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Monte Carlo simulation in the semi-grand canonical ensemble as a ‘thermodynamic’ reverse Monte Carlo technique, with application to a polymer melt

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Abstract

We describe the use of Monte Carlo simulation in the semi-grand canonical ensemble (SGMC) to analyse and interpret experimental data for non-equilibrium states of matter such as glasses and many processed polymer melts. Experiments that provide information about atomic-level ordering are amenable to this approach. Closure of the inverse problem of determining the structural detail from limited data is achieved by selecting the lowest-free-energy ensemble of configurations that reproduces the experimental data. The free energy is calculated using the thermodynamic potential of the appropriate semi-grand canonical ensemble defined by the experimental data. To illustrate the method we examine uniaxially oriented polyethylene melts of average chain length C_{78} . The simulation results are analysed for features not explicitly measured, such as the density, torsion angle distribution, and free energy, to understand more fully the underlying features of these non-equilibrium states.

1. Introduction

Reverse Monte Carlo (RMC) was introduced in 1988 by Pusztai and McGreevy [1]. Since that time, the method has produced many useful contributions to the interpretation of structural measurements, especially in the interpretation of diffraction experiments [2]. Despite its successes, users of RMC must continually address questions of non-uniqueness of the solutions thus generated. The non-uniqueness as well as an element of arbitrariness arises, in part, because of the incorporation of user-defined weightings into the acceptance criterion. By formulating the inverse problem strictly in terms of thermodynamic variables, we incorporate experimental data into an ensemble that provides a thermodynamically consistent resolution to the problem of uniqueness. The semi-grand canonical Monte Carlo (SGMC) method obtains

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closure to the inverse problem through the selection of the ensemble of states with the lowest free energy.

2. Description of the SGMC method

A formalism for the incorporation into a Monte Carlo simulation of experimental data was presented by Rutledge [3], based on the earlier work of Briano and Glandt for the treatment of polydisperse systems of differentiable particles in the semi-grand canonical ensemble [4]. The semi-grand canonical ensemble is well suited to address the problem of structure because it allows an otherwise homogeneous system to be differentiated in terms of measurable structural characteristics. In the traditional language of thermodynamics, the system is expressed as a mixture of isomers whose origins are physical rather than chemical; the concentrations of such physical isomers are known, for example, from experimental measurements. The resulting method correctly interprets the intensities of physical measurements as information about the concentrations of physical species in the system, and casts the inverse problem as one of finding the (thermodynamically rigorous) potentials responsible for the observed concentrations. Although similar in implementation to the empirical potential methods described by Soper [5] and Lyubatsev and Laaksonen [6], the potentials determined by SGMC are only as approximate as the physical isomers to which they apply, or the measurements by which the potentials are iteratively determined. To emphasize this fact, we refer to the method simply as a semi-grand canonical Monte Carlo (SGMC) simulation. As demonstrated in [3], the potential determined by SGMC can in certain circumstances be the ‘interatomic potential’, which usually constitutes a whole or part of the ‘force field’ used to compute the configuration energy $U(\mathbf{r}^N)$; more generally, the potential determined by SGMC represents a physical field conjugate to the structural entities measured by the experimental data, and may supplement any force field invoked *a priori*.

To incorporate information about the physical isomers, we expand the canonical ensemble to include the set of normalized experimental values $\{\langle x_i \rangle\}$ and its thermodynamic conjugate variables $\{\mu_i\}$ in the Metropolis acceptance criterion as:

$$p_{\text{acc}} = \min \left\{ 1, \exp \left(-\beta \left[U(\mathbf{r}^N)_{\text{new}} - U(\mathbf{r}^N)_{\text{old}} - \sum_{i=1}^K \mu_i (\langle x_i \rangle_{\text{new}} - \langle x_i \rangle_{\text{old}}) \right] \right) \right\}. \quad (1)$$

The form of equation (1) is important, because it ensures the existence of a single ensemble that minimizes the free energy of the ensemble characterized by constant N , V , T and $\{\mu_i\}$.

