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Effects of physisorption of xenon on the thermal conductivity of resorcinol-formaldehyde aerogels

Jianyu Lou, Steven Harrington, and Da-Ming Zhu
Department of Physics, University of Missouri–Kansas City, 5110 Rockhill Road, Kansas City, Missouri 64110

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The effects of adsorption of xenon to the thermal conductivity of a resorcinol-formaldehyde aerogel were investigated in a temperature range from 20 to 120 K. It was found that at temperatures below 75 K, the adsorbed xenon has little effect on the thermal conductivity. Rapid rises of the thermal conductivity develop at temperatures around 75–80 K with magnitudes roughly proportional to the amount of xenon adsorbed. The effect is explained as due to adsorbed xenon atoms that enhance the neck connection between aerogel particles. [S1063-651X(99)09411-8]

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I. INTRODUCTION

Aerogel materials have extraordinarily low thermal conductivity due to their unique microscopic structures and morphology, which can be characterized as consisting of nanometer-sized particles which form tortuous chains interconnected into an open skeleton [1–14]. The low-volume fraction of the material reduces the number of passage channels available to transport thermal energy [3,4,11]. The tortuous nature of the solid paths and the smallness of the particles that form the paths limit the propagating speed and the mean free path of thermal excitation [15]. The smallness of the pore sizes also limits the mean free path of gas molecules existing in the pore structure, further reducing the overall thermal conductivity [11,16,17]. These factors make this class of materials one of the best thermal insulators with various potential applications.

However, due to the extraordinarily large surface area, adsorption of atoms or molecules onto an aerogel surface might significantly influence its thermal conductivity and other properties. In particular, adsorption might increase the connection between aerogel particles by forming menisci or bridges between them. Since the size of the aerogel particles is typically on the order of tens of nanometers, adsorption of a few equivalent layers of atoms or molecules could results in significant changes in the tortuosity and connectivity, and thus the thermal conductivity of the system.

The thermal conductivity of aerogels has been previously studied as a function of gaseous pressure [6,8,11]. Presumably the presence of gas molecules would not only introduce the gaseous conductance, but also cause a certain degree of adsorption on the surface of aerogels. These studies were, however, focused on the effect of the smallness of pore size on the gaseous conductance. The influence of adsorption of gas molecules on the surface of an aerogel upon its thermal transport properties has not yet been systematically investigated. Considering the extremely low thermal conductivity of aerogels, any modification of the structure and morphology due to adsorption of atoms or molecules might produce a measurable change in the thermal conductivity. The change, when incorporated with results from other approaches, will in turn provide information leading to a better understanding of the structures and the properties of the materials. The purpose of this study is to investigate the effects of physisorption of xenon atoms on the thermal conductivity of an organic aerogel. Xenon is a noble gas and its adsorption on other surfaces, i.e., graphite, has been studied quite extensively [18]. The effects of adsorption on the thermal conductivity were investigated in this study in a temperature range from 20 to 120 K. At these temperatures, the radiative conductance is very small, so the possible change of the specific extinction coefficient of the aerogel [8] should not interfere with the effects caused by changes in the microscopic morphology of the material due to adsorption. The vapor pressure of xenon at these temperatures is low, so that the thermal conductance due to gaseous flow would not significantly contribute to the thermal conductivity of the system.

It should be noted that the study of gas adsorption on aerogel thermal conductivity is important to potential applications of the material, as many such applications are in the ambient environment where the material's large surface area will be exposed to many different substances. Even though the adsorption of air molecules at room temperature may not be significant, a continuous accumulation of adsorbates, such as water, may gradually cause a deterioration of the thermal insulating properties of the material.

II. EXPERIMENTAL METHODS

The aerogel used in this study is a piece of resorcinol-formaldehyde (RF) aerogel derived from the base-catalyzed aqueous polycondensation of resorcinol with formaldehyde. The microscopic structure of the RF aerogel has been the subject of recent studies using various techniques and simulations [19–21]. Many properties of RF aerogels, such as density, particle size, mechanical strength, and microscopic structure, are influenced by the initial resorcinol to catalyst ratio (R/C) [19,20]. As the catalyst increases, the structures of the aerogels vary from colloidal-like to well-connected polymericlike [19,20]. The specific surface area of RF aerogels is found to be comparable to silica-based aerogels [20]. RF aerogels have a lower radiative conductivity, are more durable, and thus have been suggested as an alternative solid insulator to their silica-based counterparts [11,19,20].

