Thermal conductance and wettability of xenon on resorcinol-formaldehyde aerogels

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We have performed thermal conductivity and adsorption isotherm measurements to investigate the system formed by Xe adsorbed on resorcinol-formaldehyde (RF) aerogel. Below 80 K, the thermal conductivity of the Xe/RF-aerogel system is essentially identical to that of the bare RF aerogel; however, above this temperature the thermal conductivity of the system increases significantly above that of the bare aerogel. Adsorption isotherm measurements indicate that Xe incompletely wets the RF aerogel below Xe's bulk triple point temperature. The thickness of the Xe film that forms on the RF aerogel decreases with decreasing temperature. By 80 K the total amount of Xe present on the aerogel in equilibrium with the saturated vapor pressure is less than the amount needed to form about 1.5 atomic layers of Xe on the substrate. We attribute the observed changes in the thermal conductivity of the Xe/aerogel system to changes in the wettability of the aerogel by the Xe film.

The study of aerogels is of interest from a fundamental as well as an applied perspective [1]. Aerogels are materials prepared by a sequence in which sol-gel processes are followed by a liquid-extraction step [1,2–4]. The resulting product is an extremely porous, very low density solid that can be described as a three-dimensional random network of nanometer-sized particles [1]. The ratio of liquid to solid prior to the extraction step is typically of order 9 to 1 or higher; the resulting network of solid particles occupies only a small fraction of the original gel volume, with voids substituting for the liquid that was present before the extraction [1,2–4]. One of the most remarkable features of aerogels is their extraordinarily low thermal conductivity [5–10]. Thermal conduction through the solid is intrinsically low due to limited number of solid paths and the nanometer-scale size of the particles that constitute the solid network, thereby limiting the mean free path of the excitations [5–10]. Another salient characteristic of aerogels is their extremely large specific surface areas, which typically are in the range of hundreds of m²/g [1–4]. Because of these two unique features, it is intriguing to ask whether or not the thermal conductivity of an aerogel with adsorbed gases would be significantly different from that of the bare aerogel.

Recently the low temperature thermal conductivity of the system formed by Xe adsorbed on resorcinol-formaldehyde (RF) aerogel was investigated [11]. The thermal conductivity of this system was observed to drop abruptly near 80 K [11]. It was speculated that this drop could be the result of a change in the wetting behavior of the Xe/aerogel system [11]. Wetting refers to the growth mode of a film as the saturated vapor pressure of the adsorbate, P_0, is approached [12]. There are three different wetting modes: ''Complete wetting'' refers to the situation where the adsorbate forms a uniform film on the substrate, with a thickness that grows asymptotically as P_0 is approached. ''Incomplete wetting'' refers to the situation where the adsorbate forms a film of finite thickness at P_0, at which point bulk particles of the dense phase start to form. ''Nonwetting'' behavior refers to the situation where no film will form on the substrate at all,

and bulk will form at P_0. On a porous substrate, such as an aerogel, capillary condensation can occur. This term refers to the formation of the bulk dense phase at pressures below P_0 in the crevices and pores within the substrate [13].

We report here on the combined results of adsorption isotherm and thermal conductivity measurements for the Xe/aerogel system. These results show that the changes of the thermal conductivity of a gas/aerogel system are indeed correlated with different wetting behaviors of the gas on the aerogel surface. Such a correlation can be understood in terms of the different connectivities existing between the particles in the Xe/aerogel system under the different wetting modes. The results demonstrate that thermal conductivity measurements can be a very sensitive probe in the study of the wetting properties of gases on aerogels and on other porous materials.

We have used resorcinol-formaldehyde (RF) aerogel both in our thermal conductivity and in our adsorption isotherm measurements. RF aerogels are organic aerogels derived from base-catalyzed aqueous polycondensation of resorcinol with formaldehyde [2]. Many of the properties of RF aerogels are influenced by the initial ratio of resorcinol to catalyst (R/C) [3,4]. As the initial amount of catalyst increases, the structure of the aerogel goes from colloidlike to well-connected polymerlike [3,4]. The RF aerogel we used had an R/C ratio of 200. Electron micrographs show that the structure of the aerogel, at this R/C ratio, consists of interconnected strands formed mainly by colloidlike particles [4]. RF aerogels have specific surface areas comparable to their silica-based counterparts; they have lower radiative thermal conductivities and are more durable [2–4]. Because of this combination of characteristics, RF aerogels have been suggested as alternatives to silica-based aerogels in insulation applications [3].

