Impermeable Atomic Membranes from Graphene Sheets

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Abstract:

We have fabricated membranes one atom in thickness from graphene sheets and have shown that they are not only impermeable to gases but can support pressure differences larger than one atmosphere. We use such pressure differences to tune the mechanical resonance frequency by ~ 100 MHz. This allows us to measure the mass and elastic constants of graphene membranes. By measuring the gas leak rates from membrane-sealed nanochambers, we present strong evidence that graphene is vacancy-free over square microns. Our results show that single atomic sheets can be integrated with microfabricated structures to create a new class of atomic-scale membrane-based nanomechanical devices.

Summary of Research:

Membranes are fundamental components of a wide variety of physical, chemical, and biological systems, used in everything from cellular compartmentalization to mechanical pressure sensing. They divide space into two regions, each capable of possessing different physical or chemical properties. Graphene, which is a single layer of graphite, represents the ultimate limit in thickness for such membranes. Here we give the first demonstration of graphene as a membrane separating two environments.

We fabricated graphene-sealed microchambers—shown schematically in Figure 1—on silicon wafers by a combination of standard photolithography and mechanical exfoliation of graphene sheets. On a silicon wafer coated with 280 nm of oxide, we defined holes with areas ranging from 1 to 60 µm² and depths between 250 nm and 3 µm. We then mechanically exfoliated Kish graphite onto the surface by cleaving it with Scotch tape and then rubbing it onto the surface. This resulted in graphene sheets with thicknesses from 1 to ~ 75 layers becoming suspended over the holes to form sealed microchambers containing ~ 1-100 µm³ of confined gas.

We can tune the strain of these membrane-sealed microchambers by placing them into an environment with higher or lower external pressure. Figure 2 shows an atomic force microscope (AFM) topographic image of a microchamber with vacuum on the inside and atmospheric pressure on the outside. Over time, air leaks through the graphene-SiO₂ interface and the internal and external pressures equilibrate, as shown by the AFM line traces through the center of the membrane in Figure 3. We can estimate the leak rate by monitoring the deflation over time, and using the ideal gas law to convert the pressure change to the change in the number of particles. We find that air and argon show similar leak rates, while helium is 2 orders of magnitude faster. The helium leak rates ranged from 10⁵ atoms/s to ~ 10⁶ atoms/s with no noticeable dependence on thickness from 1-75 atomic layers.

The lack of dependence of the leak rate on the membrane thickness indicates that the leak is not through the graphene.
sheets, or though defects in these sheets. This suggests that the leak is either through the glass walls of the microchamber or through the graphene-SiO$_2$ sealed interface. The former can be estimated from the known properties of helium diffusion through glass to give a leak rate of $\sim 1-5 \times 10^6$ atoms/sec, which is close to the range of values measured. This analysis leads us to conclude that the graphene layer is vacancy-free and impermeable to all standard gases, including helium.

Using the optical drive-detection scheme reported in Ref. 2, we can mechanically vibrate the graphene membranes and thus measure their resonance frequency. The ability in these microchamber devices to apply a pressure difference across the graphene membrane, allows us to tune the membrane’s resonance frequency by as much as 100 MHz. Figure 4 shows the results of some typical resonance measurements on a 1.5 nm thick membrane, at various external pressures (and negligible internal pressure).

From the AFM static deflection measurements of Figure 2, we can extract the mechanical stiffness, $E_t/(1-\nu) = 390 \pm 20$ N/m, where $E_t$ is the thickness-independent Young’s modulus and $\nu$ is Poisson’s ratio. Using this value for $E_t/(1-\nu)$ we can fit a theoretical model to the data of Figure 4 to determine the mass per area, $m$, of the membranes. For a monolayer device, we find $m = 9.6 \pm 0.6 \times 10^{-7}$ kg/m$^2$. This mass is 30% higher than the theoretical value for a single layer of graphene of $7.4 \times 10^{-7}$ kg/m$^2$.

In this work, we have given the first demonstration of using a one-atom-thick membrane to separate two disparate environments. We have used AFM and optically-driven mechanical resonance measurements to characterize the leak rates of gas into and out of graphene-sealed microchambers, and shown that the graphene itself is impermeable to all standard gases, including helium. We have shown that these devices offer the ability to both to measure the membrane’s elastic constants, and to tune its mechanical resonance frequency by as much as 100 MHz. We envision the use of graphene membranes in applications ranging from nanoscale pressure sensing, to investigations of nanoscale thermodynamics, to high-vacuum scanning tunneling microscope (STM) studies of liquids and gases, where the fluids are separated from vacuum environment by graphene membranes.

References: