

# Physical Adsorption of Argon and Nitrogen on Graphite

In this experiment you will record an adsorption isotherm of  $N_2$  molecules and a second one of Ar atoms on a graphite substrate at a temperature of 77.4 K. A feature of the  $N_2$  isotherm corresponding to a known density of molecules on the graphite substrate allows one to calculate the total substrate area. With the substrate area thus determined, the Ar isotherm can be used to determine the density of Ar atoms at single (mono)layer completion, allowing for a determination of the monolayer Ar-Ar spacing. This number can then be compared to the known nearest neighbor spacing of Ar atoms in the solid 3-D phase, and the Ar-Ar separation derived from the Lennard-Jones potential.

## 1 Introduction

Adsorption is the process in which atoms or molecules of a substance in one phase (usually gas) become bonded to the surface of a second substance in a different phase (usually solid). Adsorption is to be distinguished from absorption, the process in which one substance interpenetrates the bulk volume of a second substance.

There are many examples of adsorption in everyday life. Activated charcoal, which can have a surface area of up to several thousand square meters per gram, is capable of adsorbing many different substances. It is used to filter contaminants from drinking water, and is also used in gas masks to remove toxic substances from breathing air. Silica gel ( $SiO_2$ ) packets, which adsorb water vapor, are often packed in with moisture sensitive merchandise. And adsorption is a key part of many catalytic processes, as many chemical reactions will not take place except in the presence of a particular kind of surface. For example, molecular hydrogen and oxygen can be mixed at room temperature with no effect. However, these molecules dissociate when adsorbed on a platinum surface, and will then combine (vigorously!!) to form water molecules.

Before proceeding it is useful to present some definitions. In this write-up we will be discussing a system where a substance in the gas phase becomes bonded to the surface of a second, solid substance.

**Adsorbate:** the substance originally in the gas phase which becomes bonded to the surface of a second, solid substance.

**Adsorber:** the solid substance on the surface of which the adsorbate becomes bonded. The adsorber is also referred to as the adsorbent or, more commonly, the substrate.

There are two broad types of adsorption processes, characterized by the strength of the bond between the adsorbate and substrate. In physical adsorption, or physisorption, the bonds between atoms or molecules being adsorbed and the substrate are due to dipole-dipole interactions, and are relatively weak. In chemical adsorption, or chemisorption, a chemical bond is formed between the adsorbate and the substrate. Such bonds, which involve the exchange or sharing of electrons between the adsorbate and the substrate, are much stronger. Typical physisorption binding energies are 50-500 meV per atom or molecule; chemisorption binding energies are typically an order of magnitude greater.

Some significant differences between physisorption and chemisorption:

1. Physisorption is reversible, i.e., the adsorbate will desorb (become unbound from the substrate) when the substrate temperature is raised, and return to its original condition in the gas phase. Chemisorption is usually not reversible; i.e., raising the substrate temperature will typically not result in the adsorbate returning to its original condition in the gas phase.
2. Physisorption does not result in the dissociation of adsorbed molecules. Chemisorption often results in the dissociation of molecules during the adsorption/chemical reaction process.
3. With physisorption, multiple layers of the adsorbate can form on the substrate. Chemisorption is typically characterized by the formation of a single layer of adsorbate on the substrate.
4. Chemisorption typically occurs over a wide range of temperatures, often exceeding temperatures at which the adsorbate will condense from the gas phase to the liquid phase. Physisorption occurs with the substrate temperature typically near or below temperatures at which the adsorbate will condense from the gas phase to the liquid phase.

In physisorption the force of attraction between adsorbate and substrate is due to instantaneous fluctuating electric dipole moments in both the atoms or molecules of the adsorbate and the atoms of the substrate. Even in an atom or molecule with no permanent electric dipole moment, fluctuations in the electron charge distribution will give it an instantaneous (short lived, but averaging to zero over a longer time interval) dipole moment which will induce a dipole moment in a nearby atom or molecule. The interaction between the original and induced dipole moments results in an attractive force between these two moments. Such dipole-dipole forces are known as “van der Waals” forces. In addition to being the main force resulting in physisorption, the van der Waals force is the main force resulting in the condensation and solidification of inert atoms (e.g., Ne, Ar, Kr) and many simple molecules such as  $N_2$ ,  $O_2$  and  $CH_4$ .

Figure 1 shows how the potential energy of a physisorbed atom or molecule varies as a function of the distance  $z$  from the substrate surface. At larger  $z$ , the potential falls off as  $1/z^3$ . This can be derived by considering the force between a dipole and its image in the plane of the substrate. For smaller  $z$ , the potential energy increases rapidly (adsorbate-substrate force becomes repulsive) as the electron charge distribution of the adsorbate atom/molecule begins to overlap the electron charge distribution in the substrate.