The ability to make this assertion is dependent on the form of the thermodynamic potential. The necessary form of additional constraints is:

$$\ln(p) \propto \beta \mu_i \langle x_i \rangle \quad (2)$$

where x_i is some observable quantity and $\lambda_i = -\beta \mu_i$ is an iteratively determined Lagrangian multiplier. This particular form was shown by Jaynes [7] to be the least restrictive solution to the problem of maximizing entropy in a system constrained to reproduce $\{\langle x_i \rangle\}$. Any other form adds some degree of unnecessary constraint to the system, by incorporating information that is not contained in the experimental measurement.

We may now ask, ‘does the maximum entropy probability distribution given in equation (2) lead to equation (1) as the correct description for an *interacting* system?’ Guiaşu [8] has shown that an arbitrary weighting of each of the states does not affect the ability to find the most likely solution, and that this solution would now maximize the weighted entropy.

Because our weighting is the Boltzmann factor for each configuration, Guiaşu’s weighted entropy is equal and opposite to the *free energy* of the system. Thus, the problem of entropy

maximization in the non-interacting system becomes a problem of free-energy minimization in the interacting system, where each state is weighted by its configuration energy $U(\mathbf{r}^N)$. The minimum-free-energy solution will be of the form:

$$\ln(p) \propto -\beta(U(\mathbf{r}^N) - \sum_{i=1}^K \mu_i \langle x_i \rangle) \quad (3)$$

leading directly to the Metropolis criterion given in equation (1). This formulation in turn leads to a unique ensemble of configurations that reproduces the observed experiment.

The process of iteratively obtaining the values for μ_i is a specific example of a ‘potential determination’ method. Tóth and Baranyai make a very useful comparison of potential determination methods and the RMC method for producing a structure from experimental data [9]. They conclude that potential determination methods are ‘very promising’ once they can incorporate incomplete measurements and measurement error. Below, we describe our ideas towards the resolution of these issues, based upon formulation of the problem as an SGMC simulation.

The ‘problem’ of incomplete measurements is only a problem insofar as one demands that the solution be constrained to data that does not (yet) exist. The incomplete portion of any measurement is treated as any other unmeasured characteristic of the system; it is otherwise unconstrained and determined through the minimization of the free energy. A more complete knowledge of the experimental results can always be incorporated using additional constraints as additional knowledge becomes available. Below, we use an incomplete representation of the orientation distribution function (ODF) to obtain information about the system. Specifically, we employ measurements of the birefringence, which provides only the second moment of the orientation distribution, yet we can obtain a prediction of the full ODF, using the results of the SGMC simulation.

The issue of how to interpret measurement error was answered by Jaynes [7]. He points out that the fluctuation of a system and the experimental uncertainty of a measurement are two very different things. The first is a well-defined quantity that is intrinsic to the system; the second depends on external considerations and varies accordingly. The determination of the *value* of the potential relies only on the intrinsic properties of the system; its *uncertainty* is tied to the experimental error. This is a fundamental point—the physics of the problem do not depend on the accuracy of the measurements. In an SGMC simulation, given a set of measured values $\langle x_i \rangle$, the corresponding potentials μ_i must be determined iteratively. Several numerical procedures have been described for this purpose [3, 10, 11]. The termination of these procedures is dictated by the accuracy with which μ_i must be determined in order to ensure that the simulated $\langle x_i \rangle_{\text{sim}}$ reproduces the measured values of $\langle x_i \rangle_{\text{exp}}$ to within the experimental error, δ_i . That is:

$$(\langle x_i \rangle_{\text{sim}} - \langle x_i \rangle_{\text{exp}})^2 \leq \delta_i^2. \quad (4)$$

Finally, figure 1 shows a schematic of the SGMC method that summarizes the steps discussed above.

In closing this section, we assert that the determination of a unique lowest-free-energy solution requires a method such as SGMC, which captures the intrinsic fluctuations of the system. If other factors such as the ease of modelling or computational expense are important, one may very well choose an alternative method such as the traditional RMC model. However, this should be done with the understanding that thermodynamic rigor is being sacrificed for other benefits, such as avoiding the need to run potentially time-consuming iterative determinations of the potential, or fully atomistic energy calculations.

