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Conformation of graphite oxide membranes in solution

Terence Hwa
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

Etsuo Kokufuta
Institute of Applied Biochemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Toyoichi Tanaka
Department of Physics and Center for Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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We report an experimental study of polymerized membranes using graphite oxide (GO) suspension. Dry samples of GO are analyzed using electron microscopy and electron diffraction. They are found to be composed of thin solid membranes. The conformation of these membranes in solution is investigated using light scattering and is found to be fractal.

There has been a considerable amount of interest in understanding the properties and behaviors of surfaces and membranes [1]. Applications of this new branch of science range from cell-membrane interactions in biology [2] to world-sheet dynamics in string theory [3]. One class of membranes that is being intensively studied recently is that of *polymerized (or tethered) membranes* [4]. These membranes are two-dimensional analogs of linear polymer chains; their study is a natural extension of polymer physics [5]. Just like polymers, such membranes collapse into compact forms [6] when placed in inappropriate solvents. They can "swell" and take on fractal conformations ("crumpled") in appropriate solvents. However, due to rigidity as well as much more pronounced excluded-volume interactions, the membranes can also be "flat" (like stretched polyelectrolytes [5]) under suitable circumstances such as appropriate solvents and low temperature [7,8].

There has been much theoretical work concerning the nature of the crumpled [4,9–11] and the flat [12,13] membranes, and the transition between the two phases [14]. In the flat phase, the membrane is characterized by an effective width w which scales with the linear size L as L^{ζ} [15,16]. In the crumpled phase, the membranes are self-similar and characterized by a fractal dimension D_f [4]. A Flory estimate gives $D_f = 2.5$. However, the expected crumpled phase has never been observed in simulations of self-avoiding membranes [15].

Despite the many activities in theory and simulations, there has been very little progress in this field from the experimental side. One major obstacle lies in the difficulty in obtaining such membranes. While making large two-dimensional sheets (e.g., writing papers) is easy, it becomes much more difficult to obtain small and thin sheets which can equilibrate in experimentally feasible times. For instance, the thickness of a 10×10-μm^2 membrane should be less than 100 Å for a reasonable aspect ratio of 1000:1. To obtain such thin membranes, some of the approaches attempted have been isolation of the red-blood-cell membrane skeleton (spectrin network) [17], and partial polymerization of phospholipid vesicles [18]. However, the work in spectrin network is marred by various technical difficulties associated with biological samples, while the randomly polymerized network may belong to a different universality class from polymerized solid membranes [19].

Recently, we have succeeded in synthesizing thin membranes of graphite oxide (GO) by exfoliating graphite [20]. In this Rapid Communication, we first describe briefly the method used to prepare the GO suspension. The sample obtained is then characterized using electron microscopy and diffraction and found to be composed of solid thin membranes (≤ 100 Å thick). The conformation of the membranes is probed using quasistatic light scattering. Our results indicate that the membranes in solution fold into fractal shapes. The observed fractal dimension is rather close to the Flory estimate for a crumpled membrane.

GO, also known as graphitic acid, has been known for over a century [21]. There exist a number of ways of GO preparation, all involving treating graphite with strong oxidizing agents such as potassium chlorate [22] or potassium permanganate [23]. Although the reaction is itself simple, great care must be taken in controlling the rate of reaction so that the reaction proceeds safely to completion. The synthetic method used in this experiment is based on Ref. [23], though the optimal reaction condition is found by trial and error as is usual in any chemical reaction. The product obtained after careful purification is a solid with a brownish yellow color. Its chemical properties have been investigated in Ref. [24]. It consists of layers of carbon networks loosely attached via association with oxygen. On average, one oxygen atom is added for every two carbon atoms.

GO does not disperse well in pure water, but the dispersibility is much improved in alkaline solution. We tested GO dispersibility in an aqueous solution containing different amounts of NaOH (pH 7–14) and found maximum dispersibilities at pH values close to 11. The pH dependence of the dispersibility is attributed to dissocia-

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tion changes of the carboxyl groups (COOH) attached to GO resulting from the oxidation of graphite. An increase in the basicity yields negatively charged GO through the dissociation of COOH, bringing about the increased dispersibility. However, high basicity is accompanied by an equally high concentration of cations (Na^+ in this case). This tends to decrease the dispersibility through electrostatic screening of the negative charges on GO by the cations. Therefore, there is an optimum *p*H value in the GO dispersibility depending on the balance between these factors.

