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LETTER TO THE EDITOR

Universal amplitudes ratio at the collapse transition of polymers in two dimensions

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Abstract. First values of the universal ratio of the mean square radius of gyration and the mean square end-to-end distance for 2D linear polymers at their collapse transition are calculated by the scanning simulation method. Two models are considered: (i) self-avoiding walks (SAWs) with nearest-neighbour attractions for which this ratio is found to be 0.179 ± 0.003 at the Θ point; (ii) self-intersecting trails at their tricritical point for which the value 0.166 ± 0.002 is obtained. This provides yet another indication that these models may belong to different tricritical universality classes. We have also computed this ratio for trails at the high temperature limit (with non-interacting intersections) and found 0.141 ± 0.001 in excellent agreement with earlier estimates of this ratio for SAWs in their swollen phase.

There has been much interest recently in understanding the statistical properties of linear polymers at their collapse transition [1-23]. Usually linear polymers have been modelled by SAWs of N steps on a lattice, where an attraction energy ε ($\varepsilon < 0$) is assigned to a pair of nearest-neighbour monomers. As the temperature T changes, there is a tricritical temperature $T = \Theta$ (the collapse transition point) which separates a swollen phase of the chain at high T from a collapsed phase at low T. A polymer under various solvent conditions has also been modelled by trails [13, 14]. Trails are lattice walks that can visit an already visited site, but cannot go on any bond more than once. One can associate an attraction energy ε with each intersection [14], which leads to a new tricritical behaviour, first studied by Shapir and Oono [15].

While a lot of effort has been invested to calculate by different methods the tricritical exponents which characterise the asymptotic scaling properties of 2D polymers at the collapse transition, no attention has previously been given to another universal property, namely the ratio between the mean square radius of gyration $\langle G^2 \rangle$ and the mean square end-to-end distance $\langle R^2 \rangle$ [24]. We have thus decided to perform the first numerical calculations of this ratio both for SAWs and for trails at tricriticality using the scanning simulation method.

Many years ago Domb and Hioe [25] calculated the ratio $A = \langle G^2 \rangle / \langle R^2 \rangle = 0.140 \pm 0.001$ for swollen SAWs in 2D using exact enumeration. The Monte Carlo result is in excellent agreement with this value [26]. Recently Cardy and Saleur [27] derived a relation between this ratio and another universal ratio based on conformal invariance. Exact enumerations, however, could not confirm the validity of their relation [28].

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Duplantier [29] first addressed the value of this ratio at the Θ point. He calculated the first correction of order $\varepsilon = 3 - d$ to the mean field value $A_{MF} = 1/6$. Inserting naively $\varepsilon = 1$ to the expansion he predicts $A = 0.170$ in 2D. However this extrapolation is not very credible in predicting the 2D tricritical properties.

Another debated question is whether SAWs and trails belong to the same universality class. While there is a wide consensus for that to be the case if both models are in their high temperature regimes (swollen phases) [13, 15, 16], the situation at their respective collapse transitions is not as clear. We briefly summarise the conclusions of many works [3-23] on their respective tricritical exponents.

(i) The value of the tricritical size exponent (ν_t) seem to coincide in both models [8, 10, 20].

(ii) The partition function exponents in the bulk (γ_t) [8, 10, 20], with one end ($\gamma_{1,t}$) and both ends ($\gamma_{11,t}$) [8, 22, 23] attached to a surface, seem to differ but the differences are too small to make definite claims.

(iii) The values of the specific heat exponent (α_t) and the crossover exponent (ϕ_t), to the accuracy they have been computed to date, to differ for both models [8, 10, 19, 23]. Comparison between the universal ratios at the respective collapse points will also shed more light on this question.

We use the results for $\langle G^2 \rangle$ and $\langle R^2 \rangle$ obtained with the scanning method by Meirovitch and Lim for trails at $T = \infty$ (number of conformations: 4.5×10^6) [20] and for SAWs at their Θ point 30×10^6 conformations) [10]. We also analyse recent results for tricritical trails (20×10^6 conformations) with the same technique [30]. In those simulations results are obtained for partial chains of length $N = 10, 20, 30 \ldots$ where at finite temperatures the general scanning procedure takes into account the interaction energy ε associated with each interaction. In order to investigate the behaviour of chains over a wide range of temperatures and to locate the tricritical temperature, many simulations are required. With the scanning simulation method it is a relatively simple task because one can obtain results at many different temperatures from a single sample simulated at any given temperature. For the details of the scanning simulation method for SAWs and trails, see [10, 16, 20, 23].