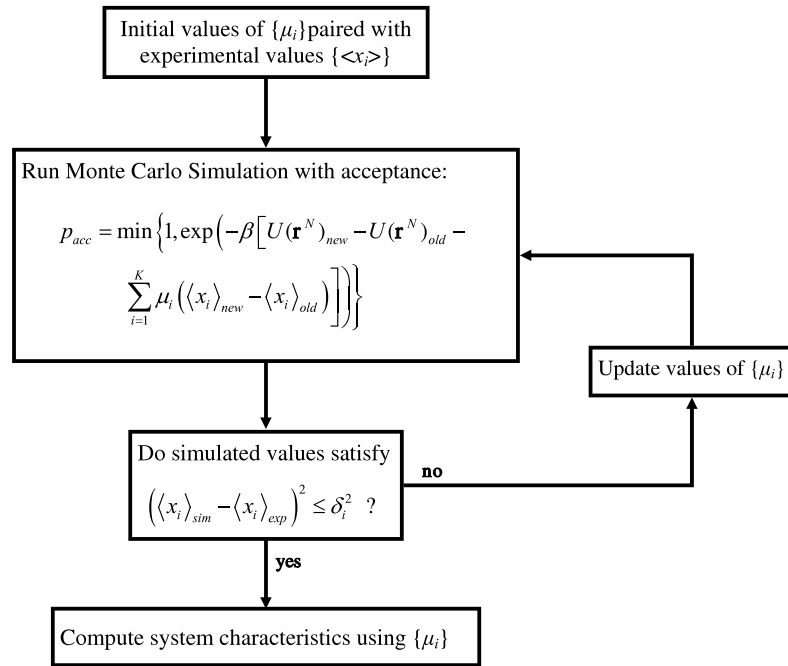


Figure 1. Schematic of the SGMC method.

3. Simulations

In the illustrative example considered here, the observable quantity x is the second Legendre coefficient $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ of the angle θ of the structural unit with respect to the axis of orientation. This value is proportional to the birefringence for a uniaxially oriented system. Using a united atom polyethylene force field described elsewhere [12], we have run simulations on polyethylene chains with average size C_{78} . The correct form of the probability density follows from equation (3):

$$\ln(p) \propto -\beta(U(r^N) - \mu \langle P_2(\cos \theta) \rangle). \quad (5)$$

We have run simulations for a series of values of μ under conditions described elsewhere [13], to obtain the functional form of the orientation potential, as well as the changes in other structural properties. Thus, no iterative procedure was required in this example; the value of μ required for any value of $\langle P_2(\cos \theta) \rangle$ may be estimated by interpolation of the results provided.

4. Results and discussion

The potential μ is the conjugate thermodynamic variable to $\langle P_2(\cos \theta) \rangle$. Using the relationship between these two variables presented in figure 2, we report all subsequent structural dependences using $\langle P_2(\cos \theta) \rangle$ as the independent variable.

Figure 3 shows the density of the system as a function of orientation. The density of the system is constant for orientations less than approximately $\langle P_2(\cos \theta) \rangle = 0.1$. For more oriented systems, the minimization of free energy is accomplished through changes in the molecular structure that produce a denser melt. By correlating this phenomenon with other

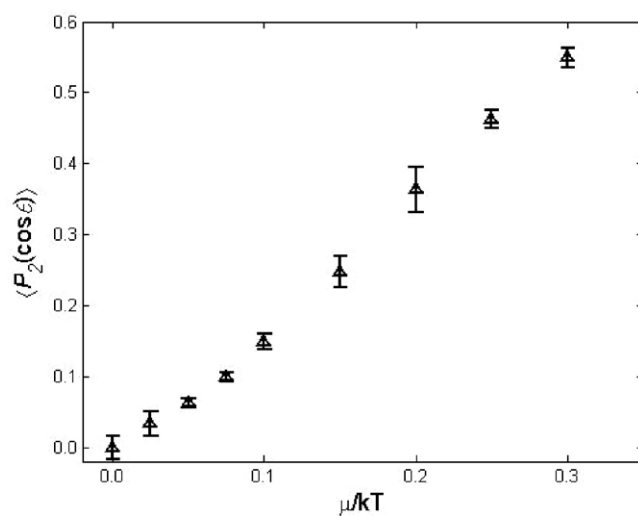


Figure 2. Orientation of C_{78} PE molecules with increasing orientation potential.