The binding energy  $V_0$ , the “hard core” distance  $z_h$ , and the attraction coefficient  $C_3$  are determined by the constituent atoms or molecules of the adsorbate and the substrate. For a given substrate and with rare gases as the adsorbate, both  $V_0$  and  $C_3$  increase in the order He, Ne, Ar, Kr, and Xe. Simple molecules like  $N_2$ ,  $O_2$ ,  $CH_4$ ,  $CF_4$ , etc. can be cataloged the same way [1-3].

It is possible to cover a substrate surface with a monolayer of atoms or molecules of any of the above adsorbates, provided certain conditions are met. First, the temperature of the surface must yield an energy much less than  $V_0$  ( $k_B T_{\text{surface}} \leq 1/10 V_0$ ) for the particular adsorbate-substrate combination. For reference,  $k_B T = 8.62$  meV at 100 K;  $k_B$  is the Boltzmann constant,  $k_B = 8.62 \times 10^{-5}$  eV/K. Second,  $|V_0|$ , the absolute value of the adsorbate-substrate binding energy, must be greater than the absolute value of the adsorbate-adsorbate binding energy. The latter binding energy is also due to a van der Waals interaction, which results in an attractive force between the atoms/molecules. If this binding energy condition is not met, the adsorbate may not always “wet”, or distribute itself across the substrate, but may cluster into its three-dimensional (3-D) phase. At liquid nitrogen temperature (boiling point = 77.4 K at 1 atmosphere pressure) and with graphite as the substrate,

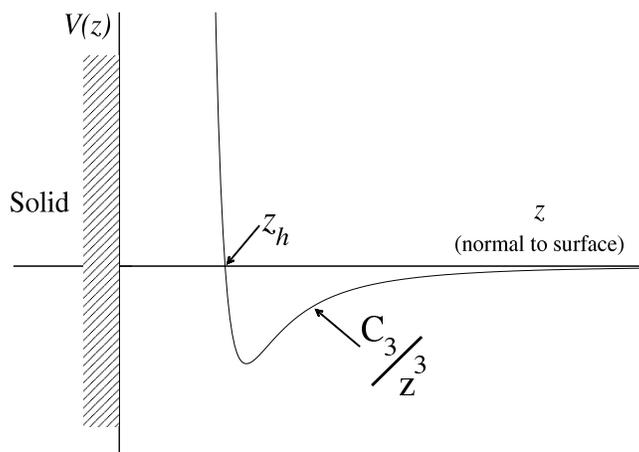


Figure 1: Potential energy between adsorbate atom and adsorption surface, modeled on van der Waals force.

it is possible to form a monolayer of Ar, Kr, Xe, N<sub>2</sub>, CH<sub>4</sub>, etc, but not of Ne, H<sub>2</sub>, or He, as  $V_0$  for these species is too small relative to  $k_B T$  at 77.4 K for adsorption to occur.

Adsorbates can exist in a number of different phases (gas, liquid, solid, registered/unregistered relative to the substrate geometry), depending on the temperature and the density of adsorbed atoms/molecules on the substrate. One relatively simple but yet very powerful method of studying the behavior of adsorbed atoms or molecules is the adsorption isotherm. In this method, gas is introduced to the substrate, which has typically been cooled to a low temperature. Some of the gas adsorbs, and some remains in the gas or vapor phase after the system reaches equilibrium. The number of adsorbed atoms/molecules as a function of the vapor pressure of the remaining gas is plotted on a graph to generate the adsorption isotherm. This procedure is called “measuring an adsorption isotherm”.

The isotherm measurement method has been highly refined by chemists and physicists and is used as a tool to investigate how the adsorbed film evolves as atoms/molecules are added to form a single layer, and then as they are added to form additional layers [4]. The goal is to map out the 2-D phase diagram for the adsorbate, analogous to the standard phase diagram describing the behavior of bulk 3-D matter. In this regard, our system is capable of detecting the phase transition in which adsorbed N<sub>2</sub> molecules go from a 2-D fluid where they are not bound to particular substrate sites, to a state where they form a “registered”, or commensurate structure, i.e. they occupy specific sites relative to the graphite substrate (approximately one N<sub>2</sub> molecule on every third carbon hexagon in the graphite substrate; see Fig. 6). The signature of this transition is a small “bump” in the coverage (number of adsorbed molecules) vs. vapor pressure curve. Several other methods used to study these 2-D phases and provide a fuller picture of the state of the adsorbate are heat-capacity measurements, which can detect the transition from one state to another (e.g. solid to liquid) and neutron-diffraction measurements which can provide information about the structure (molecule orientation, separation, location relative to substrate) of the adsorbed film [5,6].

Monolayer formation of  $N_2$  at 77.4K is also widely used in industrial settings to measure the surface area of various adsorbents, e.g. activated charcoal, silica gel, and zeolite, which consists of crystalline aluminosilicate. The standard area occupied by a  $N_2$  molecule,  $\approx 16 \text{ \AA}^2$ , is used as a reference area.

