

Granular polymer solution

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(Received 14 March 2001; published 27 February 2002)

We have measured the spectrum of fluctuations in the size of a granular polymer in a granular solvent. The system consists of a linear chain of plastic spheres immersed in a planar fluid of self-propelled balls. The time average of the end-to-end length r of the chain scales with the number of links N according to $\langle r^2 \rangle \sim N^{2\nu}$, with $\nu = 0.75 \pm 0.01$. This provides an experimental test of the theoretical value $\nu = \frac{3}{4}$ of the critical exponent for a self-avoiding random walk in two dimensions. The measured probability distribution $P(r)$ is compared with the universal function of the scaling theory.

DOI: 10.1103/PhysRevE.65.031306

PACS number(s): 45.70.-n, 36.20.-r, 05.40.-a, 89.75.-k

Granular matter consists of macroscopic particles (balls, beads, grains, sand, etc.) that can be agitated into fluidlike motion by external forces [1]. Recently, there has been interest in velocity fluctuations in granular gases [2–4] and knots in granular chains [5]. In these experiments, the motion of the grains (steel spheres) is driven by vibrating the container. In this paper, we study a granular polymer solution, consisting of a chain of plastic spheres surrounded by a fluid of self-propelled balls. The motion of the chain is driven by the random collisions of the balls against the chain. This Brownian-like force of agitation mimics the natural driving force of molecular motion. The granular solution represents a mechanical model of a linear polymer in a planar solvent. The granular chain is an experimental realization of a self-avoiding random walk, which is the theoretical model for a polymer with excluded volume. Theoretical studies of the self-avoiding random walk in two dimensions are abundant, but experimental tests of the two-dimensional theories are scarce. A molecular polymer can be confined to a region that is at best quasi-two-dimensional and tends to uncoil (expand) when adsorbed onto a flat surface. Our granular polymer is flexible and exactly two-dimensional. It is an experimental system that is architecturally equivalent to the theoretical model.

A fundamental quest of polymer statistics is to find the average size of a long flexible chain. For a self-avoiding random walk in d -dimensions, scaling theory [6–8] predicts that the mean-square end-to-end length $\langle r^2 \rangle$ of the walk obeys the power-law relation $\langle r^2 \rangle \sim N^{2\nu}$, where N is the number of steps in the walk and ν is a universal critical exponent that depends only on d . For $d=3$, the exact value of ν is unknown, although theory and experiment [7,8] predict the value 0.59. For $d=2$, analytical theories [6–9], based on field theory, spin models, and the renormalization group, predict the exact value $\nu = \frac{3}{4}$. Extensive computer studies [7,8], based on exact enumeration and Monte Carlo simulation, predict numerical values of ν that are consistent with this analytical value. The radius of gyration exponent, which is theoretically equivalent to the end-to-end exponent,

has recently been measured for DNA bound to a fluid lipid membrane [10] and found to be 0.79 ± 0.04 . Scaling theory predicts that the probability distribution $P(r)$ of the end-to-end length r is a universal function of the scaled length r/N^ν [6–8]. Recently [11], this function has been numerically computed using Monte Carlo simulation, and analytically calculated to second order in $\epsilon \equiv 4-d$ using renormalization group theory. To our knowledge, the end-to-end distribution $P(r)$ has never been experimentally measured. In this paper, we present a direct measurement of the end-to-end exponent ν and distribution $P(r)$. This provides a granular test of the two-dimensional theory of the self-avoiding random walk using an exactly-planar polymer solution.

