95,060

Title: Properties of Rare-Gas Solids

Desired Starting Date: March 1, 1974 (Present Grant Expires
on February 28, 1974)

Item 1: Technical Progress Report*

During the present Grant period we have made considerable progress in our goal of understanding the properties of rare-gas solids and rare gases. We have completed our study of superfluid He film flow into beakers of solid Ar and out of beakers of solid Ar. This study has taught us a lot about surface forces and other surface effects. The study also has given interesting information about superfluid critical velocities and hydrodynamics of films. In the current Grant period we have also completed a theoretical study of Kapitza resistance. We showed that the experimental data on this effect may be explained by theory if suitable surface attenuations and surface densities are assumed. We have also almost completed our study of thermal conductivity of solid Ar. We have a considerable amount of good experimental data from 2°K to 83.8°K, the Ar triple point, and we have analyzed the data using modern theories of thermal conductivity and realistic interatomic potentials. Finally we have initiated an experimental study of interactions between rare gases and physiological systems. For this study we have some very encouraging, preliminary data on the diffusion rate of Ar molecules through membranes.

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Pollock,

The principal investigator has devoted approximately 50% of his time to this research during the Grant period since the beginning of the current Grant term. He will continue to devote 50% of his time to this research.

The work for the current year will be briefly described below under these six headings:

A. Liquid Helium Film Flow into and out of Solid Argon Beakers, B. Kapitza Resistance, C. Thermal Conductivity of Solid Argon and other Molecular Solids, D. General Activity in Rare-Gas Solids, E. Vapor Pressure of Molecular Solids, and F. Interaction of Rare Gases with Biological Materials.

A. Liquid Helium Film Flow into and out of Beakers of Solid Argon

The purpose of this experiment was to study the flow of liquid He films over a surface whose interactions with Helium we understand. During the current Grant period we completed this study and achieved all our intended goals. This experiment was the Ph.D. thesis problem of Thomas O. Milbrodt. Dr. Milbrodt received his Ph.D. in September 1973, during the Current Grant period. He remained on the Grant as a post-doctoral research associate until December 15, 1973. We have been successful in finding for him a suitable position in which he can carry on his professional career. Dr. Milbrodt will start in January 1974 as an assistant professor in the Physics Department of Bowling Green State University.

The research is described in detail in the numbered bibliography in papers 32 and 33. These are, respectively, a reprint of an article: "He-II Film Transfer Rates for Solid-Ar beakers", Phys. Rev. 8, 930-7 (1973), and a copy of the Ph.D. thesis: "Helium II Film Transfer Rates for Solid-Argon Beakers" by T. O. Milbrodt.

Since the experiment is described in all its aspects in the two items above, we include here only a brief summary of the main points of the research. In this experiment we grew beakers of solid Ar by freezing liquid Ar in a mold. The mold was then removed, leaving free-standing beakers of solid Ar. It was possible to make beakers that were leak free, i.e. that did not leak normal liquid He and did not leak superfluid He, as far as could be determined by experimental tests. We filled these beakers with superfluid He using a He fountain and studied the flow rates for beaker emptyings. We also made many measurements of beaker filling rates, i.e. experiments in which the He level outside is initially higher than the level inside and the liquid He flows over the beaker rim into the beaker proper until the inner and outer levels are equal.

In this experiment we measured the flow rate σ , in cm^3 per sec per cm of circumference, as a function of temperature (T), height from the liquid helium surface to the beaker rim (H), and driving force under the level difference (z). We made most of our measurements at 1.66°K , although we also

took data in the range 1.47 - 1.99°K.

The dependence of σ on z gives information on critical velocities in superfluid helium and also on the rate of dissipation of chemical potential when helium flows at supercritical velocities. The theoretical relation connecting σ and z is $\sigma = (A - B \ln z)^{-1}$ where A and B are parameters determined from the theory. They, in turn, give information about vortex production in liquid He and about dissipation mechanisms. We found that our data fit this function quite well and we obtained values of A and B which can be matched to theoretical values.