Figure 2 shows a simplified schematic of an adsorption isotherm apparatus. Initially the calibrated

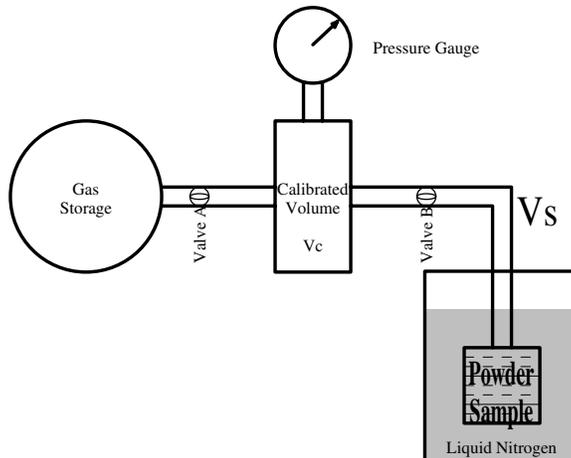


Figure 2: Simplified adsorption isotherm apparatus.

volume,  $v_c$ , and the sample volume  $v_s$  are pumped out to  $\approx 0$  pressure (pump not shown) with the sample at a high temperature relative to the temperature at which the isotherm is measured. After the pumping is completed, valve B is closed and the sample is cooled down to the temperature at which the isotherm will be measured. Gas is admitted from the storage volume to  $v_c$ . With valves A and B closed, the initial pressure,  $P_i$ , of the gas in  $v_c$  is recorded. Using the ideal gas law, the amount of gas in  $v_c$  is calculated. Valve B is then opened allowing gas to expand into the volume  $v_s$ , which includes the cooled sample at the temperature of the isotherm. After the pressure equilibrates (may take minutes to hours) in the combined volumes  $v_c + v_s$ , the final pressure  $P_f$  is recorded. The ideal gas law is again applied to calculate the amount of the original gas remaining in the gas phase. The amount of gas which has been adsorbed is just the amount not accounted for in the gas phase. Valve B is then closed, another dose of gas is admitted to  $v_c$  from the storage volume, and the process is repeated. Gas doses can be added until the vapor pressure of the adsorbate in the 3-D phase is reached. At this point, droplets of solid or liquid adsorbate are formed.

The variation of  $V_0$  at different locations on the substrate surface is a measure of the uniformity, or homogeneity of the substrate surface. If a significant fraction of the surface sites that adsorbed atoms/molecules can occupy have different binding energies, an isotherm like that shown in Fig. 3a will result. This kind of isotherm will result from having many different crystal planes (corresponding to Miller indices 100, 110, 111, etc.) with their different values of  $V_0$  exposed to the adsorbate. In contrast, with substrates having only one crystalline plane exposed to the adsorbate, isotherms show “steps”, as in Fig. 3b, corresponding to the single layer and successive layer completions. On some highly uniform substrates, isotherms can exhibit upwards of seven steps. The graphite substrate used in this experiment is only uniform enough to show a small hint of second layer completion with Ar as the adsorbate.

Since the attractive potential decays as  $1/z^3$  away from the substrate, molecules adsorbed on the first layer are much more strongly bound to the substrate than molecules on successive layers.

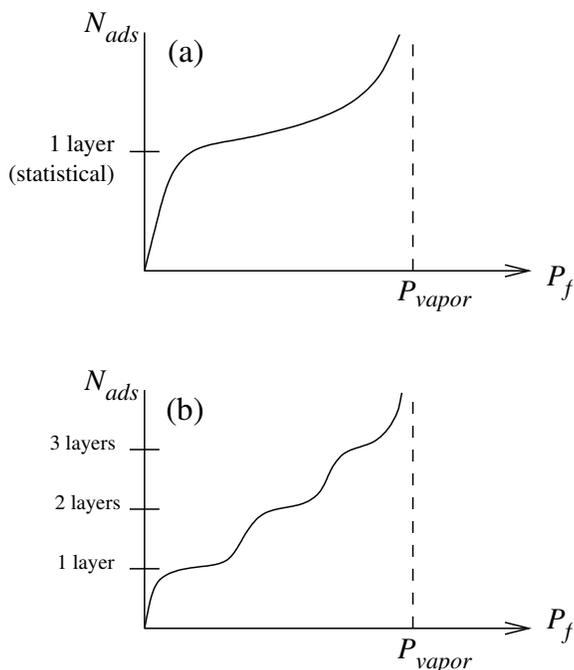


Figure 3: Typical adsorption isotherms. (a) Isotherm for heterogeneous substrate. (b) Isotherm for highly uniform substrate.

Thus, as more adsorbate is added to the system after first layer completion, one can expect the equilibrium vapor pressure to increase rapidly. And indeed, both isotherms in Fig. 3 exhibit this behavior. In terms of a criterion for first layer completion, the "knee" where the isotherm first bends over and the vapor pressure starts to increase rapidly is assumed to define this condition. Knowing the amount of adsorbed gas at the knee, one can calculate the number of adsorbed atoms or molecules needed to complete the first layer.