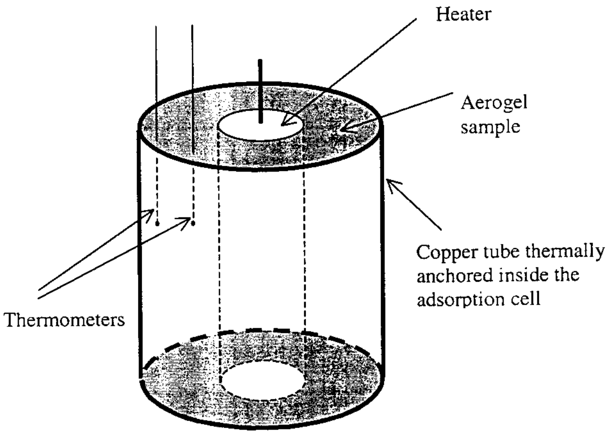

FIG. 1. Experimental setup: The shaded region represents a piece of monolithic RF aerogel. The aerogel was placed inside a copper cylinder that was anchored to a temperature stage inside an adsorption cell. Two thermocouple joints were inserted to the sample and different radius distances. A resistance heater was placed in the center of the sample to generate temperature gradient.

Thermal conductivity measurements with adsorption of xenon were conducted in a closed-cycle refrigerator. The experimental sample was a piece of cylindrical shaped monolithic RF aerogel synthesized with an R/C ratio of 200 and density of 0.195 g/cm^3. Electron microscopy results show that, at this R/C ratio, the structure of the RF aerogel consists of interconnected chains formed mainly by colloidal-like particles [19,20]. The total surface area of the sample was 530 m^2, as determined from measurements of vapor pressure isotherms. A resistance heater was fitted into a hole drilled along the axis of the sample, as shown in Fig. 1. The sample was then tightly fitted into a copper tube anchored to a temperature stage inside an adsorption cell through a copper block. The axis of the cylinder was oriented so that the temperature gradient was perpendicular to the gravitational field. This configuration was used to eliminate the possibility of xenon convection between the central heater and the copper tube when the center of the sample was heated.

The thermal conductivity of the aerogel was measured using a steady-state method. A constant heating power Q was applied to the resistance to create a temperature gradient along the radial direction. The heating power Q was determined by measuring the applied voltage and the current through the heater. Two thermocouple joints embedded at distances R_1 and R_2 from the central axis of the sample were used to measure the temperature difference ΔT at the two positions. The temperature drop created by the heating power from the heater to the copper cylinder was typically controlled at about one degree. The thermal conductivity of the sample is determined by

$$\kappa = [Q/2\pi L(\Delta T)]\ln(R_1/R_2). \qquad (1)$$

where L is the height of the cylinder. Due to the low thermal conductivity of the aerogel, thermal equilibrium time of the adsorption cell is quite long. For the evacuated sample the equilibrium time is about 20 min at 80 K. We found that the equilibrium time increases with temperature. When the aerogel sample was adsorbed with xenon, the equilibrium time increased slightly. We typically waited for twice the equilibrium time before recording a data point after the heating power was applied to the sample.

