

Continuous Self-Avoiding Walk with Application to the Description of Polymer Chains

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We develop the continuous self-avoiding walk (CSAW) methodology for investigating temperature dependent thermodynamic properties of finite polymer chains without imposing a lattice. This leads to a new concept: the free energy theta temperature, $T_{\theta F}$, at which the free energy is proportional to chain length. Above $T_{\theta F}$, the polymer chain-solvent mixture leads to a single phase, whereas below $T_{\theta F}$ the polymer solvent system has a positive surface tension with a tendency to phase separation to form a globular phase. For finite chains this coil-globule transition lies above the geometric theta temperature at which the distribution describes a Gaussian coil. CSAW provides the basis for a new approach to predict globular properties of real polymers.

A number of powerful mathematical models have been developed to describe the behavior of linear polymer molecules in a good solvent. These include the self-avoiding walk (SAW) on a lattice,^{1,2} the bead-rod model,³ and the continuum Edwards model.^{4,5}

Here we develop SAW methodology on continuous space (CSAW) to enable the investigation of temperature-dependent geometric and thermodynamic properties (enthalpy and entropy) of finite polymer chains at finite temperatures. CSAW leads to a new critical point: the free energy theta temperature, $T_{\theta F}$, at which the free energy is proportional to chain length. Above $T_{\theta F}$, the polymer chain-solvent mixture leads to a single phase, the solvation phase, whereas below $T_{\theta F}$ the polymer chain solvent system has a positive surface tension and tends toward phase separation to form a globular phase. In addition, CSAW enables the prediction of properties for polymers using realistic interaction potentials.

The random walk on a lattice was proposed by Polya⁶ in 1921 and has been studied broadly and systematically. It has a powerful theoretical significance for mathematics, and the lattice walk model has been the basis for many applications in physics, chemistry, and biology.

The self-avoiding walk (SAW)^{1,2} is a random pathway that does not contain self-intersections, serving as a model for linear polymers and playing a central role in understanding polymer statistics. The SAW has been shown to be equivalent to the $N=0$ case of the N -vector model,⁷ making SAW an important test case for the theory of critical phenomena.

Many properties of polymer materials (e.g., rubber elasticity, liquid crystallinity) are well characterized in terms of single-chain conformations and dynamics. Indeed the use of SAW to describe long flexible polymer chains with excluded volume⁸ has led to remarkably simple scaling properties that dominate the behavior of many physical properties, allowing a generic understanding of features common to many chemically different systems. However, these scaling rules are limited to infinite

temperature and do not include realistic interaction parameters needed to distinguish the properties of real materials. Of particular interest here are the properties of polymer chains in solution. The phase behavior of such systems is of fundamental interest with enormous practical applications for predicting the processing and mechanical properties of various plastic materials.

The continuous self-avoiding walk (CSAW) on continuous Euclidean space describes polymer chains with fixed bond length and bond angle, but with continuously variable torsion and VDW interactions. Previous studies of SAW^{1,2} were based on Euclidean lattices, lattice self-avoiding walk (LSAW).

To define the continuous self-avoiding walk, we start with a united atom force field, in which each monomer is represented by one united atom or bead. Here we use the Siepmann-Karanorni-Smit force field^{9,10} (SKSFF) based on fitting to alkanes. This uses a Lennard-Jones 12-6 van der Waals (vdW) potential (well depth is $\epsilon/k_B = 47$ K and inner wall distance is $\sigma = 0.393$ nm) plus a torsional potential, while the bond distances ($R_b = 0.154$ nm) and bond angles ($\theta = 114.0^\circ$) are fixed. The torsion potential is short ranged and hence does not affect the global scale properties of the polymer chain.

