Density Functional Theory of Simple Polymers in a Slit Por:

1. Theory and Efficient Algorithm

Justin B. Hooper, John D. McCoy
Department of Materials & Metallurgical Engineering
New Mexico Institute for Mining & Technology
Socorro, New Mexico 87801

and

John G. Curro†
Sandia National Laboratories
Albuquerque, New Mexico 87185

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Abstract

Previous applications of DF theory required a single chain Monte Carlo simulation to be performed within a self-consistent loop. In the current work, a methodology is developed which permits the simulation to be taken out of the iterative loop. Consequently, the calculation of the self-consistent, medium-induced-potential, or field, is decoupled from the simulation. This approach permits different densities, different forms of $U_m(r)$, and different wall-polymer interactions to be investigated from a single Monte Carlo simulation. The increase in computational efficiency is immense.
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1. Introduction

Density functional (DF) theory was first extended to molecular systems by Chandler, McCoy, and Singer. This general methodology has been previously reviewed, and applied to a number of polymer problems as discussed elsewhere.

In the current paper, a new solution methodology is introduced which greatly enhances the efficiency of the technique. This work has implications for a number of other similar polymeric theoretical methods which entail a single (or few) chain simulation in a self-consistent loop.

In the companion paper, referred to as Paper II, simple polymer chains in a slit-pore are investigated with the new methodology. The remainder of the paper consists of a review of DF theory in section 2 followed by a discussion of the new solution methodology in section 3.

2. Density Functional Theory

The excess Helmholtz free energy of the inhomogeneous system, $A - A_0$, where the "0" indicates the ideal system, is expanded through second order about the bulk, homogeneous system as

$$
(A - A_0) = (A - A_0)_{\text{bulk}} + \sum_i \int_V d\mathbf{r} \left[ \psi_i(\mathbf{r}) - \psi_i^0(\mathbf{r}) \right] \Delta \rho_i(\mathbf{r})
$$

$$
+ \frac{1}{2} \sum_{i,j} \left[ \int_V d\mathbf{r} d\mathbf{r}' \frac{\delta^2(A - A_0)}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} \right]_{\text{bulk}} \Delta \rho_i(\mathbf{r}) \Delta \rho_j(\mathbf{r}')
$$

where the conjugate variable to the density, $\rho_i(\mathbf{r})$, is the "external field" or "spatially varying chemical potential", $\psi_i(\mathbf{r}) = \mu_i - U_i(\mathbf{r})$; $\mu_i$ is the usual chemical potential; and $U_i(\mathbf{r})$, the external field. The sums are over site type, and the integrals, over the system volume. The coefficients in the functional
expansion are evaluated in the bulk state; and the expansion variables, \( \Delta \rho_i(r) \), equal \( \rho_i(r) - \rho_{i,\text{bulk}} \). The thermodynamic identity

\[
\psi_i(r) = \frac{\delta A}{\delta \rho_i(r)} \tag{2.2}
\]

was used to simplify the first order term.

In applications, the fields, \( \psi_i(r) \), rather than the densities are the independent variables. As a result, it is more convenient to work in terms of the grand potential functional, \( W \), which is found from the Legendre transform

\[
W = A - \sum_i \int_V d\mathbf{r} \psi_i(\mathbf{r}) \rho_i(\mathbf{r}) \tag{2.3}
\]

This, combined with equation (2.1) results in

\[
\Delta W = \Delta W_0 - \sum_i \int_V d\mathbf{r} \left[ \psi_i(\mathbf{r}) - \psi_i,\text{bulk} \right] \rho_i(\mathbf{r})
+ \sum_i \int_V d\mathbf{r} \left[ \psi_i^0(\mathbf{r}) - \psi_i^0,\text{bulk} \right] \rho_i(\mathbf{r})
+ \frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' \frac{\delta^2(A - A_0)}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} \Delta \rho_i(\mathbf{r}) \Delta \rho_j(\mathbf{r}') \tag{2.4}
\]

where the \( \Delta W = W - W_{\text{bulk}} \).

At this point, the expression for \( \Delta W \) is completely general since the ideal system has not been defined. Indeed, if no ideal system is used, the minimum of equation (2.4) is found in Fourier space to be

\[
\hat{\rho}(\mathbf{k}) = \hat{\delta}(\mathbf{k}) \rho_{\text{bulk}} - \left[ \hat{\Delta}_{\text{bulk}}(\mathbf{k}) \right]^{-1} \cdot \hat{U}(\mathbf{k}) \tag{2.5}
\]
where matrix notation is used; \( \mu \) is set equal to \( \mu_{\text{bulk}} \); and \( A'' \) is the second derivative of the Helmholtz free energy indicated in equation (2.4) with \( A_0 = 0 \). Clearly, this is a poor approximation except for very small fields.