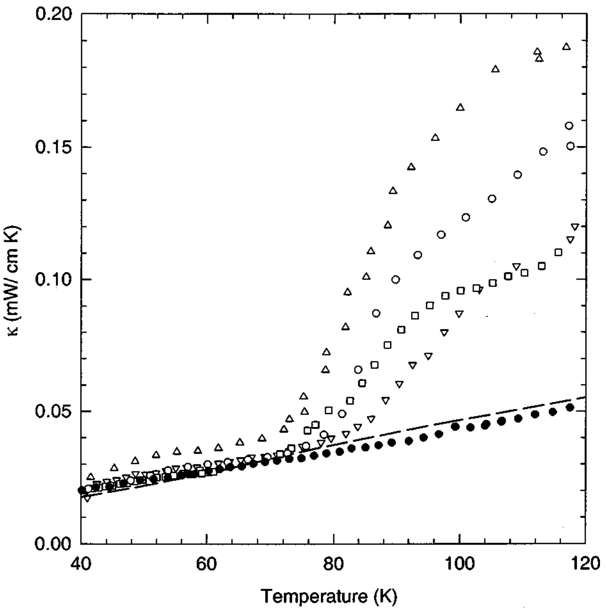

FIG. 2. Thermal conductivity of RF aerogel adsorbed with xenon. (●) Evacuated RF aerogel; (▽) adsorbed with 1.7×10^{21} xenon atoms; (□) adsorbed with 2.4×10^{21} xenon atoms; (○) adsorbed with 7.7×10^{21} xenon atoms; (△) adsorbed with 1.04×10^{22} xenon atoms. The capacity of an effective single layer on the RF-aerogel sample is equivalent to 3.2×10^{21} xenon atoms. The dashed line is the thermal conductivity of a silica aerogel with density 0.235 g/cm^3 (Ref. [3]).

The aerogel sample was first evacuated to 10^{-7} torr at a temperature of 350 K over a period of one week. The sample was then cooled in the vacuum to low temperatures, and the thermal conductivity of the evacuated RF aerogel was measured. Figure 2 shows the measured thermal conductivity of the evacuated RF aerogel. The magnitude and the temperature dependence of the RF aerogel's thermal conductivity appear to be very close to that of a silica aerogel in the temperature range studied [3,7]. The thermal conductivity of the evacuated RF aerogel measured in this study is also consistent with that previously measured at room temperature [11].

After the initial thermal conductivity measurements of the evacuated RF aerogel, a known amount of xenon gas was dosed into the cell at a temperature close to the bulk melting temperature of xenon (161 K). The sample was then slowly cooled down to 20 K over a period typically of 12–24 h. The thermal conductivity of the aerogel adsorbed with xenon gas was then measured.

III. EXPERIMENTAL RESULTS

Figure 2 shows the thermal conductivity of the RF aerogel adsorbed with different amounts of xenon atoms together with that of the evacuated aerogel. An apparent feature demonstrated in Fig. 2 is that the adsorption of xenon had little effect on the solid thermal conductivity of the RF aerogel at temperatures below 75 K. Above that temperature the thermal conductivity rises rapidly. Figure 3 shows the thermal

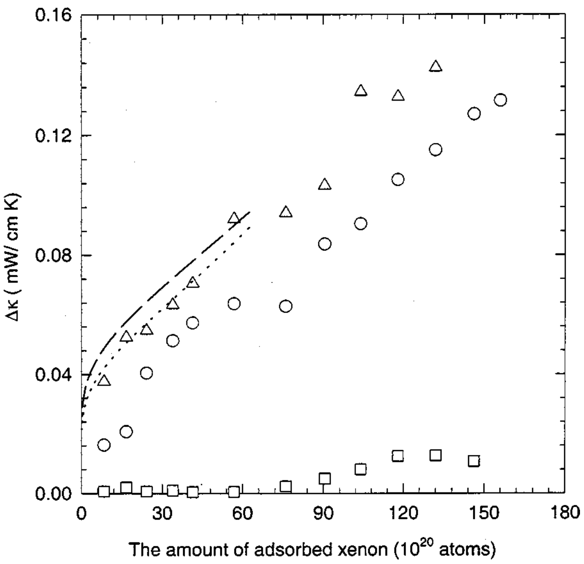

FIG. 3. The thermal conductivity increases of the RF aerogel due to the adsorption of xenon at different temperatures. (□) $T=60\,\mathrm{K}$; (○) $T=90\,\mathrm{K}$; (△) $T=110\,\mathrm{K}$. The dotted and dashed lines are the results of a calculation described in the text for thermal conductivity increase due to formation of menisci of xenon at 90 and 110 K, respectively. The lines stop at the maximum size of menisci allowed for the given size of particles.

conductivity increase versus the adsorbed amount of xenon atoms at different temperatures. The increases at temperatures below 75 K are similar to that plotted for $T=60\,\mathrm{K}$. It is clear that the increase in the thermal conductivity in this temperature range is very small when compared to that observed at 90 and 110 K. The slopes of the increases of the thermal conductivity at 90 and 110 K appear to be similar to each other.