In the experiment reported here, we disperse 1 mg of purified GO in 10 ml NaOH solution ($0.01M$). The suspension is vigorously agitated (by manual shaking or by ultrasonicator), and then left standing for several days. Afterwards, the suspension is centrifuged for 20 min, and the precipitate is discarded. The remaining suspension contains 0.1% to 1% (wt.%) of GO [25]. The suspension is homogeneous in appearance and brown in color. Inspection in optical microscope reveals micron-sized particles executing Brownian walks as well as tumbling and spinning. For typical concentrations, interparticle distance is about 10 times the particle size. Particle-particle adhesion is not observed and the suspension is stable for weeks.

The physical structure of GO particles is first examined by electron microscopy. A drop of GO suspension is left on a sample holder made of thin carbon or silicon film. The suspension is dried in air and the remaining GO is examined using a transmission electron microscope. A typical picture is shown in Fig. 1, indicating that the suspension is composed of thin films. The typical thickness of these films is estimated to be between 50 and 100 Å by comparing the transmitted electron intensity with the background intensity. The connectivity of the GO thin films is probed by diffracting electrons. Figure 2 shows a resulting diffraction pattern for a single piece of film. The sharpness of the rings indicates an ordered atomic structure. The interatomic spacing is estimated to be close to that of the graphitized carbon (~2.5 Å). Also, the sixfold orientational order of the starting graphite remains in GO to some extent.

The conformation of GO in solution is readily probed using light scattering. Recall that the structure factor for a fractal object is [26].

$$S(q)=q^{-D_f}F(qR)\,,$$

where q is the scattering wave vector, R is the radius of gyration, and D_f is the fractal dimension. A flat membrane has $D_f=2$ while a compact object has $D_f=3$. A crumpled membrane may have $2<D_f<3$.

The size R of the membrane cannot be controlled in the synthesis and has a broad distribution (i.e., polydispersed). It is therefore important to understand the size dependence of the structure factor which enters through the scaling function $F(qR)$. For $qR \ll 1$, the membrane appears as a point scatterer to the incident light. $S(q)$ cannot be q dependent, implying, $F(x\rightarrow 0)\rightarrow x^{D_f}$. How-

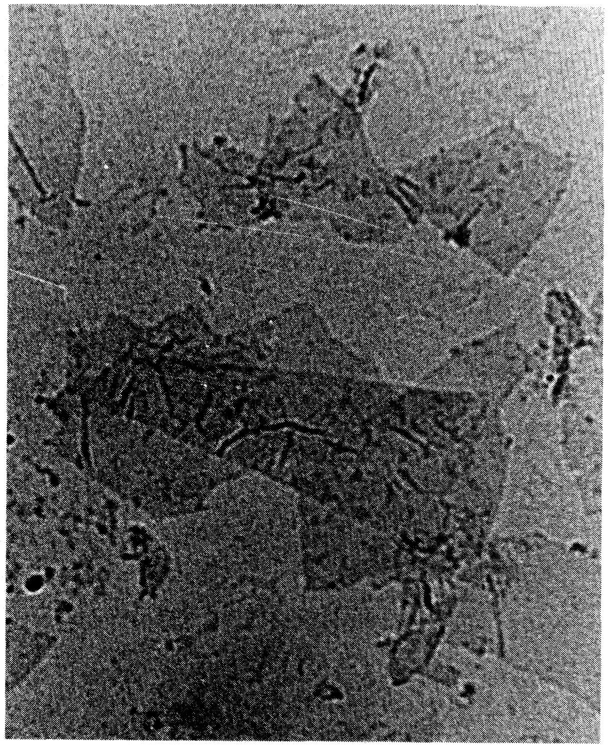

FIG. 1. A transmission electron microscope picture of some dried graphite oxide membranes. The area shown has a linear dimension of a few micrometers.