Our main interest in this experiment was to test and extend our understanding of the surface forces between He and argon. This information is contained in the dependence of film thickness on film height and appears in the analysis of our experiment as $\sigma(H)$. We compared our results with the van der Waals theory of surface forces in which the He-Ar interatomic potential is taken to a Lennard-Jones potential derivable, using combining rules, from the He-He and Ar-Ar interatomic potentials. According to this theory we would expect an H Dependence $\sigma \propto H^{-\frac{1}{2}}$. We also compared our results with the theory of surface forces of Dzyaloshinskii, Lifshitz, and Pitaevskii. This is a theory based on the exchange of photons between any substrate and adsorbate as measured by the complex dielectric constant of the substrate and adsorbate. Since the absorption spectra for solid Ar and liquid He are known, one can derive from these spectra data, the force

between liquid He and solid Ar. The result is $\sigma = (\rho_s/\rho) \cdot 5.05 \times 10^{-5} H^{-0.21}$, where (ρ_s/ρ) is the superfluid fraction of liquid He at the temperature of the experiment. Our experimental results support the theory of Lifshitz and are also close to the results of the usual van der Waals calculation.

The details of this work are given in the papers numbered 32 and 33 in the attached bibliography.

This experiment has been well received by the low-temperature physics community. The principal investigator gave an invited paper on the work at the June 1973 meeting of the American Physical Society and has also given eleven other seminars and colloquia on this research. A complete list of these will be given in Section D. Dr. Milbrodt and the principal investigator are grateful to the A.E.C. for supporting this work and making it possible to do this experiment.

B. Kapitza Resistance

During the present Grant period we have completed our projected theoretical study of Kapitza Resistance. This work was the Ph.D. thesis topic of Mr. Jon Opsal. The purpose of this study was to try to understand and resolve the apparent paradoxes between experimental measurements and theoretical calculations of Kapitza resistance (R_k). Kapitza resistance is essentially the temperature jump at the inter-

face between a solid and liquid He when heat flows across the interface.

Typical experimental values of R_k are about $1 \text{ m}^\circ\text{K}/(\text{mW cm}^{-2})$ near 1°K , i.e. when a heat flux of 1 mW/cm^2 flows across the interface between a solid and liquid He, the temperature on the He side of the interface differs from the temperature on the solid side by 1 mK . The phenomenon has been much studied since 1941 when Kapitza first discovered it.

The theoretical explanation of Kapitza resistance due to Khalatnikov, and to Mazo and Onsager treats the heat flow across the liquid-solid interface in terms of quantized elastic waves, i.e. phonons, which are incident on the interface and are then reflected or transmitted. The idea is that many of the phonons are reflected because of the large differences in acoustic impedance between the solids and liquid helium. Theoretically calculated values for R_k are typically an order of magnitude or more ^{larger} ~~smaller~~ than the experimental values. Our work on this problem is aimed at trying to resolve this paradox: Why are the calculated and measured values of R_k in such disagreement? Is the phonon acoustic mismatch theory incorrect in some essential way? Can the theory be modified so as to bring theory and experiment into agreement? Are the experiments somehow measuring something different from the theoretically derived quantities?

The model that we adopted for our work was to apply the Khalatnikov theory to a realistic model of the interface between a solid and liquid He. Real solids may have surfaces

that are more or less deformed and in such deformed surfaces we expect a lower acoustic impedance than at perfect surfaces. Also at the He side of the interface between liquid He and a solid, there is a condensed layer of He atoms, and for about the first $18 \text{ \AA}$ the density of the liquid is increased. Our idea was to recalculate $R_k(T)$ for a Cu-liquid He interface including these two effects respectively, attenuation in the solid and impedance matching due to condensed He.