We first look at this ratio for trails at $T = \infty$; in figure 1(c) we plot $A = \langle G^2 \rangle / \langle R^2 \rangle$ against $1/N$ for $60 \leqslant N \leqslant 300$. For very long chains the graph is expected to asymptotically approach its $N \to \infty$ value. For the chain length studied here it is decreasing monotonically as N increases. Therefore we take the value of this ratio at a last point as an upper bound and take the linearly extrapolated value as a lower bound. Our estimation for the infinite chain is $A = 0.141 \pm 0.001$, which agrees well with the value 0.140 ± 0.001 of SAWs at $T = \infty$ [25, 26]. The best estimate of the Θ temperature for SAWs on a square lattice has been calculated [10], $K_\Theta = -\varepsilon / k_B \Theta = 0.658 \pm 0.004$. In a recent simulation work [30] of trails of up to $N = 300$ steps on a square lattice we obtain $K_t = -\varepsilon / k_B T_t = 1.092 \pm 0.006$. In figure 1($a$) results are presented for $\langle G^2 \rangle / \langle R^2 \rangle$ for SAWs at $K_\Theta = 0.658$ for $60 \leqslant N \leqslant 170$. Our analysis is only based on the data for $60 \leqslant N \leqslant 140$ since the statistics of data for $N \geqslant 150$ is not reliable due to the small number of accepted SAW configurations [10]. We take a linearly extrapolated value as an asymptotic value of A_Θ by using a least squares fitting in the range $60 \leqslant N \leqslant 140$ which yields $A_\Theta = 0.179 \pm 0.003$. In figure 1($b$) the same ratio is shown for trails at $K_t = 1.092$ for $60 \leqslant N \leqslant 300$. Also using the same analysis described above we only rely on the data for $60 \leqslant N \leqslant 250$ (since the acceptance rate is larger for this case) which yields $A_t = 0.166 \pm 0.002$. Our error estimates are based on the available data and the possibility of systematic deviations at larger N may not be ruled out [31].

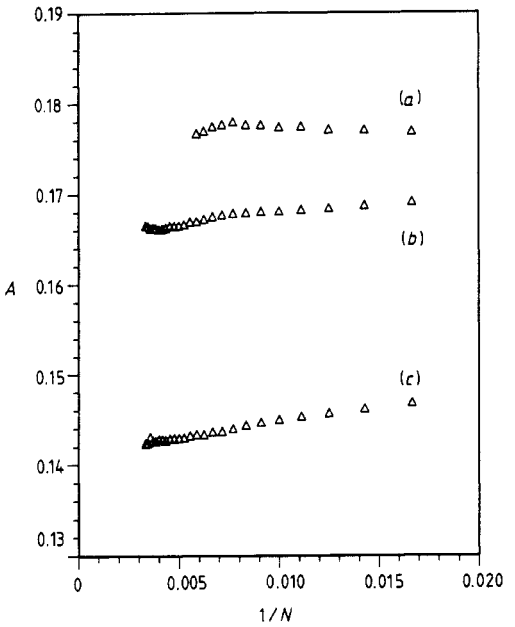

Figure 1. The universal ratio $A = \langle G^2 \rangle / \langle R^2 \rangle$ of the mean square radius of gyration and the mean square end-to-end distance, $\langle G^2 \rangle / \langle R^2 \rangle$ against $1/N$ for (*a*) SAWs at the Θ temperature $K_\Theta = -\varepsilon / k_B \Theta = 0.658$ for $60 \leqslant N \leqslant 170$, (*b*) tricritical trails at $K_t = 1.092$ for $60 \leqslant N \leqslant 300$, and (*c*) trails at $T = \infty$ for $60 \leqslant N \leqslant 300$.

Here the errors also include the uncertainty of the tricritical temperatures. This value of A_t for tricritical trails is very close to the mean field value $A_{MF} = 1/6$ which is obtained for unrestricted random walks. We have shown elsewhere [22, 23] that at the special temperature T^* such that $-\varepsilon / k_B T^* = \ln 3 = 1.098$ the trails have the mean field value for the exponent $\gamma_t = 1$. The question of whether T^* is the tricritical temperature or it is slightly below T_t is not settled yet but it is likely that our finding of $A_t \approx A_{MF}$ may be related to the special properties of the trails at T^*. Further studies of these questions are certainly worthwhile.

To summarise, we have provided the first estimates for the universal amplitude ratios $A = \langle G^2 \rangle / \langle R^2 \rangle$ for two models of polymers at their collapse transitions in 2D. For SAWs at the Θ point we find $A_\Theta = 0.179 \pm 0.003$ which is larger than its value in the swollen phase and is also larger than the value predicted from the extrapolation of the first-order ε expansion below, $D = 3$ [29]. For trails in the swollen phase our value of 0.141 ± 0.001 confirms that this model is in the same universality class of swollen SAWs. At the tricritical point, however, our estimate for $A_t = 0.166 \pm 0.002$ differs from A_Θ. Although we may not rule out completely the possibility of strong downtrend in A_Θ and/or uptrend in A_t for longer chains which will make them converge to the same value [31], the results for the chains' length available in our simulations seem to indicate that the tricritical behaviour for SAWs and trails may not be identical.

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Note added in proof. After this letter had been submitted a preprint by Camacho and Fisher in which amplitude ratios for two-dimensional self-avoiding polygons and planar vesicles are studied, was received [32].

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