## 2 Apparatus

The substrate used in this experiment is exfoliated graphite, commercially available under the trade name Grafoil (Union Carbide Corporation, Carbon Products Division, 270 Park Avenue, New York, NY 10017). A major worldwide research effort studying adsorbed films on Grafoil substrates has been going on for more than three decades, and faculty in our own department have made a major contribution to this effort. Grafoil is made of very small graphite crystals which, after intercalation with  $\text{FeCl}_2$  or a similar compound, are heated rapidly, resulting in a separation of the basal planes. These exfoliated crystallites are then rolled into sheets of various thicknesses. Our experiment uses Grafoil discs of about 4.5 cm diameter cut from a sheet 0.010 inches thick. The discs are placed in a Pyrex glass container connected to the vacuum/gas handling system. Grafoil has a specific surface area of about  $20 \text{ m}^2/\text{gram}$ .

The vacuum and gas handling system is shown schematically in Fig. 4. The gas handling system is made entirely of glass with O-ring sealed valves. The system has two pressure gauges. A thermocouple gauge is used only at the beginning of the experiment when the apparatus is pumped to the lowest possible pressure. The second pressure gauge is a Baratron Capacitance gauge which

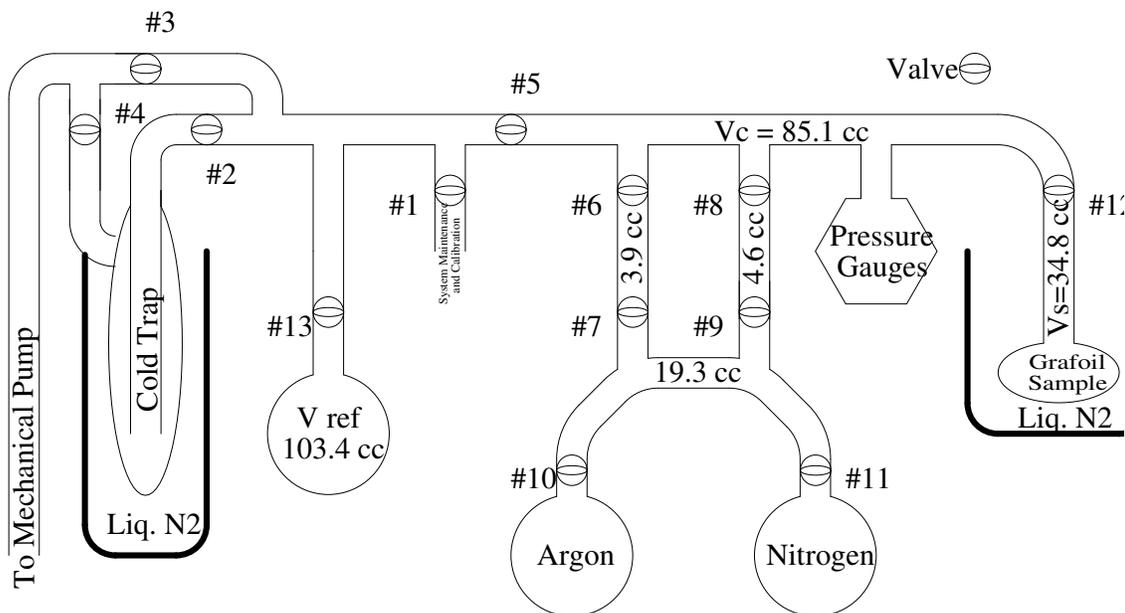


Figure 4: Schematic of gas-handling apparatus used in physical adsorption experiment.

measures absolute pressure from 0 to 1000 torr. The capacitance gauge is used to measure the pressure when taking isotherm measurements. The Baratron is a high quality gauge costing several thousand dollars. This gauge outputs 10 millivolts per Torr—or about 7.6 Volts at atmospheric pressure. A digital voltmeter is used to read pressure to 0.1 Torr, the manufacturer’s stated resolution for this device.

### 3 Procedure

See Fig. 4 for a diagram of the system. The basic procedure for measuring the isotherm is to admit gas into the calibrated volume  $v_c$  with the sample volume  $v_s$  closed off (valve 12 closed). The pressure of the gas in  $v_c$  is noted and then valve 12 is opened to allow gas to be exposed to the sample, where some of it will be adsorbed. As gas adsorbs, the pressure will decrease. When the pressure comes to equilibrium, it is noted, and using the ideal gas law along with knowledge of the volumes and of the ambient (room) temperature, the amount of  $N_2$  or Ar no longer in the gas phase can be computed. This is just the amount of  $N_2$  or Ar that is adsorbed on the sample.