Figure 1a illustrates a self-avoiding walk on a 2D square lattice. The partition function Z_n or the number of SAWs is straightforward here: $Z_0 = 1$, $Z_1 = 4$, $Z_2 = 12$, etc. Figure 1b defines the CSAW. Each step in CSAW involves adding by one additional united atom with fixed bond length and angle to the chain, but allowing continuous torsion. The partition function Z_n or the number of SAWs of CSAW is counted as $Z_0 = 1$, $Z_1 = 2\pi$, $Z_2 = Z_1 * 2\pi$ (since we fix bond length/angle, the possible positions of the second step comes from the torsion, leading to 2π), $Z_3 = Z_2 * 2\pi$, etc. For $N > 4$ united atoms, there are repulsive van der Waals (vdW) interactions that induce self-avoidance, reducing the contribution for each step below 2π (Figure 1c).

The calculations of the CSAW use the CCBB algorithm,^{11,12} a Monte Carlo approach that combines continuous configuration

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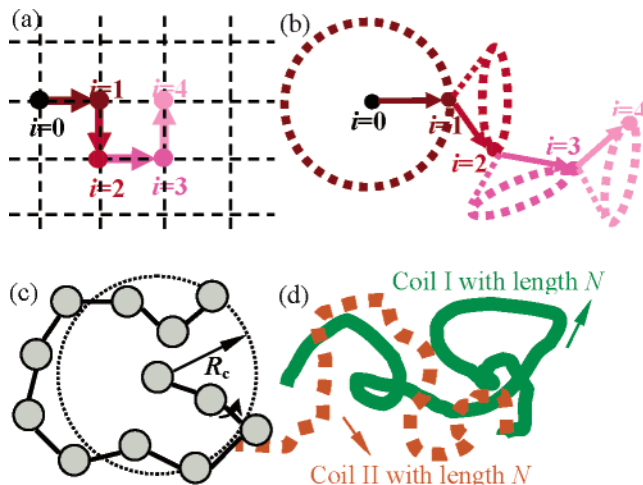


Figure 1. (a) Self-avoiding walk on a 2D square lattice. (b) Continuous self-avoiding walk on 3D space. (c) Self-avoidance in CSAW comes from the vdW repulsive interactions, which reduces the contribution for one step below 2π . A cut off distance R_c is applied for vdW interactions. (d) One chain with length $2N$, considered as connecting two coils with length N .

biased sampling (CCB) with Boltzmann-factor enrichment (BGB). CCB is a direct MC sampling, using a fast algorithm for evaluating the torsion sampling weighting function. The BFB method is an improved enrichment method, which introduces a configurational-dependent enrichment procedure with correct bias correction and automatic population control. Combining these two types of samplings (CCBB) dramatically improves MC convergence.

We first examine the following properties of CSAW and compare with traditional LSAW: The partition function Z_n or the number of n -step SAWs; the mean-square end-to-end distance of n -step SAWs $\langle R_e^2 \rangle_n$, and the radius of gyration $\langle R_g^2 \rangle_n$. At infinite temperature (athermal), LSAW leads to asymptotic forms¹³ at large n of

$$Z_n = A\mu^n n^{\gamma-1} [1 + o(1)] \quad (1)$$

$$\langle R_e^2 \rangle_n = Bn^{2\nu} [1 + o(1)] \quad (2)$$

$$\langle R_g^2 \rangle_n = Cn^{2\nu} [1 + o(1)] \quad (3)$$

where μ is the monomer partition function (also termed the connective constant). The values of μ and the amplitudes A , B , C vary from lattice to lattice, while the exponents γ , ν , and the amplitude ratio¹⁴ C/B are universal; that is they depend only on the space dimensionality d but not on the particular lattice chosen.

The properties of the traditional LSAW at infinite temperature are simple to study since it is not necessary to use energy terms to account for self-avoidance. For CSAW, we *must* include energy terms to realize self-avoidance, which arises from repulsive vdW interaction. Thus, to obtain the infinite temperature limits to compare with LSAW, we perform CSAW at extremely high temperatures (7200 K, 50 400 K, and 5 040 000 K). The molecule cannot decompose since bond lengths and angles are fixed. Only long-range vdW interactions affect global scale properties.

