ON THE POLYMER PHASE TRANSITION

D.C. RAPAPORT

Physics Department, Bar-Ilan University, Ramat-Gan, Israel

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The self-interacting, self-avoiding lattice walk model of a polymer chain has been studied by exact enumeration of short chain configurations. The apparent development of a divergence in the specific heat as the chain length is increased indicates a phase transition in the infinite chain limit.

The random walk has long been regarded as the basis for developing models of an isolated polymer chain in dilute solution [1]. However, any approach based on the random walk neglects two important long-range effects: the excluded volume, and the attractive interaction between non-neighbouring chain units which approach one another in particular spatial configurations. These effects destroy the Markovian nature of the model and are thus capable of producing a fundamental change in behaviour.

The lattice version of the chain with excluded volume - the self-avoiding walk - has been extensively studied, [e.g. 2], the walk with attractive force to a lesser extent [3–5]. The effect of the attraction is small at high temperature and the chain behaves as a self-avoiding walk, but at low temperature energy considerations require that the chain condense into an ordered, tightly packed (coiled or folded) configuration. The results presented in this note point to the existence of a phase transition at some intermediate temperature, and a specific heat which becomes infinite at the transition point. This transition presumably coincides with the onset of long-range order.

The partition function of a chain of $n + 1$ units, i.e. an $n$-step walk, embedded in a regular lattice is

$$c_n(\theta) = \sum_{m \geq 0} c_{nm} \exp(m\theta)$$

with $\theta = -J/k_B T$. $J$ is the excess energy due to each pair of non-adjacent units which approach to nearest-neighbour separation, and $c_{nm}$ is the number of $n$-step walks with $m$ such pairs. The $c_n(\theta)$ are finite polynomials in $\exp \theta$ and, with the aid of a computer we have determined the $c_{nm}$ exactly for $n \leq 9$ on the FCC lattice and $n \leq 13$ on the SC.

The reduced specific heat $C(\theta) = d^2 \log c_n(\theta)/d\theta^2$ (the true specific heat is $k_B \theta^2 C$) was determined as a function of $\theta$ for each $n$ and its maximum value $C_{\text{max}}$ computed. $C_{\text{max}}$ is plotted versus log $n$ in fig. 1, and the values of $\theta$ at which the maxima occur, $\theta_1$, are given in table 1.

Fig. 1 also contains estimates of $C_{\text{max}}$ extracted from graphed FCC Monte Carlo data on much longer

![Graph showing $C_{\text{max}}$ vs log $n$. The SC (x10) is plotted against FCC.](image-url)

Fig. 1. Reduced specific heat maximum versus log $n$. The Monte Carlo results ($n \geq 29$) are taken from ref. [3].
Table 1
Estimates of $\theta_t$ for different chain lengths $n$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\theta_t$ (FCC)</th>
<th>$n$</th>
<th>$\theta_t$ (SC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.405</td>
<td>9</td>
<td>1.020</td>
</tr>
<tr>
<td>6</td>
<td>0.405</td>
<td>10</td>
<td>0.924</td>
</tr>
<tr>
<td>7</td>
<td>0.379</td>
<td>11</td>
<td>1.005</td>
</tr>
<tr>
<td>8</td>
<td>0.356</td>
<td>12</td>
<td>0.808</td>
</tr>
<tr>
<td>9</td>
<td>0.342</td>
<td>13</td>
<td>0.810</td>
</tr>
</tbody>
</table>

chains [3]. The error bars in the Monte Carlo estimates correspond to a 2% uncertainty; no estimates of their values have been published, but they are unlikely to be smaller than this. Furthermore, no attempt was made to search for the location of $C_{\text{max}}$, so that the correct Monte Carlo $C_{\text{max}}$ may be slightly larger.

Even with these reservations the results are striking. The FCC exact data establish a smooth trend which persists into the Monte Carlo results. The actual rate of divergence is faster than log $n$, but not easily determined. A log-log plot of the same data shows downward curvature, indicating that the divergence is not a simple power law — at least not for the chain lengths considered, and techniques such as Neville extrapolation fail to clarify matters. The SC results have yet to settle down, but the overall trend appears similar to the FCC.

Little can be said regarding the trends in $\theta_t$, except that in the FCC case a possible limiting value is $\theta_t \approx 0.2$. This means that in the $n = \infty$ limit the specific heat is singular at finite temperature. (The irregular $\theta_t$ behaviour is the reason we chose to work with the reduced specific heat.)

Support for this type of analysis is provided by calculations for small Ising systems [6] which also yield specific heat maxima that diverge smoothly with increasing system size. In this case the limit is known exactly, and the observed trends correctly predict the limiting behaviour.

References