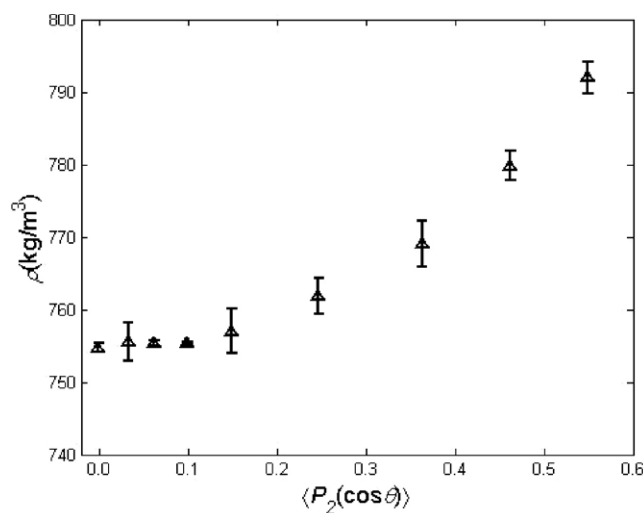


Figure 3. Density of C_{78} PE molecules as a function of potential.

structural information, we can gain a deeper understanding of the different mechanisms for orientation.

Considering figures 4 and 5 together, we can see that each describes behaviour consistent with the observation of two different regimes of orientation, with a transition that occurs around $\langle P_2(\cos \theta) \rangle = 0.1$. Figure 4 shows that the percentage of *trans* bonds in the molecule remains constant below this transition. This means that, although the molecules are being oriented, the shape of the molecule itself is not disturbed; that is, the principle axes of the molecule are rotated. Above this transition, the percentage of *trans* bonds increases, which indicates a deformation of the molecules to more extended conformations. Figure 5 tells a similar story: below the transition, the mean-square end-to-end distance is unchanged, while at higher orientation it increases.

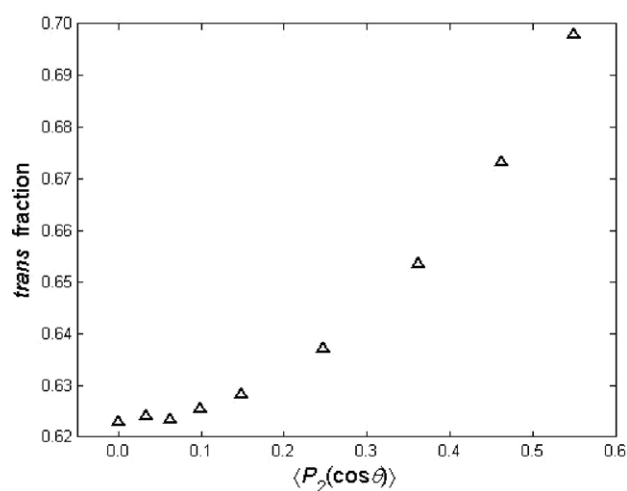


Figure 4. Fraction of *trans* bonds for the PE chains as a function of orientation.