To determine these parameters with high-precision, we use appropriate extrapolation method to reduce the error arising from finite length, the $o(1)$ term. CSAW is much more expensive than LSAW, making it impractical to sample sufficient data for

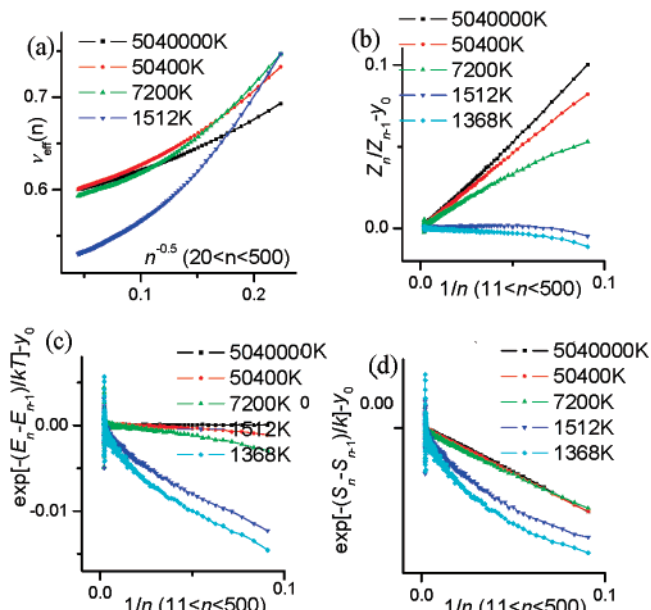


Figure 2. (a) Dependence of $\nu_{\text{eff}}(n) = 1/2 \log_2 \langle R_n^2 \rangle / \langle R_{n/2}^2 \rangle$ on $n^{-0.5}$ for CSAW at various temperatures. Each data point is averaged from three samplings, with a standard error smaller than the symbol. (b) Dependence of $r_n = Z_n/Z_{n-1}$ on $1/n$ for CSAW. (c) Dependence of $\exp[-(E_n - E_{n-1})/kT]$ on $1/n$ for CSAW. (d) Dependence of $\exp[-(S_n - S_{n-1})/k]$ on $1/n$ for CSAW. Each curve in (b) (c) (d) is shifted by y_0 to have the same origin. The shifted y_0 from high temperature to low temperature are 5.9291, 5.5204, 4.8046, 3.1893, 3.0467 in (b); 0.9939, 0.9645, 0.8747, 0.6416, 0.6235 in (c); and 0.1676, 0.1747, 0.1821, 0.2012, 0.2047 in (d).

large N to reduce finite size error. Thus for chain length up to $N = 500$ we sample enough chains or walks, $\sim 3 \times 10^8$, to reduce statistical error and then use finite size correction approaches to derive the properties. In comparison, exact enumeration¹⁵ for LSAW has been carried out for chain lengths up to $N \leq 26$ (3D) without statistical error; Monte Carlo approaches¹⁶ to LSAW have reached chain/walk lengths of $N \sim 80\,000$ with $\sim 10^7$ walks.

The $o(1)$ term of $\langle R_e^2 \rangle$ and $\langle R_g^2 \rangle$ in eqs 2 and 3¹⁶⁻¹⁸ scales as $\sim n^{-0.5}$ ($\sim n^{-0.56}$ in ref 16); hence Figure 2a plots $\nu_{\text{eff}}(n) = 1/2 \log_2 \langle R_n^2 \rangle / \langle R_{n/2}^2 \rangle$ against $n^{-0.5}$, showing that the temperature dependence of ν_{eff} is weak above 7200 K. Linear extrapolation of ν_{eff} to $N = \infty$ in the range of $0.045 < N^{-0.5} < 0.07$ leads to 0.5848(1) at 5 040 000 K; 0.5822(1) at 50 400 K; 0.5751(1) at 7200 K. Extrapolating these values leads to $\nu = 0.585 \pm 0.003$ for CSAW, which is consistent with $\nu = 0.588 \pm 0.001$ for LSAW.^{15,16} This confirms that ν is a universal scale property shared by different types of LSAW and CSAW.

