Velyaminov, J. Chem. Phys. 96, 1776 (1992).
[14] See also recent related work on Simulated Tempering (E. Marinari and G. Parisi, Europhys. Lett. 19, 451 (1992)) and Multicanonical ensembles (B. A. Berg and T. Neuhaus, Phys. Rev. Lett. 68, 9 (1992)).
[15] L. Carmesin and K. Kremer, Macromolecules 21, 2819 (1988).
[16] H.P. Deutsch and K. Binder, J. Chem. Phys. 94, 2294 (1991).
[17] Care must be exercised to ensure that detailed balance is satisfied when the system is in state \( \lambda_0 \) or \( \lambda_{M-1} \), there being only one choice for the new trial \( \lambda \)-state.
[18] J. I. Siepmann, I. R. McDonald and D. Frenkel, J. Phys. Condens. Matter 4, 679 (1991).
Figure 1: (a) The pre-weighted distribution $p(\lambda_m)$ for a system of athermal polymers of chain length $N = 40$ and volume fraction $\rho = 0.4$, contained in a volume $V = 40^3$. (b) The reweighted distribution $\tilde{p}(\lambda_m) = \exp(-\eta_m)p(\lambda_m)$ expressed on a logarithmic scale.

Figure 2: (a) The pre-weighted distribution $p(\lambda_m)$ for a system of athermal polymers of chain length $N = 80$ and volume fraction $\rho = 0.5$, contained in a volume $V = 40^3$. (b) The reweighted distribution $\tilde{p}(\lambda_m) = \exp(-\eta_m)p(\lambda_m)$ expressed on a logarithmic scale.

Figure 3: (a) The pre-weighted distribution $p(\lambda_m)$ for a system of thermal polymers of chain length $N = 40$, $\rho = 0.2$ at temperature $T = 2.0$, contained in a volume $V = 40^3$. (b) The reweighted distribution $\tilde{p}(\lambda_m) = \exp(-\eta_m)p(\lambda_m)$ expressed on a logarithmic scale.
Figure 4: Distributions of the number of overlaps between ghost monomers and normal monomers at various fixed $\lambda$.

Figure 5: The measured form of the function $M^3/P_a(M)$

Figure 6: The measured value of the chemical potential for a system of athermal polymers of chain length $N = 40$ at volume fraction $\rho = 0.2$ for system sizes $L = 40, 47, 60$. A constant corresponding to the infinite volume estimate $\mu_{\text{ex}} = 19.50$ has been subtracted from the data. Also shown (broken curve) is the predicted finite-size dependence of $\mu_{\text{ex}}$ following from equation 16 utilising predetermined equation of state data [12].

| $\lambda_m$ | $\eta_m$ | $p(\lambda_m)$ | $\eta_m$ | $p(\lambda_m)$ | $\eta_m$ | $p(\lambda_m)$ | $\eta_m$ | $p(\lambda_m)$ |
|------------|-----------|----------------|-----------|----------------|-----------|----------------|-----------|----------------|
| $\lambda_0 = 0.00001$ | 0.00 | 0.00 | 12.60 | 0.000 | 24.28 | 0.000 |
| $\lambda_1 = 0.35$ | 0.00 | 0.00 | 12.60 | 0.000 | 24.28 | 0.000 |
| $\lambda_2 = 0.55$ | 0.00 | 0.00 | 12.60 | 0.000 | 24.28 | 0.000 |
| $\lambda_3 = 0.7$ | 0.00 | 0.00 | 12.60 | 0.000 | 24.28 | 0.000 |
| $\lambda_4 = 0.8$ | 0.00 | 0.00 | 12.60 | 0.000 | 24.28 | 0.567 |
| $\lambda_5 = 0.9$ | 0.00 | 0.00 | 12.60 | 0.423 | 12.18 | 0.168 |
| $\lambda_6 = 0.97$ | 0.00 | 0.222 | 3.79 | 0.299 | 3.72 | 0.142 |
| $\lambda_7 = 1.0$ | 0.00 | 0.977 | 0.00 | 0.277 | 0.00 | 0.113 |

Table 1: The weight determination procedure described in the text for $N=40$, $\rho = 0.2$. All runs are 50000 MCS.