If an ideal monatomic gas is taken as the ideal system, the densities and fields are related by

\[
\rho_i(x) = \rho_{i,\text{bulk}} \exp[-\beta U_i^0(x)] \\
= \exp[\beta \psi_i^0(x)]
\]

(2.6)

where \( \beta = 1/kT \); \( k \) is the Boltzmann constant; \( T \) is the temperature; and the bulk chemical potential is set to \( kT \ln(\rho_{i,\text{bulk}}) \). Through equation (2.2), the Helmholtz free energy difference can be found to be

\[
\Delta \beta A_0 = \sum_i \int_V d\mathbf{r} \rho_i(x)[\ln(\rho_i(x)) - 1] - \sum_i \int_V d\mathbf{r} \rho_{i,\text{bulk}}[\ln(\rho_{i,\text{bulk}}) - 1]
\]

(2.7)

or, as is expected from thermodynamics,

\[
\Delta \beta W_0 = -\sum_i \int_V d\mathbf{r} \Delta \rho_i(x).
\]

(2.8)

Equations (2.6) and (2.8) in combination with equation (2.1) result in a minimum of

\[
\rho_i(x) = \rho_{i,\text{bulk}} \exp[-\beta U_i(x) - \sum_j \int_V d\mathbf{r}'(A - A_0)_{i,j,\text{bulk}}(x - \mathbf{r}') \Delta \rho_j(x')]
\]

(2.9)

which is a vast improvement on equation (2.5), but only includes bonding constraints weakly through \((A-A_0)''\).

The ideal system we use is at the next level of complexity where bonding is explicitly included in the ideal system:

\[
\rho_i(x) = \rho_{i,\text{bulk}} \sum_k \int \ldots \int d\mathbf{r}_1 \ldots d\mathbf{r}_{k-1} d\mathbf{r}_{k+1} \ldots d\mathbf{r}_N \exp[-\beta \sum_j U_j^0(x_j)] S(x_1, \ldots, x_N)
\]

(2.10)
where \( n_i \) is the number of sites of type "i"; the sum \( \Sigma' \) is over all sites of type "i" on a single chain; the sum \( \Sigma \) is over all sites on a single chain; and \( S(r_1, \ldots, r_N) \) denotes the bonding constraints upon the chain. In terms of the \( \psi \)'s, this becomes

\[
\rho_i(r) = \sum_k \int_dr_1 \ldots dr_{k-1} dr_k \ldots dr_N \exp \left[ \beta \sum_j \psi^0_j(r_j) \right] S(r_1, \ldots, r_N). \tag{2.11}
\]

By using the thermodynamic relationship

\[
-\rho_i(r) = \frac{\delta W}{\delta \psi_i(r)}, \tag{2.12}
\]

the expression for \( \Delta W^0 \) is found to be

\[
\Delta\beta W_0 = -\frac{1}{N} \sum_i \int_V \Delta \rho_i(r) \tag{2.13}
\]

where \( N \) is the total number of sites on a chain.

Now, equation (2.2) in combination with equation (2.13) must be minimized with respect to \( \rho_i(r) \); however, since the \( \psi \)'s cannot be completely removed from the expression for \( \Delta W \), a method related to that of undetermined multipliers is used. Usually, a \( \lambda(r) \) function would be introduced to ensure that the minimum of \( \Delta W \) with respect to both \( \rho(r) \) and \( \psi^0(r) \) would coincide to the constraint of equation (2.11). In the present case this insurance can be achieved in a slightly different manner by substituting equations (2.11) and (2.13) into the \( \Delta W \) expression to get
\[ \Delta W = -kT \sum \int \mathrm{d}x_1 \cdots \int \mathrm{d}x_N \exp \left[ \beta \sum_j^{\infty} \psi_j^0(x_j) + \frac{kTV}{N} \sum_i \rho_{i,\text{bulk}} \right] \]

\[ - \sum_i \int V \left[ \psi_i(x) - \psi_i^{\text{crit}} \right] \rho_i(x) + \sum_i \int V \left[ \psi_i^0(x) - \psi_i^{0,\text{crit}} \right] \rho_i(x) + \frac{1}{2} \sum_{i,j} \int \int V \frac{\delta^2(A - A_0)}{\delta \rho_i(x) \delta \rho_j(x')} \Delta \rho_i(x) \Delta \rho_j(x') \]

(2.14)

Here the partial functional derivative with respect to \( \psi^0(x) \) enforces the constraint equation without an explicit \( \lambda(x) \).