There are two levels of granularity in our experiment: a granular system of connected spheres (polymer) interacting with a granular environment of self-propelled balls (solvent). The spheres are ping-pong balls, each of mass 2.2 g and radius 1.9 cm. The spheres are linked together on a single thread so as to form a linear chain. Neighboring spheres are separated by spacers 7.0 mm in length. The spacers act as rigid bonds that freely rotate. The self-propelled balls are motorized balls, known commercially as “squiggle balls.” Each ball has a mass of 120 g and a radius of 4.0 cm. A battery-powered motor inside the ball rotates its plastic shell at approximately 3 rev/s. When placed on a surface, the ball rolls without slipping. During a collision, the ball rebounds in a random direction. In a system of balls, each ball moves with a distribution of speeds between 0 m/s and about 0.75 m/s. During a sufficiently long time, each ball appears to visit every square centimeter (cell) of the surface (phase space). In this sense, the motion of these “motorized molecules” is ergodic. Motorized molecules have recently been used to illustrate the fundamental principles of statistical mechanics, including the fundamental postulate, the ergodic hypothesis, and the canonical statistics [12]. A schematic of the granular polymer solution is shown in Fig. 1. The linear chain and the motorized balls are confined to a two-dimensional container consisting of a horizontal surface and a circular wall. One end of the chain is attached to the center of the area. The length of the completely stretched chain is less than the radius of the container. The inner surface of the circular wall has irregularities, in the form of wavy protrusions, to help randomize the motion of the balls. The concentration of motorized balls is approximately 50 balls/m².

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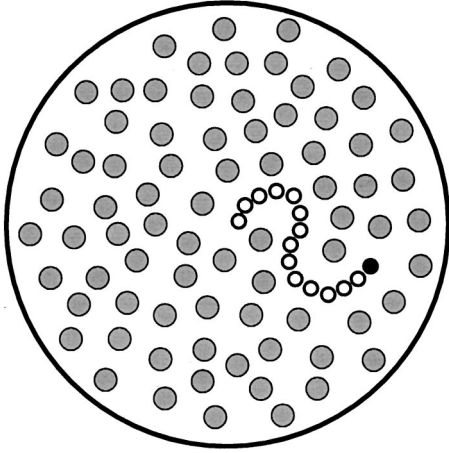


FIG. 1. The granular polymer solution consists of a linear chain of plastic spheres immersed in a planar fluid of self-propelled balls.

Until now, experiments [2–4] have focused on the velocity states of a granular gas (unconnected grains) using an electromechanical vibrator to shake the walls of the container. This source of agitation is *extended*, *peripheral*, and *periodic*. In our experiment, we focus on the position states, or conformations, of a granular polymer (chain of grains). The energy source is a set of electromechanical balls moving randomly within the container. This source of agitation is *granular*, *internal*, and *random*. The “thermal reservoir” of motorized balls provides the “temperature bath” that allows the polymer to explore phase space. The temporal sequence of states that the chain visits during its dynamical evolution corresponds to the set of random conformations of a self-avoiding random walk in two dimensions.

The experiment consists of measuring the end-to-end length $r(t)$ of the chain as a function of time. The free end of the chain is marked with a different color than the rest of the chain. This is the granular analogue of labeling elements of a molecular polymer, via deuterium substitution, in order to measure correlation functions in neutron scattering experiments. In our experiment, a video camera mounted above the center of the container records the motion of the granular polymer. The mean-square end-to-end length $\langle r^2 \rangle$ of the chain is defined as the time average of the dynamical function $r^2(t)$:

$$\langle r^2 \rangle \equiv \frac{1}{\tau} \int_0^\tau r^2(t) dt.$$

We have measured $r(t)$ and computed $\langle r^2 \rangle$ of chains containing N links for $5 \leq N \leq 15$. Each link has unit length. Thus for a chain with N links, the minimum end-to-end length is $r=0$ (closed loop) and the maximum end-to-end length is $r=N$ (straight line). Data was recorded at a video rate of two frames per second, while the collision rate of the solvent balls with the chain was on the order of five balls per second. The observation time τ ranged from 1000 seconds for $N=5$ to 1600 seconds for $N=15$. These values of τ are long enough to ensure that the time average of $r(t)$ is independent of τ . We tested this ergodic behavior by comparing

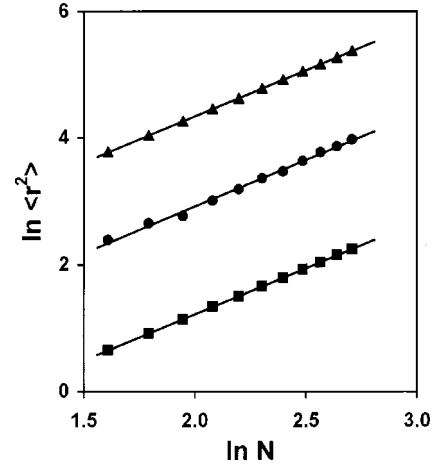


FIG. 2. The scaling behavior $\langle r^2 \rangle \sim N^{2\nu}$. Experimental data (●) for the granular polymer are compared with the theoretical data for self-avoiding random walks on the triangular (▲) and the square (■) lattices. To distinguish the three lines, the theoretical values $\langle r^2 \rangle$ have been multiplied by a constant. The slopes of the best-fit lines are 1.47 (●), 1.46 (▲), and 1.45 (■).