The details of the calculation are given in two publications numbers 34 and 35 in the attached bibliography. The first of these is a preprint of a paper to be published shortly in Physics Letters, entitled: "The Combined Effects of Phonon Attenuation and Impedance Matching on Kapitza Resistance". The second is a preprint of a longer paper to be published in the Physical Review, entitled: "Improved Calculations of Kapitza Resistance: The Combined Effects of Phonon Attenuation and Impedance Matching on Kapitza Resistance."

The basic result of our work is that if one assumes suitable attenuation in the solid, and also includes impedance matching due to the increased He density at the interface, then the usual theory of Kapitza resistance does predict values of $R_k(T)$ in agreement with experiment for a Cu-He⁴ interface over the range from 0.03 to the lambda temperature (T_λ). Since the calculation and its results are presented

in such detail in the two preprints, which are included, we shall not give a detailed exposition here.

The student whose Ph.D. thesis this work comprises, Mr. Jon L. Opsal, has finished his work and we were very fortunate in obtaining for him a position as assistant professor in the Physics Department of Portland State University in Portland, Oregon. Mr. Opsal assumed his duties in September 1973, and finished writing his thesis there. He has by now taken his final oral exams, his thesis has been approved, and he has completed all the Ph.D. requirements. His thesis is now being printed and bound and he will receive the Ph.D. degree in Winter quarter 1974.

C. Thermal Conductivity of solid Ar and other Molecular Solids.

In the current Grant period we have extended our measurements of thermal conductivity of solid argon to the range 2-83.8°K. This is the entire temperature range over which we aimed to take data and it includes many of the regions of theoretical interest. We have made several independent runs on large-grained solids; the data are reproducible and in agreement with the measurements of other workers over the common T ranges.

The apparatus we have designed, built, and used for these thermal conductivity measurements is rather versatile and can be used for measuring thermal conductivity of other molecular solids at low temperatures. Indeed this was

another of the goals of this research project: To develop apparatus and techniques for growing good quality crystals of cryogenic solids and for measuring thermal conductivity at low T. Now that this path is clear we shall proceed to growing large single crystals of Ar, if possible, and to investigate other substances. These experiments are described below in the Proposed Technical Program, section A.

The maximum value of thermal conductivity that we observe is about 70 mW/cm K, near 7°K. We judge from this that our phonons are scattering from internal strains and dislocations in the solid Ar crystals. It was our original intention to grow such excellent quality single crystals of Ar that the phonons would scatter ultimately at low T only from the crystal boundaries. We now probably know fairly well how to do this, but it will require some redesigning and rebuilding of some of the apparatus. This is only about three month's work and we shall undertake it in the forthcoming renewal period. Since our present data are so interesting and useful we have decided to pause and take time to analyze the data now using modern theories of thermal conductivity.

The theoretical analysis is now essentially complete. We have analyzed the part of the thermal conductivity for T above the maximum using the theory of Krumhansl with different two-body potentials with suitable potential parameters. Our theoretical calculation uses quasi-harmonic force

constants, i.e. the force constants are associated with the cell size determined from x-ray measurements. This has enabled us to calculate T dependent thermal conductivities. Working out the proper computer programs for calculating thermal conductivity was a difficult problem but it is now all finished.

The theoretical results agree very well with experiment and we have learned many interesting new things about realistic interatomic potentials and thermal conductivities. For example, it had been observed in our work and work of others that experimental values of thermal conductivity decreased faster than the expected T^{-1} for increasing temperatures below but near the Debye temperature. We have been able to show that at least part of this is the result of the expanding lattice, i.e. when our quasiharmonic force constants are used then the calculated thermal conductivity falls off faster than T^{-1} also.

We have also analyzed our data below the thermal conductivity maximum. This gives information on the defect structure of the crystals.

The details and results of this research will be written up and submitted for publication within the next four months. We have presented an early version of the experimental data at the June 1973 A.P.S. Meeting (Bull. Am. Phys. Soc. 18, 772 (1973)). We plan to present the theoretical results at the A.P.S. Meeting in March 1974 in Philadelphia.