The first measurement will be the Ar isotherm, since it is a bit easier. It is common practice to express the amount of adsorbed gas as a volume ( $V_{ads}$ ) in units of  $cm^3$  STP, which is just the amount of gas in the stated number of cubic centimeters at standard temperature and pressure, 273.15 K (0 Celsius), and 760 Torr. There are  $2.69 \times 10^{19}$  molecules (or atoms) in  $1 cm^3$  STP. Figure 5 shows some actual data taken with this system.

See Fig. 4 for values of the various volumes in the system. Knowing these volumes will help in devising a strategy for setting up the doses. Consult Fig. 5 to get an idea of the number of points (gas doses) you will need to map out the features of interest of the isotherm. Make an estimate of the size of the doses needed to increase the coverage by a certain amount.

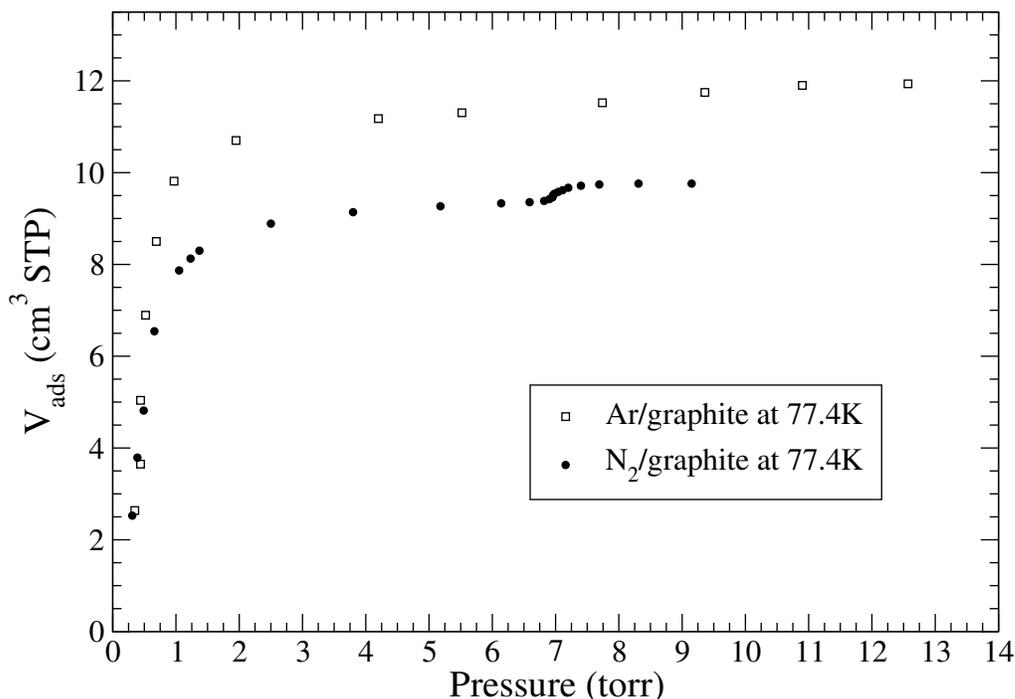


Figure 5: Sample data taken with adsorption system.

Here is an example. Say that you want to estimate the dose pressure required to put about  $2.5 \text{ cm}^3$  STP in the graphite. Assume the current room temperature is  $300 \text{ K}$  ( $27 \text{ }^\circ\text{C}$ ). According to the sample data, this gives an equilibrium pressure of about  $0.3 \text{ torr}$ . So the total gas in the sample volume  $v_s = 34.8 \text{ cm}^3$  plus the calibration volume  $v_c = 85.1 \text{ cm}^3$  plus the graphite is

$$V_1(\text{total}) = \frac{273 \text{ K}}{300 \text{ K}} \times \frac{0.3 \text{ torr}}{760 \text{ torr}} \times (34.8 + 85.1) \text{ cm}^3 + 2.5 \text{ cm}^3 = (0.043 + 2.5) \text{ cm}^3 = 2.54 \text{ cm}^3$$

Since this amount of gas is originally in just the calibration volume, the pressure needed to provide this gas is what you get if you put it all in the calibration volume at room temperature, i.e.,

$$P_1(\text{initial}) = \frac{2.54 \text{ cm}^3}{85.1 \text{ cm}^3} \times \frac{300 \text{ K}}{273 \text{ K}} \times 760 \text{ torr} = 24.9 \text{ torr}$$

Clearly, in this initial dose, nearly all of the Ar goes on to the graphite and very little is left in the vapor. But as you add more doses, the pressure will start to rise significantly past the “knee” in the isotherm, and you need to reduce your dosing pressure.

The above calculation assumes that the cell is initially completely empty. But after the first dose, this is not the case, and you must work out the calculation assuming that some gas is already on the graphite and in the sample volume.

**Big hint:** Open up a spreadsheet and create formulas that calculate the adsorbed volume (STP) at any given dose based on the dosing pressure and previous doses. This will save time in the analysis and give you something to do while you wait for equilibrium.

Depending on how large a dose is desired, you can vary the sequence of valve openings and closings to transfer different amounts of gas from the appropriate storage bulb to the calibrated volume,  $v_c$ , and then to the sample volume,  $v_s$  (see additional details on gas transfer procedure below). One comment on  $v_s$ : the stated value for this volume has been adjusted from the true geometric volume to reflect the fact that part of  $v_s$  is at liquid nitrogen temperature when the isotherm is being measured, yet the ideal gas law is applied as if all of this volume were at room temperature.

It is important that you keep accurate records and reduce the data while you take it. Otherwise it is likely that you will discover later that you missed the nitrogen step at 7 Torr or don't have enough points to map out the desired feature(s) of the isotherm. The data you need to collect are:

1. initial pressure,  $P_i$ , in volume  $v_c$ ;
2. final pressure,  $P_f$ , in volume  $v_c + v_s$ ; and
3. ambient (room) temperature.

The values for the volumes are:

$$\begin{aligned} v_c &= 85.1 \pm 0.2 \text{ cm}^3 \\ v_s &= 34.8 \pm 0.1 \text{ cm}^3, \end{aligned}$$

with the graphite substrate at 77.4K.

For calculations, use the ideal gas law,  $PV = nk_B T$  ( $n$  is the number of atoms/molecules). The cumulative number of molecules adsorbed on the surface after  $m$  doses is:

$$n_{\text{adsorbed}} = \left( \frac{v_c}{k_B T} \right) \sum_{j=1}^m [P_i(j) - P_f(j)] - \left( \frac{v_s}{k_B T} \right) P_f(m), \quad (1)$$

where  $T$  is in degrees Kelvin, and  $k_B$  is Boltzmann's constant,  $1.3805 \times 10^{-23}$  J/K. The pressure conversion factor from torr to pascals (N/m<sup>2</sup>) is: 1 torr =  $1.333 \times 10^2$  N/m<sup>2</sup>. There are  $2.69 \times 10^{19}$  molecules (or atoms) in 1 cm<sup>3</sup> STP. It is instructive to derive the above formula by going through the calculations for the initial several doses.

*Note regarding valves:* When closing valves on the system, be careful to not over tighten them. Watch the O-ring at the tip to see when it comes in contact with the valve body. After contact is first made, gently continue tightening the valve a small amount until a dark and slightly widened band is visible all the way around where the O-ring is contacting the glass surface. A gentle touch is definitely in order - overtightening the valves is poor form! When opening the valves, be careful not to open them so far that the O ring seal on the shaft is broken. The valves should not be opened more than the 5mm maximum travel indicated on the valve bodies.

Before starting to take data, it is necessary to pump out all of the system *except the storage bulbs containing Ar and N<sub>2</sub> gas*. After pumping the system out, the cell is cooled to liquid nitrogen temperature and then data taking commences. Procedures for these steps are outlined below.

With the system at room temperature, pump out the entire system (including the graphite sample) **except for the Ar and N<sub>2</sub> storage bulbs (valves 10 and 11 should be closed)**. The thermocouple gauge should go down to 40-50 millitorr (also known as microns of mercury). When the pressure gets near this value, put the dewar for the pump trap in place and fill it with liquid nitrogen.

*Note:* One should be careful to not leave the pump directly evacuating the system and sample volume for long periods of time without going through the liquid nitrogen trap, as oil vapors from the pump will migrate toward the Grafoil and contaminate the surface. This is particularly true if the Grafoil is cold, as the Grafoil itself will act as a very good pump (adsorption in action!).

After the system reaches its lowest pressure (may take 10-15 minutes of pumping), close the sample valve, 12, and valves 5, 6, 7, 8, and 9. The volume between valves 5, 6, 8, and 12, including the pressure gauges, is the calibrated volume,  $v_c$ . The volume past valve 12 is the sample volume,  $v_s$ . Gas is admitted from one of the storage bulbs (assume the gas pressure in these bulbs to be somewhere between 500 and 750 Torr) into the volume between valves 7, 9, 10, and 11, and then into a combination of the remaining volumes depending on how large a dose is desired.

Put the dewar in place around sample and fill it with liquid nitrogen to within a few centimeters of the top. Cover the top of the dewar with aluminum foil to reduce the amount of atmospheric  $O_2$  absorbed by the liquid nitrogen; absorbed oxygen will raise the boiling temperature of the liquid nitrogen bath. As you progress with your measurements, check the liquid nitrogen level occasionally and replenish it to keep the level of liquid approximately constant.

Check that valves 5, 6, 7, 8, 9, 10 and 11 are closed. Start admitting Ar to the system by opening valve 11 and allowing gas into the volume bounded by valves 7, 9, 10 and 11 ( $19.3 \text{ cm}^3$ ). At this point you will probably want to let some gas into the  $3.9 \text{ cm}^3$  volume between valves 6 and 7, and then allow gas from this smaller volume into  $v_c$ . (The volume between valves 8 and 9 is  $4.6 \text{ cm}^3$ , similar to the volume between valves 6 and 7.) If an even smaller dose is desired for a subsequent point in the isotherm, you may want to just let some of the remaining gas from the  $19.3 \text{ cm}^3$  volume into the  $3.9 \text{ cm}^3$  volume, and then open valve 6 to  $v_c$ . If a larger dose is desired, you will probably want to recharge the  $19.3 \text{ cm}^3$  volume from the storage volume and then let gas from this volume into  $v_c$ . The possibilities are numerous. Valve 5 is used to pump out excess gas if too much gas for the dose desired has been admitted to  $v_c$ . For the initial doses, you will probably find that expanding from the  $3.9 \text{ cm}^3$  volume, containing a significant fraction of  $3.9 \text{ cm}^3$  STP Ar, into  $v_c$  results in too much gas in  $v_c$ . Some of this gas can be removed by closing valve 6 and then opening and closing valve 5 very quickly.

*Note:* When pumping any significant quantity of gas out of the system, do not pump it through the liquid nitrogen trap. If a significant amount of gas (e.g. Ar or  $N_2$ ) condenses in the trap, it will prevent the system from pumping down to a low pressure. The trap is bypassed by pumping through valve 3 with valves 2 and 4 closed.

After you have the desired amount of gas in  $v_c$ , make sure all the valves defining  $v_c$  (5, 6, 8 and 12) are closed. The pressure in the volume  $v_c$  is the initial pressure,  $P_i(1)$ , for the first dose. Note it. Now open valve 12. After the pressure comes to equilibrium (may take some minutes), note it. This pressure in the volume  $v_c + v_s$  is the final pressure,  $P_f(1)$ , for the first dose. **Before setting up the next gas dose, close valve 12.** Add the desired amount of gas to the calibrated volume  $v_c$ . Next make sure all the valves defining  $v_c$  (5, 6, 8 and 12) are closed. Note the pressure in  $v_c$ ; this is  $P_i(2)$ , the initial pressure for the second dose. Open valve 12, and after the pressure has come to equilibrium, note it. This pressure in the volume  $v_c + v_s$  is the final pressure,  $P_f(2)$ , for the second dose. Repeat this sequence for successive isotherm data points.

Take measurements for an Ar isotherm in the pressure range from 0 to 30 Torr, plotting the equilibrium vapor pressure on the  $x$  axis and amount of adsorbed Ar on the  $y$  axis as you acquire the data. Take smaller steps (smaller dosing pressures) as you get close to the knee. To help estimate gas dose sizes, you can use the number  $11 \text{ cm}^3$  STP as an approximate number for the

amount of adsorbed Ar necessary to complete the first layer.

After taking Ar adsorption data up to about 30 Torr pressure, *carefully* follow the procedure immediately below to pump the Ar out of the system. **Not following this procedure may cause the pressure inside the glass system to exceed atmospheric pressure, which can result in damage (glass may explode when over pressured) to the system and possible injury to those nearby.**

1. Close valves 2 and 4.
2. Open valves 3, 5, 6, 7, 8, 9 and 12.
3. Lower the liquid nitrogen dewar from around the sample.
4. After the pressure in the system drops below 100 millitorr, open valves 2 and 4 and close valve 3.
5. Gently warm the cell with a hair dryer and continue pumping on the system (everything except the storage volumes) until the pressure again reaches its lowest value.

Measure an N<sub>2</sub> isotherm in the pressure range of 0 to  $\approx 10$  torr using the same procedure as for Ar. Plot the equilibrium vapor pressure on the  $x$  axis and amount of adsorbed N<sub>2</sub> on the  $y$  axis as you acquire the data. Try to take small steps near the knee which indicates completion of the first layer. and especially small steps (add small gas doses) near 7 Torr pressure to map out the small sub-step defining the fluid-registered structure phase transition. Our system is capable of mapping out this sub-step in considerable detail.

Figure 5 shows some sample Ar data taken on this system by Jason Alferness. A temperature of 77.4K is above temperatures at which adsorbed Ar undergoes any 2-D phase transitions, thus there will be no feature or “step” in the isotherm as there is in the N<sub>2</sub> isotherm. A number for the amount of Ar necessary to complete the first layer can be derived from the data by extrapolating the straight portion of the isotherm above the knee to its  $y$ -axis intercept.

When you finish the isotherm, pump out the gas (except from the storage bulb) following the same procedure as after the Ar isotherm. After the gas is pumped out, close valve 2. With valve 4 still open, remove the liquid nitrogen dewar from around the trap and gently warm the trap with the hair dryer. When the trap is warmed up to room temperature, close valve 4 and turn off the mechanical pump.

## 4 Analysis

As previously mentioned, the density of nitrogen molecules on the graphite substrate at the fluid to registered solid transition is approximately 1 nitrogen molecule on every third graphite hexagon (see Fig. 6). The spacing between adjacent carbon atoms in the hexagon is known to be 1.42 Å,

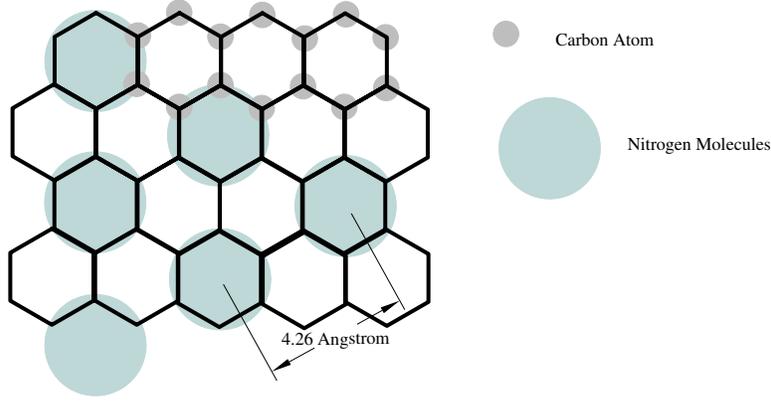


Figure 6: Geometry of commensurate  $N_2$ /graphite phase. 1/3 of graphite “hexagons” are occupied by an  $N_2$  molecule. The structure is called  $\sqrt{3} \times \sqrt{3}R 30^\circ$ , because its unit cell is  $\sqrt{3}$  longer on its side and rotated  $30^\circ$  with respect to the graphite unit cell.

the area of the graphite hexagon therefore being  $5.24 \text{ \AA}^2$  [7]. With a nitrogen molecule on every third graphite hexagon, the nitrogen density is 1 molecule/( $15.7 \text{ \AA}^2$ ).

To determine the density of Ar atoms at single layer completion, one need only take the ratio of the STP volume of Ar required for single layer completion to the STP volume at the top of the step in the  $N_2$  isotherm. The total amount of adsorbed  $N_2$  at this “2-D fluid to commensurate structure transition” occurs at approximately 7 Torr (at 77 K). At the top of the small step where the isotherm flattens out again, the area of the graphite is

$$1.04 \times 3 \times (\text{area of carbon hexagon}) \times (\text{number of adsorbed } N_2 \text{ molecules}) .$$

See reference 5, Chan, et al., 1984, for a discussion of this point.

Once the single layer density of Ar atoms is determined, one can determine the Ar-Ar separation by assuming that each Ar atom occupies a hexagonal area on the substrate. Note: this is not the same area as that of the graphite hexagons. This value of the Ar-Ar separation can be compared to the nearest neighbor distance in crystalline Ar (see table in the text, Introduction to Solid State Physics by Charles Kittel, or check in other solid state texts).

The interaction between atoms of noble gases is well described by the Lennard-Jones potential,

$$V(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] , \quad (2)$$

where  $r$  is the atom-atom separation. The parameters  $\varepsilon$  and  $\sigma$  are empirically determined from various kinds of measurements. For Ar, the parameters have the values:  $\varepsilon = 1.04 \times 10^{-2} \text{ eV}$ , and  $\sigma = 3.40 \text{ \AA}$ (see Kittel). The  $r^{-6}$  attractive term arises from the dipole-dipole, or van der Waals interactions discussed earlier, and  $r^{-12}$  repulsive term arises from the short range repulsive forces which increase very rapidly as the electron charge distributions of the atoms begin to overlap. A

plot of this potential looks similar to the one shown in Fig. 1. The quantity  $\sigma$  is the (close range) separation at which the potential energy is 0.

Given the value of  $\sigma$ , determine the equilibrium separation of 2 Ar atoms where the interaction is described by the Lennard-Jones potential. Compare this separation to the Ar-Ar distance at single layer completion, and to the nearest neighbor distance in crystalline Ar. That these numbers are all close is not surprising since the dominant force (dipole-dipole interactions) is the same in all three cases.

## *References*

1. J. G. Dash, Between Two and Three Dimensions, *Physics Today*, December 1985, page 26.
2. M. Bienfait, J. G. Dash, and J. Stoltenberg, *Physical Review B*, **21**, 2765 (1980).
3. O. E. Vilches, *Annual Reviews of Physical Chemistry*, **31**, 463 (1980).
4. X. Duval, J. Regnier, A. Thomy, *Surface Science Reports*, **1**, 1, (1980).
5. M. H. W. Chan, A. D. Migone, K. D. Miner, and Z. R. Li, *Physical Review B*, **30**, 2681 (1984).
6. J. K. Kjems, L. Passell, H. Taub and J.G. Dash, *Physical Review Letters*, **32**, 774 (1974); J. K. Kjems, L. Passell, H. Taub, J.G. Dash and A. D. Novaco, *Physical Review B* **13**, 1446 (1976).
7. T. T. Chung and J. G. Dash, *Surface Science*, **66**, 559 (1977).

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