$\langle r^2 \rangle$ for different subsets of the total observation time and found good agreement. It appears that during the time interval of observation, the chain uniformly visits a coarse-grained volume of phase space that is representative of the equilibrium state of a self-avoiding random walk.

The experimental data, $\langle r^2 \rangle$ as a function of N , is graphed as a log–log plot in Fig. 2. For comparison, we also graph the theoretical data based on the exact enumeration of self-avoiding walks on the square lattice [8] and the triangular lattice [13]. The error in each value of $\langle r^2 \rangle$, which is less than 3%, is too small to appear on the graph. Note that the theoretical results are based on spatial averages of a single particle walking in a discrete (lattice) space, while the experimental results are based on temporal averages of a single chain meandering in a continuum (off-lattice) space. The graphs in Fig. 2 show that the theoretical data for the self-avoiding walks closely matches the experimental data for the granular polymer. Even for these modest values of N , the data points form a straight line. The slopes of the best-fit lines in Fig. 2 are 1.45 (square-lattice theory), 1.46 (triangular-lattice theory), and 1.47 (granular polymer experiment). Note that the triangular lattice has a higher connectivity than the square lattice and thus provides a better approximation to the off-lattice topology. The slopes of the best-fit lines through large N subsets of the experimental data points are 1.55 ($N=10-15$), 1.60 ($N=11-15$), 1.50 ($N=12-15$), and 1.42 ($N=13-15$), whose average is 1.52. The slope values, 1.47 and 1.52, for the granular-polymer system are consistent with the conjectured exact value, $2\nu = 3/2$, for the self-avoiding random walk in two dimensions. Note that for a random walk, the exact value is $2\nu = 1$ in any dimension. It is well known that critical exponents can reveal their identity in walks of modest length ($N \approx 15$), even though in principle the exponents are defined for walks of infinite length [8]. Another technique to extract the critical exponent from finite- N data is to construct a converging sequence of approximate exponents [8]. Let the average length

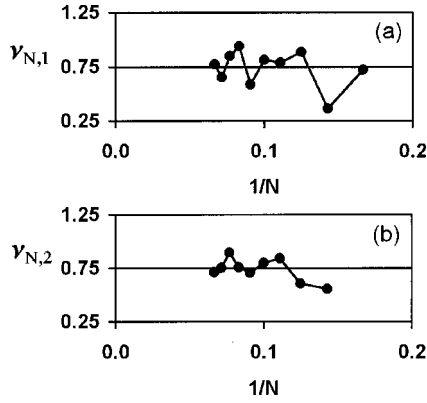


FIG. 3. Convergence of the critical exponent $\nu_{N,J}$ as $N \rightarrow \infty$ for (a) $J=1$ and (b) $J=2$.

of a chain containing N links be denoted by $R_N \equiv \langle r^2 \rangle^{1/2}$. From the measured values of R_N and R_{N-J} , we calculate $\nu_{N,J} \equiv [\ln(R_N/R_{N-J})]/\ln[N/(N-J)]$. A graph of $\nu_{N,1}$ as a function of $1/N$ is shown in Fig. 3. The values of $\nu_{N,1}$ oscillate around the value 0.75 with decreasing amplitude as N increases. Similar damped oscillations occur in computer experiments [8]. To reduce the effect of the oscillations, we compute the sequence $\nu_{N,2}$ which is graphed in Fig. 3.

Based on the linearity of the granular-polymer data, the slopes of the best-fit lines, and the converging sequences of log-ratio exponents, we conclude that $\langle r^2 \rangle \sim N^{2\nu}$, with $\nu = 0.75 \pm 0.01$. This value of the end-to-end exponent also reflects the close agreement (equality of slopes within 0.68–1.4%) between the granular-polymer data and the exact-enumeration data as displayed in Fig. 2. An analysis of the exact-enumeration data corresponding to a similar range of N as the granular-polymer data predicts values of the critical exponent between 0.745 and 0.750 [8]. The radius of gyration exponent for adsorbed molecular polymers has been measured to be 0.79 ± 0.04 [10] and 0.79 ± 0.01 [14].