This work has been the thesis work of Mr. David K. Christen. The study is essentially completed and Mr. Christen will shortly start to write his Ph.D. thesis. He will get his degree in Spring of 1974. To continue these studies we propose to assign a promising new graduate student, probably Mr. Juan Bautista. In the Budget for the forthcoming year we ask for funds to keep Mr. Christen on as a research associate until the Fall of 1974 and to take on Mr. Bautista. During this time one of Mr. Christen's duties will be to help carry out the necessary redesign and reconstruction of the apparatus described above. We intend that Mr. Bautista's thesis project will be on the growth and thermal conductivity of large single crystals of Ar. That should be an extraordinarily interesting research topic but not too difficult.

D. General Activity in Rare-Gas Solids

During the current Grant period the principal investigator and his students have continued to maintain close contact with several other laboratories working in the fields of rare gases and liquid helium. We have also continued to maintain an up-to-date bibliography of papers published in the fields of our research: rare-gas solids, liquid helium, Kapitza resistance, and the law of corresponding states.

In June of this year the American Physical Society held its Spring Meeting in East Lansing at the Michigan State

University campus. The principal investigator gave an invited paper on research performed under this Grant. The title of the talk was: "The Transfer Rate of Superfluid Helium from Solid Argon Beakers" and the abstract appears in Bull. Am. Phys. Soc. 18, 772 (1973). At the same Meeting Mr. David K. Christen gave a talk as described in Section C above which was well received.

Our work on superfluid He film flow into and out of solid Ar beakers has been well received. The principal investigator has subsequently given several colloquia and seminars on this research as follows: In October 1973, Physics Colloquia at The University of Michigan, Wayne State University, and Notre Dame University. In November 1973, colloquia at Michigan State University, University of California at Santa Barbara, and the University of California at Irvine. Also in November 1973, Low Temperature Seminars at U.C.L.A. and at the California Institute of Technology. In December 1973, Low Temperature Seminars at the University of Oregon and at the University of Washington and a Physics Colloquium at Portland State University. In January 1974, the principal investigator is scheduled to give a colloquium at the University of Windsor in Windsor, Ontario.

The last seven talks were given during a series of visits, during 13 days in late November and early December, to laboratories of low temperature physics. During this

visit the principal investigator also briefly visited the University of California Medical Center in San Francisco to discuss the research on interactions between rare gases and biological systems with active researchers there.

E. Vapor Pressure of Molecular Solids

During the current Grant period we published the paper "Sublimation and Vapor Pressure of Ar³⁶" by Jon L. Opsal, Charles W. Leming and Gerald L. Pollack. This appears as paper no. 36 in the attached Bibliography.

This research was the first part of the thesis of Jon L. Opsal and a natural extension of our earlier research. We made measurements in the range from 23.8 - 87.4°K making corrections for thermal transpiration and mercury streaming. Further experimental and theoretical details are given in Mr. Opsal's Ph.D. thesis and in the above Physical Review paper.

F. Interaction of Rare Gases with Biological Materials

During the current Grant period we have started work on some interdisciplinary studies of the interaction of rare gases with biological materials.

Rare gases are used in important applications in medicine and industry. Since a good deal of effort in our research program has been aimed at understanding the interaction among rare gas atoms themselves and among rare

gas atoms and other atoms we are in a good position to understand the properties of rare gases in general. We believe that this kind of study is a natural supplement and extension of our previous work.

During the current Grant period we have studied diffusion of Xe through biological and artificial membranes. Our first goal in this is to understand the interaction between Xe and membranes. It has been known for some time that Xe is a general anesthetic, i.e., if one replaces the N_2 in air by Xe then the resultant Xe + O_2 gas mixture is a general anesthetic for humans. There is some evidence that the site of action of this anesthetic, and indeed all general anesthetics, may be in the membranes of biological systems. Our ultimate goal is to study how rare gases interact with membranes in order to understand the mechanism of general anesthesia. The mechanism of general anesthesia is not known. We feel that our familiarity with rare gases and their properties combined with the observation that Xe is a general anesthetic puts us in a unique position to study this very important problem. The idea is that once we know how Xe produces anesthesia we will likely know why general anesthetics work in general, i.e. we will understand the mechanism of general anesthesia. This may make it possible to design a more ideal anesthetic.

This problem has interested the principal investigator for a long time and good students also have been attracted

to this problem. Since the work has so many aspects to it we have been relying for advice on discussions with many people in different fields. We have undertaken an interdisciplinary study of the effects of rare gases.

During the Grant period we have carried out these experiments in a laboratory loaned to us by the School of Osteopathic Medicine on the M.S.U. campus. We have also been in close contact and used the facilities of the Cyclotron Laboratory of Michigan State University. In addition to this we have maintained contact and sought advice from the Department of Biophysics, members of the staff of the A.E.C. Plant Research Laboratory, pharmacologists, physical chemists, anesthesiologists, and biological chemists.

So far we have developed a technique, built apparatus and made many measurements on the diffusion coefficient (d cm/sec) for diffusion of radioactive Xe-133 through frog skin membranes and through dialysis tubing membranes; the former is a living membrane system and the latter is an artificial membrane. The quantity we measured d is the molar flux (moles/cm²-sec) through the membrane per unit concentration difference (moles/cm³) across the membrane.

In the course of the work during the past year we have overcome several interesting problems. For example, Xe is only slightly soluble in water and, as with almost all gases and all liquids, the gas stays in solution only

if a suitable partial pressure of Xe is maintained at the free surface. This has required special techniques involving vessels that are completely full of liquid and closed, etc. There have also been problems to overcome involving the handling of radioactive materials and measuring the amount of Xe present. Fortunately this problem has excited the interest of several other people in the University community so we have been able to borrow important equipment to support our work.

Our measurements now give reproducible values for d to within about 25%. We shall next try to improve this by a factor of three or better. After that we shall extend the measurements to other kinds of membranes, e.g. toad bladders and turtle membranes, which are easy to work with and easy to obtain. Finally we shall try to determine the T dependence of the diffusion and from this deduce the transport mechanism from first principles. We think that, should this entire attempt be successful, the results will be very interesting and useful to physicists as well as biologists. We anticipate being able to complete both of these studies in the next year and also to publish the results during that time. With a little good luck we shall be able to include in next year's Technical Progress Report two preprints of completed work. Further description of the problem and our plans appear below, in Section E. of the Proposed Technical Program.

* This research has been supported by the U.S. Atomic Energy Commission under Grant No. AT(11-1)-1574.

Numbered Bibliography for Current Grant Period

32. "He-II Film Transfer Rates for Solid-Ar Beakers",
by T. O. Milbrodt and Gerald L. Pollack, Phys. Rev. 8,
930-7 (1973). Reprint.
33. "Helium II Film Transfer Rates for Solid-Argon Beakers",
by Thomas O. Milbrodt, Ph.D. Dissertation, Department
of Physics, Michigan State University, 1973. Copy of
thesis.
34. "The Combined Effects of Phonon Attenuation and Impedance
Matching on Kapitza Resistance", by Jon L. Opsal and
Gerald L. Pollack. To be published in Physics Letters.
Preprint.
35. "Improved Calculations of Kapitza Resistance: The
Combined Effects of Phonon Attenuation and Impedance
Matching on Kapitza Resistance", by Jon L. Opsal and
Gerald L. Pollack, submitted to Physical Review. Preprint.
36. "Sublimation and Vapor Pressure of Ar³⁶", by Jon L. Opsal,
Charles W. Leming, and Gerald L. Pollack, Phys. Rev. B 7,
4682-6 (1973). Reprint.
37. Technical Progress Report for Grant AT(11-1)-1574.