IV. DISCUSSIONS

Several mechanisms can contribute to the increase in the thermal conductivity of an aerogel adsorbed with xenon. First, the increase may be simply due to gaseous conductance of the xenon vapor. The vapor pressure of xenon increases with temperature and is close to one atmosphere at its bulk melting temperature. However, the vapor pressure of bulk xenon at 75 K is on the order of millitorr [22]. The estimated gaseous heat conduction, determined for xenon in free space and from the temperature dependence of the xenon vapor, is too small to account for the increase in the measured thermal conductivity of the aerogel [24]. The smallness of the open pore in the aerogel further limits the mean free paths of gaseous molecules and thus reduces its thermal conductance. It has been found that the gaseous conductance becomes significant in aerogels only when the vapor pressure is above about 10 torr [6,8,11]. That agrees very well with the results of a calculation taking into account the limited mean free path of gaseous molecules inside an aerogel [16,17]. Using the same equation we find, again, that the contribution due to the conduction of gaseous xenon is negligible in the temperature range we have measured [24].

Another scenario that could cause an apparent increase in the thermal conductivity is the desorption-and-readsorption process of the adsorbate. When the temperature gradient is first established across the sample, the equilibrium vapor pressure on the warmer side is higher than that on the colder side, causing the adsorbate to desorb from the warmer side and readsorb on the colder side. Thermal energy is carried by the adsorbate in the process generating an additional heat transfer. Such an effect is transient because as the adsorbate is transported to the lower temperature side, the thickness of the adsorbed layer in that region increases. Correspondingly, the vapor pressure in that region increases as well. The desorption-and-readsorption process eventually diminishes when a dynamic balance, in which the local vapor pressure throughout the sample reaches equilibrium, is reached. The excess heat transfer due to desorption and readsorption might be quite significant shortly after the heating power was turned on, but the temperature gradient appeared to approach a stable value after that heating power was turned on for about half an hour. Since the experimental data were taken 1 h after turning on the heating power, we believe this transient effect is not significant in the data presented in Fig. 2.

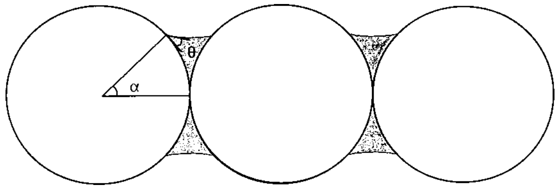

FIG. 4. Schematic diagram of the structure of a hypothetical RF aerogel (from Ref. [19]). The shaded regions represent xenon atoms adsorbed on the aerogel. The maximum amount of xenon that can be adsorbed in the neck region depends on the contact angle.

We suspect that the increase is due to changes of the connectivity of aerogel particles at the microscopic level caused by adsorption of xenon. As mentioned above, electron microscopy images indicate that the structure of RF aerogels with an R/C ratio of 200 is colloidallike and consists of small particles connected to form the open structure [19,20]. For evacuated aerogels, their conductivity depends strongly on the connections between neighboring aerogel particles that form the skeleton structure of the material. The thermal linkage of the structure is determined by the size of the neck between adjacent particles. The contact size in the neck area can be increased if the adsorbed molecules form menisci at the connecting neck. The increase depends on the total amount molecules adsorbed as well as the wetting properties of the substance on the surface. In order to elucidate this mechanism, we carried out the following model calculation.