Using $\nu = 0.585$ for CSAW and assuming $o(1) \sim N^{0-0.5}$, we estimate the amplitude B and C in eqs 2 and 3. Table 1 summarizes the results and compares with LSAW, showing that B and C from CSAW are quite different from LSAW, but C/B is universal. For CSAW the universal quantity C/B is *not* sensitive to the temperature, while B and C are sensitive to the temperature.

To analyze the quantities in eq 1, we follow the ratio method shown in eq 4, in which r_n is analyzed against $1/n$ ¹⁵ to second order in $1/n$.¹⁹

$$r_n \equiv \frac{Z_n}{Z_{n-1}} \approx \left[1 + \frac{\gamma-1}{n} \right] y = \left[1 + \frac{\gamma-1}{n} + \frac{\text{const}}{n^2} \right] y \quad (4)$$

The result is shown in Figure 2b, which leads to γ and μ for CSAW at different temperatures (to second order in $1/n$). Using

TABLE 1: Universal Quantities (γ , ν , C/B) and Non-Universal Quantities (μ , A , B , C) from CSAW Compared with Various Lattices for LSAW

		γ	μ	A	ν	B	C	C/B
LSAW	SC	1.1585 ²⁰	4.68401 ²⁰	1.205 ²⁰	0.588(1) ¹⁶	1.21667(50) ¹⁶	0.19455(7) ¹⁶	0.1599(2) ¹⁶
LSAW	BCC	1.1612(8) ²¹	6.530356(2) ²¹	1.16(1) ²²	0.591(2) ²¹	1.06(1) ²²	0.166(2) ²²	0.158(3) ²²
LSAW	FCC	1.163(2) ²⁰	10.03643(6) ²⁰	1.16(2) ²²	0.5875(15) ²³	1.03(3) ²²	0.161(3) ²²	0.158(3) ²²
LSAW	DA	1.161(2) ²⁴	2.8790(2) ²⁴	1.24(1) ²²	0.592(3) ²⁴	1.42(1) ²²	0.226(2) ²²	0.158(3) ²²
CSAW	∞ K	1.164(2)	5.9(4)	0.004(1)	0.585(3)	5.2(1.5)	0.8(0.2)	0.1600(6)
CSAW	5040000K	1.1646(4)	5.9291(1)	0.004160(2)	0.5848(1)	5.2190(4)	0.83517(4)	0.16002(2)
CSAW	50400K	1.1663(8)	5.5204(1)	0.005305(2)	0.5822(1)	6.708(2)	1.0775(1)	0.16063(6)
CSAW	7200K	1.158(1)	4.80463(5)	0.00785(1)	0.5751(1)	7.067(1)	1.1437(2)	0.16184(5)

^a See eqs 1, 2, and 3 for definitions.

this γ and μ , we obtain A from eq 1. These results are compared with LSAW in Table 1. We see that the universal quantity γ is not sensitive to the temperature and consistent with LSAW, while lattice dependent quantities μ and A are sensitive to the temperature and quite different from LSAW. μ for CSAW is ~ 5.9 , which is less than 2π due to the self-avoidance.

In eq 1, two terms μ^n and $n^{\nu-1}$ contribute to the partition function Z_n . The first term μ^n is the product of monomer partition function μ . The gamma term, $n^{\nu-1}$, has not been previously analyzed and we propose here a simple model to explain its origin.

The dominant N dependent term in the free energy is proportional to N (the volume term), where $A/RT = -aN$. Now we want to analyze the form of the dominant corrections $f(N)$, writing

$$A/RT = -aN - bf(N) - c \quad (5)$$

Consider one chain with length $2N$, as two coils with length N , but connected as shown in Figure 1d. The free energy is $-a*2N - bf(2N) - c$. If Coil I and Coil II do not interact with other, then the total free energy would be $-2*aN - 2*bf(N) - c$. The difference gives the interaction between Coil I and Coil II as $\Delta A/RT = -bf(2N) + 2bf(N)$, which includes two parts: repulsive (self-avoiding entropy) and attractive (enthalpy).