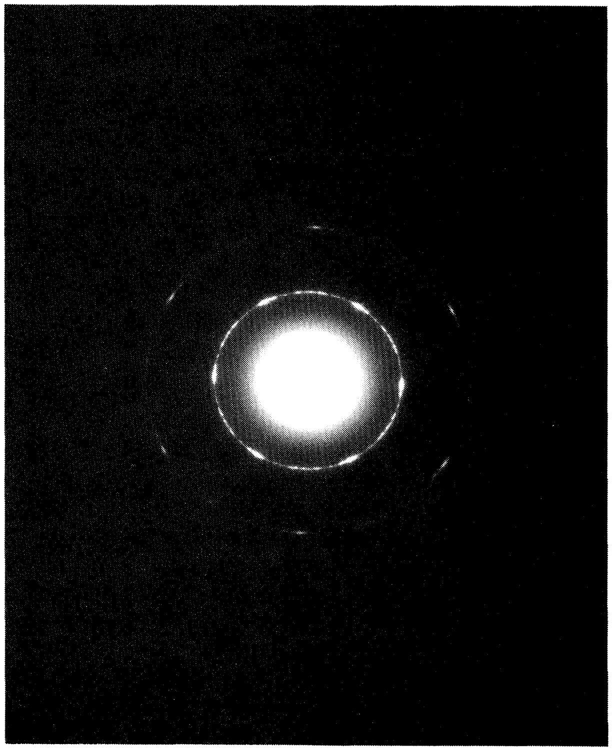

FIG. 2. An electron-diffraction pattern of the GO membranes.

ever, for $qR \gg 1$, the scattering only probes the *internal* structure of the membrane which cannot depend on the membrane size. Hence, $F(x \rightarrow \infty) \rightarrow$ const. We see that if we limit ourselves to probing only the *large* membranes, then the structure factor takes on the simple form $S(q) \sim q^{-D_f}$, independent of the polydispersity. In our light-scattering experiment, we use the 514-nm line of the argon cw laser. The smallest q probed is approximately 2 μm^{-1}. Thus it suffices to study only membranes with $R > 0.5$ μm.

In the experiment reported here, the following approach is used for size selection: We first measure the structure factor $S_1(q)$ for a sample containing all membrane sizes. Next we remove the *large* membranes from the sample and obtain the structure factor $S_2(q)$ for the remaining small membranes. Taking the difference between $S_1(q)$ and $S_2(q)$ yields the desired structure factor for the large membranes.

In practice we take two samples from the same GO suspension. One sample is filtered by a membrane filter with 0.5-μm pore size to obtain the contribution to $S(q)$ from small particles. The other sample is filtered by a 5-μm membrane filter to remove dirt in the sample. The structure factors obtained from the two samples are shown in Fig. 3 by $\triangle$ and ∇. The solid circles are the differences between these two sets of data. They represent the contribution to the scattered light intensity from the membranes ranging from 0.5 to 5 μm in size.

Since the length of the probe is under 0.5 μm, the structure factor obtained for these large membranes reflects the *internal* density correlations of the membranes. The data are nicely fitted to a straight line on a log-log scale for the probe interval of 500–5000 Å, indicating that membranes are self-similar over this range of length scales. The fractal dimension of the membranes may be obtained from the slope of the straight line, yielding $D_f = 2.4 \pm 0.1$, where the uncertainty is obtained from sample-to-sample fluctuation. Recently, we developed techniques to select the large membranes directly. The structure factors obtained have the same scaling behaviors.

Our result is compatible with the hypothesis that membranes are crumpled in appropriate solvents. In fact, the value of the fractal dimension obtained is close to the Flory estimate ($D_f = 2.5$) for crumpled membranes. Also, the result is not in favor of a flat phase: As described in Ref. [16], a flat membrane of linear size L will have $S(q) \sim q^{-2}$ for $qw \ll 1$ where $w \sim L^{\zeta}$ is the effective width. It crosses over to $S(q) \sim q^{-2/\zeta}$ for larger q's. The value of the roughness exponent ζ was found to be 0.65 in Ref. [16]. However, recent studies [27] suggest a smaller value close to 0.5. Thus the structure factor will have to bend to as much as $\sim q^{-4}$ at large q's. Such bending clearly cannot be accommodated by the result shown in Fig. 3 even if the bending is a gradual one, given the polydispersity in L.

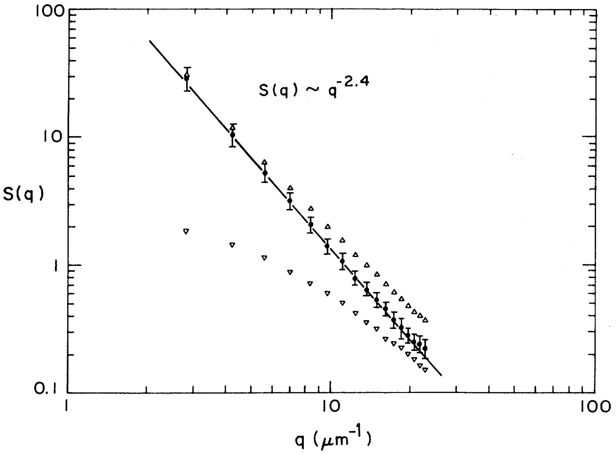

FIG. 3. The scattered light intensity of GO membranes in alkaline solution (pH = 11). $\triangle$ is the result from the polydispersed suspension with all particles under 5 μm. ∇ denotes the contribution of the small particles (< 0.5 μm). The difference (indicated by ●) is the contribution from particles with sizes between 5 and 0.5 μm. Here, the error bars indicate the magnitude of the combined errors of the two data sets.