The derivative of \( \Delta W \) with respect to \( \rho(x) \) yields the expression for the ideal field

\[ \left[ \psi_i^0(x) - \psi_i^{0,\text{crit}} \right] = \left[ \psi_i(x) - \psi_i^{\text{crit}} \right] - \sum_j \int V \frac{\delta^2(A - A_0)}{\delta \rho_i(x) \delta \rho_j(x')} \Delta \rho_j(x'). \]

(2.15)

If the chemical potentials are set equal in inhomogeneous and homogeneous systems, this simplifies to

\[ U_i(x) = U_i(x) + \sum_j \int V \frac{\delta^2(A - A_0)}{\delta \rho_i(x) \delta \rho_j(x')} \Delta \rho_j(x'). \]

(2.16)

The second derivative term is all that remains to be simplified. Using equation (2.2), the second derivative term becomes

\[ \frac{\delta^2(\beta A)}{\delta \rho_i(x) \delta \rho_j(x')} = \frac{\delta^2(\beta A)}{\delta \rho_i(x) \delta \rho_j(x')} \]

(2.17)

\[ \frac{\delta \rho_i(x)}{\delta \psi_j^0(x')} = \rho_i(x) \omega_{i,j}(x,x') + \rho_i(x) \rho_j(x') \eta_{i,j}(x,x') \]

(2.18)

where \( \omega_{i,j}(x,x') \) is the single chain site-site correlation function while \( \eta_{i,j}(x,x') \) is the correlation function for sites on different chains. Since \( h(x) \) is zero for ideal chains, the inverse is easily found to be
\[
\frac{\delta^2(\beta A_0)}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} = \frac{\delta \psi_j^0(\mathbf{r}')}{\delta \rho_i(\mathbf{r})} = \frac{\omega_{i,j}^{-1}(\mathbf{r}, \mathbf{r}')}{\rho_i(\mathbf{r})}.
\] (2.19)

For the interacting system, the direct correlation function is defined to be the deviation from ideal behavior:

\[
\frac{\delta^2(\beta A)}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} = \frac{\delta \psi_j^0(\mathbf{r}')}{\delta \rho_i(\mathbf{r})} = \frac{\omega_{i,j}^{-1}(\mathbf{r}, \mathbf{r}')}{\rho_i(\mathbf{r})} - c_{i,j}(\mathbf{r}, \mathbf{r}').
\] (2.20)

which when operated upon by its inverse (equation (2.18)) results in the generalized Ornstein-Zernike equation.

The expression for the external field becomes:

\[
\beta U_i^0(\mathbf{r}) = \beta U_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' c_{ij}(\mathbf{r} - \mathbf{r}') \Delta \rho_j(\mathbf{r}').
\] (2.21)

This is the hypernetted chain (HNC) form of the ideal external field, and is the starting point for the work in Paper II. There, alternate forms of the medium induced potential will be considered.

Finally, by substituting equation (2.15) into equation (2.4) a simplified expression for \(\Delta W\) is found

\[
\Delta \beta W = \frac{1}{2} \sum_{i,j} \left[ \int d\mathbf{r} \left( \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') - \rho_i,\text{bulk} \rho_j,\text{bulk} \right) \right] - \frac{1}{N} \sum_i \int \Delta \rho_i(\mathbf{r}) d\mathbf{r}
\] (2.22)

where the self-consistent results for the density distribution must be used. Equation (2.22) also suggests that higher order terms in a graphical expansion of the free energy could be incorporated in order to refine the theory.

3. Solution method

For a slit pore, the density profile indicated by equation (2.11) is most directly treated as a Monte Carlo simulation of a single chain in an external
field normalized to $\rho_{\text{bulk}}$ in the center of the cell (i.e., the chemical potential of the inhomogeneous density is equated to the homogeneous bulk system). Such simulations are obviously less demanding than full simulations of the many chain systems they are intended to mimic; nevertheless, there are a number of aspects of density functional theory that can reduce its computational efficiency. Foremost among these is that the single chain simulation has previously existed within a self-consistency loop. Consequently, many simulation loops were necessary, and excessive noise in the simulation results could disrupt the convergence sequence. In addition, the medium induced potential, which takes the form of an external field, can develop barriers that trap the chains in phase space. This requires that umbrella sampling be used to surmount these barriers. The main result of the current paper is the realization that the umbrella field also permits the simulation to be removed from the self-consistency loop.