Thermal conductivity measurements on the Xe/aerogel system were performed using a steady-state method [11]. The experimental details and the results can be found in Ref. [11]. The thermal conductivity as a function of temperature, for different amounts of Xe dosed into the cell, is presented
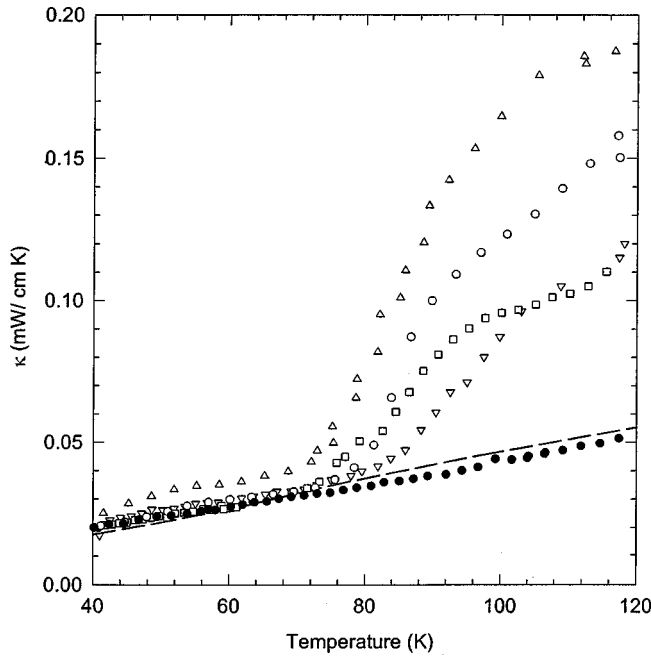
FIG. 1. Thermal conductivity κ of the Xe/RF-aerogel system, as a function of temperature, measured for different amounts of Xe admitted into the experimental cell: ($\bullet$) no Xe admitted, i.e., bare RF aerogel, ($\triangledown$) 1.7×10^{21}, ($\square$) 2.4×10^{21}, ($\bigcirc$) 7.7×10^{21}, ($\triangle$) 1.04×10^{22} Xe atoms. The monolayer capacity of the aerogel sample used in these measurements is 3.2×10^{21} Xe atoms. The dashed line represents the thermal conductivity of a bare silica aerogel with density 0.235 g/cm^3.

in Fig. 1. The data show that, as the temperature exceeds approximately 80 K, the thermal conductivity of the Xe/aerogel system increases rapidly relative to that of the bare aerogel. In the temperature range investigated here the pressure of the Xe vapor inside the cell is always below 11.8 torr, the saturated vapor pressure at 120 K. The adsorption cell for the thermal conductivity measurements was designed in such a manner as to eliminate the possibility of gaseous convection [11]. Thermal conduction by the Xe vapor in the RF aerogel is not only limited by the low vapor pressure present inside the cell, it is suppressed by the reduced mean free path of gas atoms due to the small size of the voids in the aerogel [9]. The contribution of Xe vapor is negligibly small below 100 K and is less than 5% of the thermal conductivity of bare RF aerogel at 120 K, estimated using an empirical formula that was found to describe very well the thermal conduction of a vapor in aerogels [9]. Thus, the observed change in the thermal conductivity near 80 K corresponds to a change in the thermal conductivity of the Xe/aerogel system.

The same piece of RF aerogel utilized in the thermal conductivity determinations was used as a substrate in the adsorption isotherm measurements. The isotherms were measured between 80 and 140 K. A computer-controlled, automated apparatus, detailed in Ref. [14], was used to perform these measurements. Figure 2 displays isotherms representative of the entire temperature interval explored. In all the cases shown, the amount of Xe adsorbed at the saturation
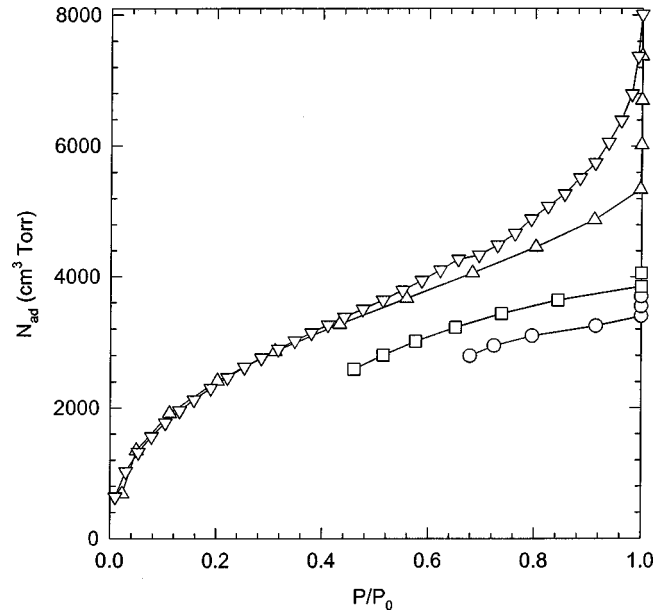

FIG. 2. Adsorption isotherms measured at different temperatures: $T = (\triangledown) 140.5$, $(\triangle) 119.8$, $(\square) 83$, $(\bigcirc) 80.6$ K. The pressures are scaled by the corresponding values of the saturated vapor pressure. The amount of Xe adsorbed on the RF aerogel, N_{ad}, is given in cm^3 Torr (1 cm^3 Torr $= 58.8$ nanomoles). The lines are guides to the eye.

pressure P_0 is finite, i.e., all the isotherms in the temperature interval studied exhibit incomplete wetting.