At $T = \infty$, there is no attractive energy (athermal) leaving only the repulsive part (self-avoiding entropy) between these two coils. Thus $\Delta A > 0$. Because $f(N) < N$ and $f(2N) < 2f(N)$, then $b > 0$. The volume occupied by the other coil scales as N and the reduced entropy scales as $\ln(\Delta V) \sim \ln N$. This suggests that $f(N)$ has the $\ln N$ form and explains the origin of the gamma term, $n^{\nu-1}$.

As the temperature decreases from infinity, the attractive energy between two coils increases. When the attractive energy exactly balances with the repulsive part between these two coils, $\Delta A = 0$ and $b = 0$. At sufficiently low temperature, the attractive energy dominates and $\Delta A < 0$ and $b < 0$. Eventually, the chain collapses leading to $V \sim N$. In this case the correction term is expected to have the form of a surface energy, leading to an $N^{2/3}$ dependence.

The point at which the attractive and repulsive parts balance is the coil-globule transition temperature, above which the polymer chains and solvent form a single phase and below which the chains tend to phase separate to form globules. To determine this coil-globule transition temperature, we plot $\ln(Z_n/Z_{n-100})$ against $\ln(n)$ in Figure 3a. We refer to the coil-globule transition temperature at which $\ln(Z_n/Z_{n-100})$ is constant at large n as the free energy theta temperature, $T_{\theta F}$, at which free energy is proportional to N and is the sum of the free energies for each monomer, leading to an ideal solution. [Note that the enthalpy and entropy analysis in Figure 2 shows that the enthalpy and entropy are *not* the sums of monomer components (the correc-

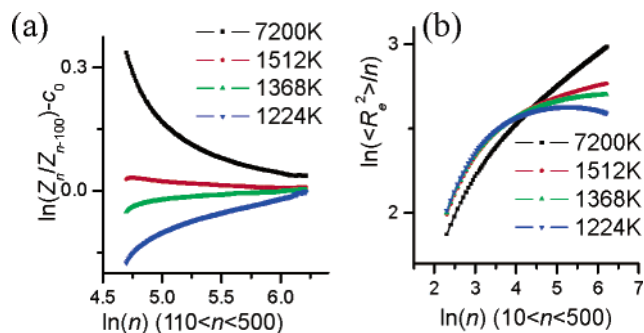


Figure 3. (a) Dependence of $\ln(Z_n/Z_{n-100})$ on $\ln(n)$ for CSAW. $\ln(Z_n/Z_{n-100})$ decreases monotonically with increasing N for $T \geq 1512$ K, while it increases with increasing N for $T \leq 1368$ K. Thus $1368 \text{ K} < T_{\theta F} < 1512$ K for N up to 500. (b) Dependence of $\ln(\langle R_e^2 \rangle / n)$ on $\ln(n)$ for CSAW. $\ln(\langle R_e^2 \rangle / n)$ increases monotonically with increasing N for $T \geq 1368$ K, while it has a maximum and decreases with increasing N for $T \leq 1224$ K. Thus $1224 \text{ K} < T_{\theta R} < 1368$ K for N up to 500.

tion term cancels).] Figure 3a shows that $1368 \text{ K} < T_{\theta F} < 1512$ K for N up to 500.

Flory defined what we will refer to as the geometric theta temperature, $T_{\theta R}$, as the temperature at which $\ln(\langle R_e^2 \rangle / n)$ is constant at large n . This is the temperature at which the chain describes a Gaussian coil. To determine $T_{\theta R}$, we plot $\ln(\langle R_e^2 \rangle / n)$ against $\ln(n)$ in Figure 3b, where we see that $1224 \text{ K} < T_{\theta R} < 1368$ K for N up to 500.

For infinite chain/walk length, $T_{\theta F} = T_{\theta R}$, so that there is only one theta point, so that at the coil-globule transition energy the chains describe a Gaussian coil. However, for finite chain lengths Figure 3 shows that $T_{\theta F} > T_{\theta R}$, (independent of the force field description).¹² Thus the coil-globule transition occurs at the free energy theta temperature that lies above the temperature at which the distribution describes a Gaussian coil.