This can be seen as follows for the case of a single site type. The Metropolis weighting of each move is determined with respect to the external, umbrella field

$$U(z) = U_E(z) + U_U(z)$$  \hspace{1cm} (3.1)

where $U_E(z)$ is the bare wall field, and we have chosen the umbrella field to be

$$\beta U_U(z) = a \left( \frac{z - z_{\text{center}}}{z_{\text{center}}} \right)^4 ;$$  \hspace{1cm} (3.2)
$z_{\text{center}}$ is halfway between the walls. This choice forces the chains to spend much of their time near the walls where good statistics are essential to the convergence of the density functional theory. The density distribution is then found from the weighted average which is the Monte Carlo equivalent of equation (2.11):

$$
\rho(z) = \rho_{\text{bulk}} \frac{\left\langle \sum_{i=1}^{N} \delta(|z - z_i|) \exp(-\Delta \beta U_{\text{chain}}) \right\rangle}{\left\langle \sum_{i=1}^{N} \delta(|z_{\text{center}} - z_i|) \exp(-\Delta \beta U_{\text{chain}}) \right\rangle}
$$

(3.3)

where the summation is over all sites; $z_i$ is the position of the $i^{th}$ site; and the brackets indicate an average taken under the umbrella field of equation (3.1). The weighting field is given by

$$
\Delta U_{\text{chain}} = \sum_{j=1}^{N} \left[ (U_M(z_j) - U_U(z_j)) \right]
$$

(3.4)

where the summation is, again, over all sites, and $U_M(z)$ is the medium induced potential given by the last term in equation (2.21).

A new method of enacting the self-consistent loop can now easily be proposed which circumvents much of the computational requirements of the previous simulation/calculation cycle. As is clear from equation (3.3), once the umbrella field is implemented, the sequence of chain configurations generated by the Monte Carlo simulation is completely independent of the medium induced potential, $U_M(r)$. In other words, since both $U_U(r)$ and all intra-chain constraints remain fixed for the entire series of chain simulations, the simulation component of the above scheme is redundant.
after the first such simulation. Consequently, a single Monte Carlo simulation can be performed to generate a sequence of chain snapshots, and this sequence, stored in memory, can be used repeatedly in the average in equation (3.3) as the medium induced potential, $U_M(x)$, is varied from iteration to iteration and density to density. This provides a massive decrease in computational demands.

Consequently, in the work presented in Paper II, before beginning the DF calculation, a single set of chain conformations was generated through an initial Monte Carlo simulation, with intra-chain contributions and $U_U(z)$ set to be consistent with the field calculations desired. For all subsequent DF calculations of the same chain model, these conformations were simply fed into the self-consistent calculations from memory, generating the appropriate density profiles. In order to obtain good results, $5 \times 10^6$ snapshots were stored, and, in order to insure that each snapshot was statistically independent, $N^2$ Monte Carlo steps were performed between each stored snapshot. Thus, the overall number of Monte Carlo steps performed for all DF calculations of a given chain type was $5N^2x10^6$.

The overall efficiency gained by implementation of this “field-decoupled” density functional technique is substantial. For a “set” of 14 densities, as investigated, the calculations, including the initial simulation, were at least an order of magnitude faster. However, since the conformations generated are applicable to any applied field so long as the intra-chain parameters remain the same, the efficiency gain for studies such as this, which investigate a large number of medium-induced potential variations on static chain parameters is even greater.

Since simulation time generally scales, at a minimum, linearly with chain length, the expected gains for studies involving longer chain lengths is
even greater. Furthermore, in comparing the traditional Monte Carlo technique employed previously, it seems likely that certain difficulties in convergence at higher densities have been experienced because the N operations attempted between iterations were insufficient to guarantee statistical independence between subsequent conformations. Therefore, it is supposed that results similar to those obtained from our new technique would require another N operations per iteration, leading to, in the case of this particular work, another order of magnitude in computational time savings.

While the method employed here is one-dimensional, this is due to the system itself, and not to an inherent limitation in the methodology. As long as the simulation takes place within the framework of internally consistent Monte Carlo moves, and the effective field in which the atoms are simulated can be decoupled from the umbrella field, this technique would be generically useful.
References