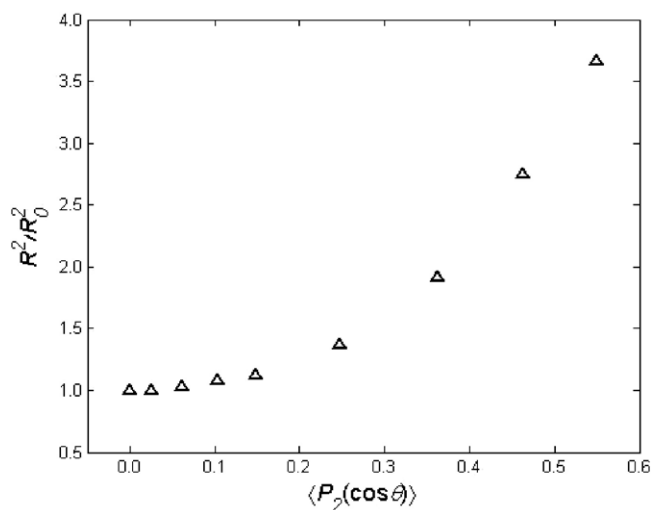


Figure 5. Relative mean-square end-to-end distance of the molecules as a function of orientation. R_0^2 is the isotropic (zero potential) mean-square end-to-end distance.

From a simple birefringence experiment, we now have a much more complete and interesting story. The initial orientation of the molecule is achieved through the reorientation of the entire molecule *without* any changes to its conformation. This allows orientation up to $\langle P_2(\cos\theta) \rangle = 0.1$, with the only penalty being a loss of orientational entropy. Further orientation can only be obtained by unraveling the molecule to produce more highly extended conformations, which comes at a cost in both internal energy and entropy. However, these highly extended conformations are able to pack more densely than the equilibrium conformations, and thereby recover some benefits through favourable intermolecular interactions. The parallel increases in figures 3–5 show how the increase in density correlates with the deformation of the molecules.

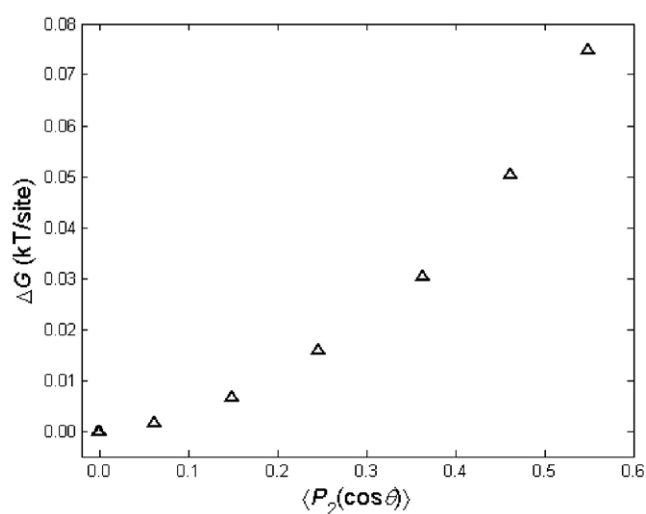


Figure 6. Work of orientation as a function of orientation. Values were determined using the self-consistent histogram method [14].

Figure 6 shows the change in free energy as the molecules orient. Rotation of the principle axes of entire molecules is achieved through relatively small amounts of work on the system. Subsequent deformation of the molecules requires larger amounts of work on the system. These values are important because they represent a lower bound on the work required to reach a particular orientation. If the experiment (in this case birefringence) captures the important characteristics of the molecule, the work put into the system (discounting losses) will be reflected by the relationship in figure 6. Significantly, the relationship between work and orientation can only be determined using a thermodynamic method such as SGMC.

5. Conclusion

We have provided a description of the SGMC method, which uses a thermodynamic basis to incorporate experimental measurements, providing a unique, minimum-free-energy solution to the inverse problem of determining the corresponding system microstructure. The method can be performed using incomplete information about a distribution, as in the above example using only one of the moments of the distribution.

We performed the simulation of PE molecules of average size C_{78} and demonstrated the ability to extract structural changes not revealed directly by the experimental measurement of orientation. The structural changes were investigated through the analysis of changes in, for example, density, molecular size and torsion distributions. The simulated systems indicate that the initial response of the polyethylene melt is a reorientation of entire molecules, followed by the distortion of the molecules to produce a denser melt. We also obtain the work required to orient the molecule, which is possible because the SGMC method is thermodynamically consistent. We propose this method to supplement conventional RMC methods in cases where the necessity of thermodynamic rigor justifies the higher computational cost.

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