Assuming that all the aerogel particles have spherical shape with identical size, and that the adsorbate condenses in the neck region, as illustrated in Fig. 4, the total amount of adsorbate formed in a single neck region would be

$$N=2\int_0^{\alpha}\pi(d^2-R^2\sin^2\varphi)R\sin\varphi\,d\varphi, \tag{2}$$

where R is the radius of the sphere, d is the distance between the adsorbate-vapor interface and the axis that connects the centers of the two neighboring spheres determined by the contact angle and the sphere radius, and α is the angle that spans between the line connecting the centers of the spheres and that connecting the center of the sphere with the adsorbate-vapor-sphere contact point. The adsorbate-vapor interface can be approximated by a section of an arc that intersects with the sphere with the contact angle θ. Over a small segment δx along the axis that connects the centers of the two sphere, the change δR in thermal resistance can be considered as due to an additional thermal energy pathway in parallel to the connected spheres due to the meniscus. Thus,

$$\delta R=\frac{\delta x}{\kappa_{\mathrm{Xe}}A_{\mathrm{Xe}}+\kappa_{\mathrm{RF}}A_{\mathrm{RF}}}, \tag{3}$$

where κ_{Xe} and κ_{RF} are the solid thermal conductivities of solid xenon [23] and RF aerogel, respectively [24], and A_{Xe} and A_{RF} are the cross-sectional areas of the solid xenon meniscus and the aerogel over δx. The thermal conductivity of RF aerogel used here is properly scaled to that with no missing volume [24]. Ignoring the thermal boundary impedance [25], the total change of the thermal resistance between the centers of the two neighboring spheres is

$$\Delta R=2\int_0^{\alpha}\frac{R\sin\varphi\, d\varphi}{\pi\kappa_{\mathrm{Xe}}(d^2-R^2\sin^2\varphi)+\pi\kappa_{\mathrm{RF}}R^2\sin^2\varphi}+2\int_{\alpha}^{\pi/2}\frac{d\varphi}{\pi\kappa_{\mathrm{RF}}\sin\varphi}. \tag{4}$$

The second term vanishes if the neck region is completely filled with adsorbate. But if the adsorbate does not completely wet the aerogel, the maximum radius of the meniscus formed would be smaller than that of the sphere [24]. Assuming a cross sectional area A_a for a unit aerogel cell consisting of the aerogel particle and an averaged pore size [3], the increase in the thermal conductivity due to adsorption is

$$\Delta\kappa=\frac{L}{A_0\Delta R}, \tag{5}$$

where L is the distance between the center of the two neighboring spheres. Combining Eqs. (2), (4), and (5), a relation of the thermal conductivity increase $\Delta\kappa$ versus the amount of adsorbate that forms the meniscus can be obtained. In Fig. 3, we plot the results obtained by choosing the radius of the aerogel particles to be 5 nm, averaged pore size to be 10 nm (which determines porosity), and a contact angle of 15°. The values for the sizes of aerogel particles and the averaged pore are close to those determined using electron microscopy [19–21]. The contact angle chosen here appears to give the best description of the data at temperatures above 90 K, but this should not be considered as an indicator of the wetting behavior of xenon on RF aerogel. The maximum size of the meniscus depends on aerogel particle size. With the particle size chosen here, the maximum size is equivalent to about two atomic layers. A more realistic model should probably include the distribution of the particle sizes and the bridges formed between particles that are originally not in contact. Nevertheless, this simple calculation can account for, at least qualitatively, some basic features of the thermal conductivity rises at temperatures above 75 K.

At temperatures below 75 K the experimentally observed increase in the thermal conductivity is too small compared to that calculated using the model. We believe that at temperatures below 75 K, xenon would not predominately adsorb in the neck region. The changes of the behavior of the thermal conductivity of aerogel adsorbed with xenon might indicate different wetting properties of xenon on RF aerogel at temperatures above and below 75 K. However, the phenomenon remains intriguing and requires further exploration. We hope the results reported here will stimulate further studies of the system using other techniques.

V. SUMMARY

We have measured the thermal conductivity of xenon-adsorbed RF aerogel at temperatures from 20 to 120 K. Below 75 K, the thermal conductivity exhibits little change due to the adsorption of xenon. Above that temperature, the thermal conductivity increases with the amount of xenon adsorbed. The dependence of the increase on the amount of xenon adsorbed indicates that adsorbed xenon provided additional heat transfer channels to the aerogel. The mechanisms that cause the different behaviors in the thermal conductivity below and above 75 K remain to be further explored.

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