The wettability of a film on a substrate is proportional to the maximum thickness that a uniform film can reach at P_0. The maximum film thickness attained at P_0 is directly related to the amount of gas adsorbed on the substrate as P_0 is reached; the latter quantity also reflects the formation of a capillary condensate. Figure 3 presents our results for the amount of gas adsorbed, N_{ad}, at P_0, for the Xe/aerogel system, as a function of temperature. It is clear from the results displayed in the figure that the maximum Xe film thickness on the RF aerogel (and, hence, the wettability) decreases as temperature decreases. The maximum amount of Xe that is
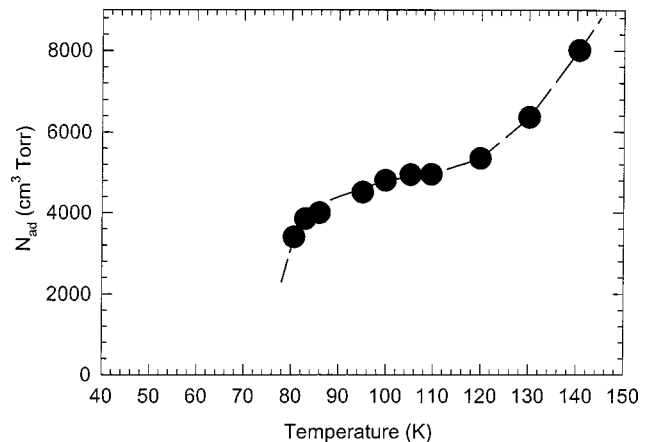

FIG. 3. Maximum amount of Xe adsorbed on RF aerogel at the saturation pressure P_0 plotted as a function of temperature. The dashed line is a guide to the eye.
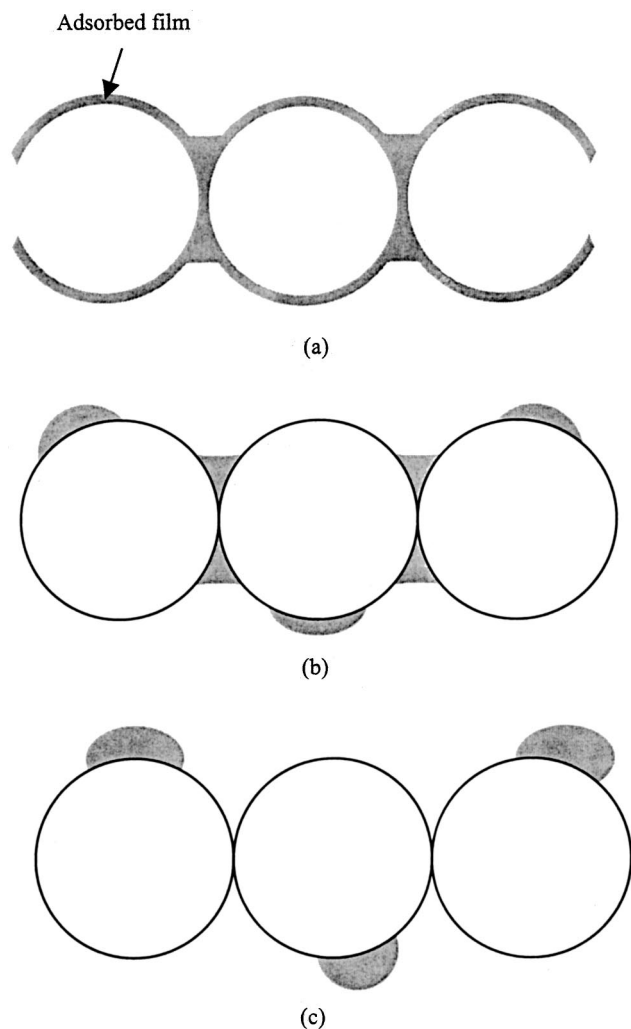
Adsorbed film

(a)

(b)

(c)

FIG. 4. Scenario for the interpretation of the thermal evolution of the wettability of Xe (represented by the shaded regions). (a) High wettability: Xe forms both a uniform film on the aerogel surface and capillary condensate in the contact regions between neighboring particles. (b) Intermediate wettability: film becomes thin and perhaps discontinuous, but the capillary condensate still exists in the contact regions. (c) Low wettability: only bulk clusters can form on the RF aerogel.

adsorbed decreases at an approximately constant rate between 115 and 140 K; the rate slows down between 90 and 115 K and then rises sharply between 80 and 90 K. 80 K was the lowest temperature at which we were able to conduct the adsorption isotherm measurements. Below this temperature the pressures are too small to be reliably determined with the manometers available in the apparatus used. At 80 K the maximum amount of Xe adsorbed on the RF aerogel is equivalent to a film 1.5 atomic layers thick.