However, a number of other possibilities may give the appearance of a self-similar crumpled phase: Due to the existence of polydispersity in the membrane *thickness* (and hence its bending rigidity), the GO dispersion may contain a mixture of membranes in the flat ($D_f = 2$) and compact ($D_f = 3$) phases. The structure factor of such a mixture will of course cross over from q^{-2} at high q to q^{-3} at low q. A broad distribution in membrane thickness may then yield an effective fractal dimension between 2 and 3 for an intermediate range of q. Another possibility is that the membranes are not equilibrated and are instead locked into some frozen conformations. It is known that random folding of a piece of paper yields an object with a fractal dimension close to 2.5 [28].

Needless to say, a lot more detailed studies are required to elucidate the nature of the observed self-similar membrane conformation. We are currently studying the behavior of GO suspensions under various solvent conditions; this knowledge will help to determine whether the observed self-similar conformation is a true thermodynamic phase. Efforts are also underway to study the *internal* motion of the membranes by means of dynamic light scattering.

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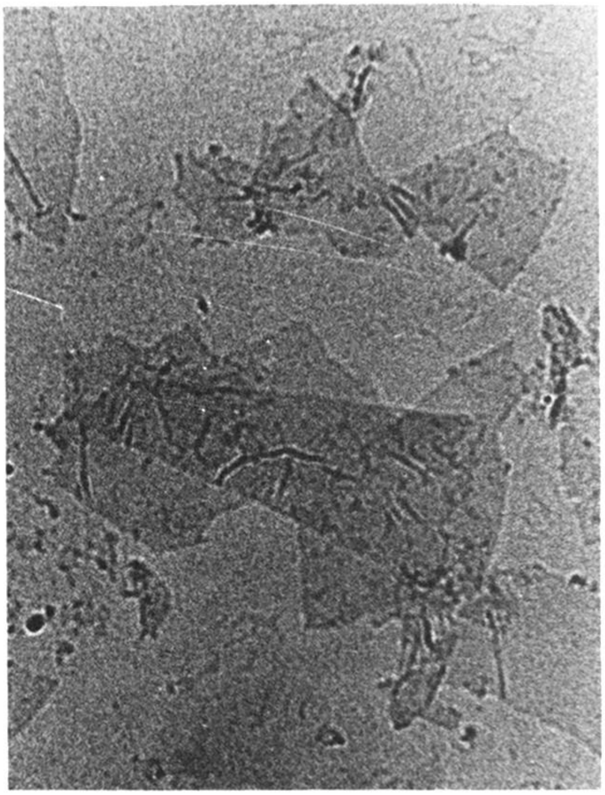

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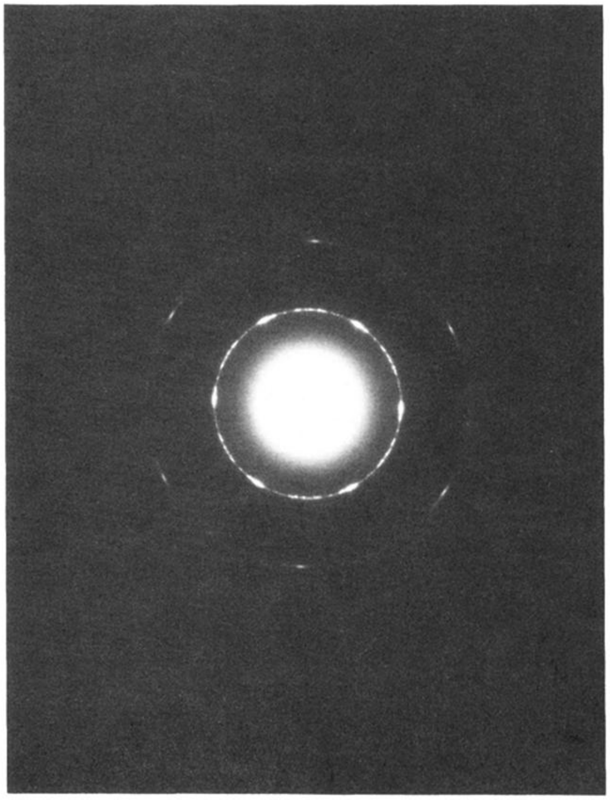

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