The spectrum of fluctuations in the end-to-end length r of the polymer chain is characterized by the probability distribution $P(r)$. The end-to-end distribution has been theoretically studied in all dimensions [7,11] and numerically simulated in two [15] and three [11,15–17] dimensions, but to our knowledge has never been experimentally measured. The measured distribution for a granular polymer with $N=12$ monomers is shown in Fig. 4. For comparison, we also graph the random-walk distribution, $br \exp(-cr^2)$ where b and c are normalization constants, and the Mazur distribution, $br \exp(-cr^7)$. The Mazur distribution, originally formulated to fit the exact-enumeration data of self-avoiding walks on the square lattice [15], is a purely empirical distribution and is used here solely because it provides a simple modified version of the Gaussian distribution that visually fits the granular polymer data. The shape of the granular polymer distribution clearly displays the major effect of the self-avoiding interaction on the random-walk statistics, namely, to concentrate the distribution around the average value [18].

Theories [6–8] of the self-avoiding walk in d dimensions predict that the limiting ($N \rightarrow \infty$) form of the distribution function of the end-to-end vector \mathbf{r} is $P(\mathbf{r}) = R^{-d} f(r/R)$,

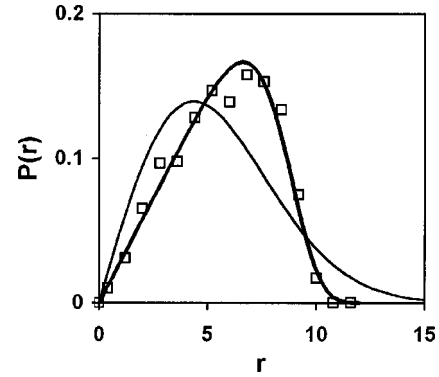


FIG. 4. Probability distribution $P(r)$ of the end-to-end length r of a granular polymer chain (\square) with 12 links. The bold curve through the experimental data points is the Mazur distribution for a self-avoiding random walk, and the light curve is the Gaussian distribution for a random walk, both with the same $\langle r^2 \rangle^{1/2} = 6.15$ as the granular chain.

where $r = |\mathbf{r}|$, $R = \langle r^2 \rangle^{1/2}$, and $f(x)$ is a universal function of the scaled length $x = r/R$. Compared to the universal exponent ν , not much is known about the universal function $f(x)$. In theory, only the asymptotic behavior of $f(x)$ for $x \ll 1$ and $x \gg 1$ is known with rigor [7]. A phenomenological representation of $f(x)$ for all x , motivated by scaling and renormalization theories, has been proposed [7,19]: $f(x) = Ax^\theta \exp(-Bx^\delta)$. The exponents θ and δ are related to the fundamental universal exponents ν and γ : $\delta = 1/(1-\nu)$ and $\theta = (\gamma-1)/\nu$ [7]. The constants A and B depend on θ and δ via the normalization conditions on $P(r)$ and $\langle r^2 \rangle$. The distribution based on this scaling function, which is referred to as the des Cloizeaux distribution, has been shown to provide an accurate fit to the large N numerical data based on Monte Carlo simulations of self-avoiding walks in two [15] and three [11,15–17] dimensions. Experimental data would be worthwhile.

In Fig. 5, we graph the scaled distribution function for granular polymer chains with N ranging from 10 to 15. Even

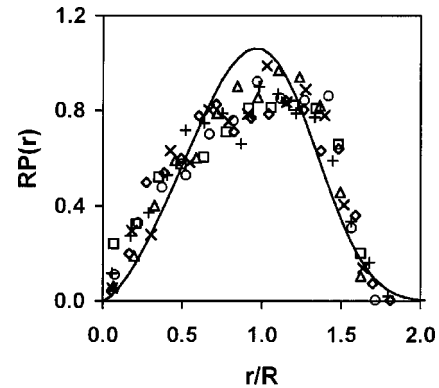


FIG. 5. The scaled probability distribution $RP(r)$, with $R = \langle r^2 \rangle^{1/2}$, as a function of the scaled end-to-end length r/R for granular polymer chains with different number of links, $N=10$ (\circ), 11 (\square), 12 (\triangle), 13 (\times), 14 ($+$), 15 (\diamond). The theoretical (solid) curve is the limiting ($N \rightarrow \infty$) distribution based on the universal scaling function of des Cloizeaux.