The manner in which changes in the thermal conductivity of the Xe/aerogel system are determined by changes of the wettability of Xe on the aerogel can be understood in terms of a simple qualitative model. The scenario we envisage is illustrated in Fig. 4, which shows a small segment of an aerogel strand in the presence of Xe at three different temperatures.

Figure 4(a) describes the situation at the high end of the temperature range investigated here. A uniform film, which may grow to be several layers thick, forms on the aerogel together with a capillary condensate forming in the spaces where neighboring aerogel particles join together. The thermal conductivity of the Xe/aerogel system is enhanced over that of the bare aerogel by two mechanisms: the presence of the uniform film coating all the particles present and the presence of the condensate in the regions between neighboring aerogel particles, which increases their area of contact. Since the volume of these regions is relatively small (the size of the particles is on the order of nanometers), the filling of these interparticle regions requires only modest amounts of Xe. Thus, the maximum amount of Xe adsorbed at P_0 is roughly proportional to the maximum film thickness (or to the wettability) of Xe on the aerogel. This is the situation present in the data of Fig. 3 at temperatures from 115 to 140 K. According to this scenario we expect that, at these relatively high temperatures, the thermal conductivity of the Xe/aerogel system will increase significantly over that of the bare aerogel.

The maximum thickness of the Xe film will be severely limited at a sufficiently low temperature since the wettability of Xe on RF aerogel decreases with decreasing temperature. Xe will still be able to form a capillary condensate in the region between adjacent particles, as shown in Fig. 4(b). In this temperature range, most of the enhancement in the thermal conductivity of the Xe/aerogel system over that of the bare aerogel is the result of the capillary condensed Xe increasing the contact area between adjacent particles. The maximum amount of capillary condensed Xe that can form in the pores, corners, and crevices of the aerogel substrate depends on the geometry of these regions; it is not as sensitive as the maximum film thickness to the wettability of the Xe/aerogel system. We expect, therefore, that for these intermediate temperatures the maximum amount of Xe measured at saturation (which is due to the limited amount of film, plus the slowly varying amount of capillary condensate) will remain essentially constant. This is exactly the behavior observed in the isotherms measured between 90 and 115 K (see Fig. 3). Thus, the scenario accounts well for the slowing down in the rate at which the maximum amount of Xe adsorbed at saturation decreases with decreasing temperature over this range.

The wettability of an adsorbate on a substrate can be characterized macroscopically by the contact angle between the substrate film and the adsorbate-vapor interfaces [12]. Lower wettabilities correspond to higher contact angles. The wetting property of Xe on mesoporous silica gel has been reported for temperatures between 139 and 165 K [15]. It was found that Xe wets the silica gel above the bulk triple point. Below the triple point, the contact angle of the Xe film increases smoothly from 0° at 165 K to 60° at 139 K, the lowest temperature studied [15]. Our adsorption isotherm results show that the wetting properties of Xe on RF aerogel are qualitatively similar to those reported for Xe on silica gel, and the contact angle between Xe film and RF aerogel will keep increasing as temperature decreases. When the contact angle exceeds 90° the capillary condensate becomes

unstable in the oblique corner regions [16,17]. At and below the temperature where this condition occurs, Xe forms only bulk clusters on the surface of the aerogel particles (and, perhaps, a film of about one layer), as illustrated in Fig. 4(c). At the temperature where the capillary condensate becomes unstable, the maximum amount of Xe present at saturation will decrease significantly. When the bulk crystallites that form on the surface of the aerogel particles are small and not interconnected, their presence will not make a significant contribution to the thermal conductivity of the Xe/aerogel system. The results from a simple calculation described in Ref. [11] show that the magnitude of the thermal conductivity increase caused by filling the neck regions between adja-

cent aerogel particles with different Xe concentrations admitted to the experimental cell agrees, roughly, with what has been observed experimentally. Thus, this model, together with the adsorption isotherm results, explains the sudden reduction of the enhancement in the thermal conductivity of the Xe/aerogel system down to values comparable to that of the bare aerogel.

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