The free energy of polymers in solution can be expressed in terms of Φ , the fraction of sites occupied by monomers as

$$F/T|_{\text{site}} = \Phi/N \ln \Phi + 1/2 (1-2\chi)\Phi^2 + 1/6 \Phi^3 + \kappa$$

At the temperature for which $\chi = 1/2$ there is no quadratic term in Φ . Thus, ignoring higher order terms in Φ leads to $\mu = 1 - 2\chi = 0$. de Gennes refers to this as “the bare theta temperature”,²⁶ which coincides in this case with the free energy theta temperature we define herein.¹²

When $\chi = 1/2$, the Φ^2 term disappears, leaving higher order terms dominated by the Φ^3 term. This three-body term²⁶ leads to repulsive interactions that result in swelling the chain above that of the Gaussian distribution. This shifts $T_{\theta F}$ to a value higher than $T_{\theta R}$.

Nidras¹⁸ introduced a nearest neighbor contact association energy into LSAW and estimated $\gamma_l = 0.9985$ and $\nu_l = 0.5001$ at the transition point, implying a theta shift ($\gamma_l < 1$ and $\nu_l > 0.5$), just as in CSAW.

The correction term $bf(N)$ in eq 4 can be analyzed in terms of enthalpy and entropy components: $b_E f_E(N)$ and $b_S f_S(N)$. Figure 2c,d plots $\exp[-(E_n - E_{n-1})/kT]$ and $\exp[-(S_n - S_{n-1})/k]$ against $1/n$. The slope at each temperature scales to b_E or b_S .

At $T = \infty$ (athermal case), $\exp[-(E_n - E_{n-1})/kT]$ is independent of $1/n$, as shown in Figure 2c. (At 5 040 000 K the slope is 0.00001 and the linearity R^2 is 0.0048.) Thus at $T = \infty$, the correction term $b_E f_E(N)$ vanishes. This confirms the prediction²⁵ by Des Cloizeau that the energy increment is uniform at high temperature. The shifts y_0 from high temperature to low temperature in Figure 2c are 0.9939, 0.9645, 0.8747, 0.6416, 0.6235, which approaches 1 at $T = \infty$. This indicates that the energy increment approaches 0 at $T = \infty$.

In contrast, at high-temperature $\exp[-(S_n - S_{n-1})/k]$ is linear with $1/n$ as shown in Figure 2d with a linearity $R^2 = 0.9981$ at 5 040 000 K. This indicates that the correction term at high temperature $-b^*f(N)$ comes from entropy not enthalpy.

The magnitudes of the slope in Figure 2c and 2d both increase as the temperature decreases. The chain in Figure 1d normally shrinks as the temperature decreases. This strengthens the interactions between the two coils, which increases the correction term $b_E^* f_E(N)$, $b_S^* f_S(N)$, and the magnitude of the slope in Figure 2c,d. The linearity in Figure 2c and 2d becomes worse as the temperature decreases. This suggests that $f_E(N)$ and $f_S(N)$ can be approximated as $\ln N$ better at high temperature than at low temperature.

Summarizing, we define the continuous self-avoiding walk (CSAW) on continuous Euclidean space, which leads to the same values for the universal constants as lattice SAW models. CSAW eliminates the use of a lattice, which has formed the framework for most general analyses of polymers, including Flory–Huggins theory and lattice SAW. CSAW allows us to study enthalpy and entropy components and study the ensemble at finite temperature. CSAW can be used to simulate real polymers including block polymer, copolymer etc. rather than the abstract description in lattice models.

CSAW leads to the new concept of free energy theta temperature, $T_{\theta F}$, as the temperature at which the free energy is proportional to chain length N . Above $T_{\theta F}$, the single polymer chain–solvent mixture leads to a single phase, the solvation phase, whereas below $T_{\theta F}$ the polymer chain has a positive surface tension and tends toward phase separation from the solvent to form a globular phase.

By eliminating the use of lattices we can study finite temperatures with CSAW, allowing us distinguish the free energy theta temperatures from the geometry theta temperature. We find that the three-body terms make $T_{\theta F}$ higher than the geometric theta temperature $T_{\theta R}$ for which the radius of gyration is proportional to N .

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