Introduction:
Statistical mechanics is a powerful platform to gain insight into a multitude of problems. One area of focus is that of polymers. In the paper “Theory of Polymer Melts: An Integral Equation Approach” authors John G. Curro and Kenneth S. Schweizer apply the Reference Interaction Site Model to a polymer melt. This is accomplished via an integral equation approach.

Background:
Curro and Schweizer were able to use RISM in conjunction with the polymer. In RISM theory the “a molecule is viewed as consisting of a collection of spherically symmetric interaction sites or chemical subunits connected by covalent bonds.” The work done by Chandler/Andersen generalized site-site Ornstein-Zernike equation for the molecular fluid to

\[ h(r) = \int d\bar{r}' \int d\bar{r}''' \omega(|\bar{r}-\bar{r}'|) C(|\bar{r}'-\bar{r}'''|)[\omega(r''') + \rho h(r'') ] \]

\( h(r), C(r) \) and \( \omega(r) \) are N x N matrices where their matrix elements for an N sites are \( h_{\alpha\gamma}(r), C_{\alpha\gamma}, \omega_{\alpha\gamma} \) respectively. \( \omega_{\alpha\gamma}(r) \) is the intramolecular probability distribution functions between sites \( \alpha \) and \( \gamma \) (see figure 1). Likewise, \( C_{\alpha\gamma}(r) \) represents the direct correlation function between sites \( \alpha \) and \( \gamma \) and \( h_{\alpha\gamma}(r) \) is the total correlation function which gives rise to the radial distribution as \( g_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) + 1 \). Closure relations are determined to be \( h_{\alpha\gamma}(r) = 1, r < \sigma_{\alpha\gamma} \) \( C_{\alpha\gamma}(r) = 0, r > \sigma_{\alpha\gamma} \) if \( C_{\alpha\gamma}(r) \) are of sufficiently short range and \( \sigma_{\alpha\gamma} \) corresponds to the distance of closest approach between sites \( \alpha \) and \( \gamma \) (see figure 1).

Using this information Curr and Sweizer considered a polymer ring. By using a ring polymer and its symmetry the matrix equations are simplify giving \( h(r) \) in terms of a single integral equation because \( h(r) = g(r) - 1 = h_{\alpha\sigma}(r) \) \( C(r) = C_{\alpha\gamma}(r) \) and the closure relations become \( h(r) = 1, r < \sigma \) \( C(r) = 0, r > \sigma \).

The author's found the Fourier Transform, \( \hat{h}(k) \), of \( h(r) \) to be

\[ \hat{\omega}(k) = \sum_{\alpha=1}^{N} \hat{\omega}_{\alpha\gamma}(k) \]

\( \hat{\omega}_{\alpha\gamma}(k) = e^{-\sigma^2 k^2 |x-y| / N} \) see figure 2.

Goals:
The goal of the project was to replicate the results reported in the paper for the radial distribution function \( g(r) \). Several approaches were discussed but ultimately doing an optimization on the functional \( I_{\text{RISM}} \) to get the function \( C(r) \), or the direct correlation function. \( C(r) \) was required to solve \( h(r) \) to get the radial distribution function \( g(r) \).
FindMinimum and NMinimize.

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\[ I_{RISM} = \rho_n^2 \int C(r) dr - \frac{1}{8 \pi^3} \int d\vec{k} \left[ \rho_n \hat{\omega}(k) \hat{C}(r) + \ln \left( 1 - \rho \hat{\omega}(k) \hat{C}(k) \right) \right] \quad (2) \]

The first integral was
solved easily using principles of change of variable of multi integral functions and the use of
the symmetry of the function the change of variable was easily simplified to a single integral in terms of
\( dr \) and integrated from 0 to \( \sigma \) resulting in the unity of the Heaviside step function. The result is
\[ \rho_n^2 \left( \frac{4 \pi \sigma^3}{3} - a_2 \left( \frac{\pi \sigma^3}{3} + a_3 \left( \frac{3 \pi \sigma^3}{15} - a_4 \left( \frac{3 \pi \sigma^3}{15} \right) \right) \right) \quad (3a) \]

The second portion to be integrated to get all of \( I_{RISM} \) as a function of \( a_i \) is more difficult than the first integral. To accomplish this \( \hat{C}(k) \)
must be found by doing the Fourier Transformation of equation (1). The FT on C(r) results in
\[ \hat{C}(k, a_1, a_2, a_3, a_4) = a_1 \sum_{i=0}^{m} \left( -a_2 k \right) k + a_3 \left( \frac{3 \pi \sigma^3}{15} - a_4 \left( \frac{3 \pi \sigma^3}{15} \right) \right) \quad (4) \]

Once this is found \( \hat{C}(k) \) can be plugged into the second multiple integral in terms of \( dk \). Similarly the
multiple integral can be simplified to a single integral.
\[ \frac{-1}{8 \pi^3} \int \left[ \rho_n \hat{\omega}(k) \hat{C}(r) + \ln \left( 1 - \rho \hat{\omega}(k) \hat{C}(k) \right) \right] 4 \pi k^2 dk \quad (5) \]