for these modest values of N , a universal behavior is evident—the scaled data representing different chains tend to cluster together so as to form a single experimental curve. For comparison, we also show the theoretical curve defined by the universal des Cloizeaux distribution: $RP(r) = 2\pi x f(x)$, where $f(x) = 0.257x^{11/24} \exp(-0.421x^4)$. We calculated the exponents and the coefficients in this scaling function using the exact two-dimensional values $\nu = \frac{3}{4}$ and $\gamma = \frac{43}{32}$ [7]. Figure 5 shows that the large N theoretical distribution approximates the overall shape of the small N granular polymer distribution. The deviations near the origin and the peak are consistent with Monte Carlo predictions [15–17]. Whereas the second moment $\langle r^2 \rangle$ of the granular polymer distribution converges to its limiting form for relatively small values of N , it appears that the distribution $P(r)$ itself converges for larger values.

In conclusion, we have presented a granular model of a polymer solution—a granular polymer in a granular solvent. Since the granular polymer is self-avoiding, freely jointed, and exactly planar, it is an ideal system with which to test the theories of polymers and self-avoiding random walks in two dimensions. We find that the granular polymer is a critical object whose size scales with its mass according to the power law $\langle r^2 \rangle \sim N^{2\nu}$. The measured value of the critical exponent, $\nu = 0.75 \pm 0.01$, agrees with the long-standing theoretical conjecture, $\nu = \frac{3}{4}$. Self-propelled balls provide a Brownian-like driving force that can be used as the source of agitation for other granular matter. A fluid of motorized molecules is itself a novel dynamical system that can provide insight into the statistical mechanics of a fluid of natural molecules.

We thank Jeffrey Nazarko for his contribution to the early stage of this research.

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- [1] H. M. Jaeger, S. R. Nagel, and R. P. Behringer, *Rev. Mod. Phys.* **68**, 1259 (1996).
 [2] F. Rouyer and N. Menon, *Phys. Rev. Lett.* **85**, 3676 (2000).
 [3] W. Losert *et al.*, *Chaos* **9**, 682 (1999).
 [4] J. S. Olafson and J. S. Urbach, *Phys. Rev. E* **60**, R2468 (1999).
 [5] E. Ben-Naim *et al.*, *Phys. Rev. Lett.* **86**, 1414 (2001).
 [6] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).
 [7] J. des Cloizeaux and G. Jannink, *Polymers in Solution: Their Modelling and Structure* (Clarendon Press, Oxford, 1990).
 [8] B. D. Hughes, *Random Walks and Random Environments Volume 1: Random Walks* (Clarendon Press, Oxford, 1995).
 [9] B. Nienhuis, *Phys. Rev. Lett.* **49**, 1062 (1982).
 [10] B. Maier and J. O. Rädler, *Phys. Rev. Lett.* **82**, 1911 (1999).
 [11] S. Caracciolo, M. S. Causo, and A. Pelissetto, *J. Chem. Phys.* **112**, 7693 (2000).
 [12] J. J. Prentis, *Am. J. Phys.* **68**, 1073 (2000).
 [13] P. Grassberger, *Z. Phys. B: Condens. Matter* **48**, 255 (1982).
 [14] R. Vilanove and F. Rondelez, *Phys. Rev. Lett.* **45**, 1502 (1980).
 [15] M. Bishop and J. H. R. Clarke, *J. Chem. Phys.* **94**, 3936 (1991).
 [16] J. Dayantis and J. Palierne, *J. Chem. Phys.* **95**, 6088 (1991).
 [17] J. P. Valleau, *J. Chem. Phys.* **104**, 3071 (1996).
 [18] C. Domb, J. Gillis, and G. Wilmers, *Proc. Phys. Soc. London* **85**, 625 (1965).
 [19] S. Redner, *J. Phys. A* **13**, 3525 (1980).