This was again integrated from 0 to \( \sigma \) but was done numerically. After numerical integration was completed \( I_{RISM} \). The integration however was
difficult to do for values past \( k=20 \) as both portions of the integrand were oscillatory in nature.
\[ \rho_n \hat{\omega}(k) \hat{C}(k) 4 \pi k^2 \text{ and } \ln \left( 1 - \rho_n \hat{\omega}(k) \hat{C}(k) \right) 4 \pi k^2 \quad (6) \]

To compensate for this the integral equation
was recast as
\[ \frac{\pi \rho_n^3}{8} \int \left( \ln \left( 1 - \rho_n \hat{\omega}(k) \hat{C}(k) \right) \right) 4 \pi k^2 \quad (7) \]

that would allow for cancellation
between the two parts. Now \( I_{RISM} \) was minimized using two different Mathematica Minimization tools,
FindMinimum and NMinimize.
FindMinimum according to Wolfram Research tends to be most efficient at doing local optimization and so tends to be used when efficiency is of the most importance. NMinimize on the other hand is more typically used to find global minimum. This has a distinct draw back in that it can more processor intensive as a much wider range must be explored. Both tools do allow for different methods to be implemented to do the optimization. A variety of trials to find the minimum were done with success. The inverse FT on $\hat{h}(k)$ with the optimized values of $a_1$, $a_2$, $a_3$, $a_4$ and the graph of of $h(r)$ output. $h(r)$ did not appear to behave well regardless of the coefficients used.

Results:

<table>
<thead>
<tr>
<th>Method</th>
<th>$k$</th>
<th>$\rho$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>Min</th>
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<tbody>
<tr>
<td>DE/NMin</td>
<td>10</td>
<td>0.01</td>
<td>-0.194479</td>
<td>9.83452</td>
<td>1.67447</td>
<td>1.90436</td>
<td>-1.53487E-005</td>
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<tr>
<td>DE/NMin</td>
<td>20</td>
<td>diverges</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMin</td>
<td>10</td>
<td>diverges</td>
<td></td>
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</tbody>
</table>

*DE=Differential Evolution

Continuing on with the project it is necessary to get $h(r)$ in a manner that is usable and consistent with physics. Progress was made in creating a frame work for further study of the PRISM model using numerical methods. There are multiple possibilities for why the solutions to $h(r)$ did not resolve. First and foremost the numerical integration integrated but timed out so it may need to be optimized. Second it is unknown whether the coefficients($a_1$, $a_2$, $a_3$, $a_4$) were the global minimum or only local minimum. More work should be done on different optimization parameters and techniques to ensure that the global minimum is being found. $k = 20$ had been working but the data had not been saved. Some alterations to the code were made but could not be resolved.
References


3. This routine written by Dr. David Wu
Mathematica code used:

*defining omega (k)*

\[ \text{omegahatag}[k_\_ , \text{alphagamma}, n] := \text{Exp}[-k^2 \text{alphagamma} \ (n-\text{alphagamma})/(6n)] \sum_{\text{alphagamma}=1}^{n} \text{Exp}[-k^2 \text{alphagamma} k^2 (-\text{alphagamma}+n)/(6n)] \]

%/. n = 10

\[ \text{omegahatag}[k_] := 1+ \]

(*defining c_hat (k)*)

\[ \text{chat}[a1\_ , a2\_ , a3\_ , a4\_ , k_] := 8 a3 p (2 k+k \text{Cos}[k]-3 \text{Sin}[k]) /k^5+4 a1 p (-k \text{Cos}[k]+\text{Sin}[k])/k^3+4 a2 p (-2+2 \text{Cos}[k]+k \text{Sin}[k])/k^4-24 a4 p (-4+k^2+4 \text{Cos}[k]+k \text{Sin}[k])/k^6 \]

(*defining I_RISM and Numerical Integration*)

\[ \text{IRISM}[a1\_ , a2\_ , a3\_ , a4\_ , \rho_] := \rho^2 (a1 (4\pi/3)-a2 (\pi/3)+a3 (\pi^2/15)-a4 (\pi/15))-1/(8 \pi^3) \text{NIntegrate}[(\text{Log}[1-\rho \text{omegahatag}[k]\text{chat}[a1,a2,a3,a4,k]]\text{Exp}[\rho \text{omegahatag}[k]\text{chat}[a1,a2,a3,a4,k]]) 4 \pi k^2,\{k,0,20\}] \]

\[ \text{NMinimize}[	ext{IRISM}[a1,a1,a3,a4,0.01],\{a1,a2,a3,a4\}] \]

(*hhat (k) solution via simple algebraic manipulation*)

\[ \text{hhat}[a1\_ , a2\_ , a3\_ , a4\_ , \text{rhom\_ , k\_}] := \text{omegahatag}[k]*(\text{chat}[a1, a2, a3, a4, k]) \]

\[ (1 - \text{rhom\_)*\text{omegahatag}[k]*\text{Chat}[a1, a2, a3, a4, k]) \]

(*unfinished is the inverse FT of hhat (k) *)