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MASTER

A STUDY OF MECHANISMS OF HYDROGEN DIFFUSION IN SEPARATION DEVICES

Third Annual Report
1979-80

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DISCLAIMER

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Abstract

The progress made in the third year of the work under the auspices of a DOE ERDA contract (DE-AS09-77-ER01023) is summarized in this Annual Report. The main results, described in detail in 9 papers (6 in print and 3 in press) listed under Publications, are in the following three areas: (i) Examination of our Diffusion Model for PdH system. (ii) Connection between our diffusion model and other physical models. (iii) Related problems. Advances made during the third year of this Project, particularly in understanding our physical model for hydrogen diffusion, make it possible for us to begin to meet some of our long-range objectives described in our initial Proposals of 1977-78.

I. Overall long-Range Objectives

The diffusion of light gases (e.g., hydrogen) in palladium-type transition metals is selective. Hence, membranes made of these metals can serve as separation devices in heavy water enrichment, in nuclear fusion reactors. The nature of light-gas diffusion in transition metals is very poorly understood. The diffusion and other transport properties are known to be governed by quantum many-body mechanisms. To realize possibly rich applications of this problem, a detailed study of the transport mechanisms has been initiated under the auspices of a DOE ERDA contract. See our first proposal for additional details.

II. Progress Made in 1979-80

To account for the observed behavior of hydrogen diffusion in palladium, we have developed a physical model starting from first principles. The model incorporates the following key facts: (i) Hydrogen atoms are embedded in a nonrigid Yang-Lee lattice. (ii) Hydrogen atoms experience pairwise, attractive long-range forces which are mediated by the metal lattice. (iii) Hydrogen atoms undergo tunnelling transitions cooperatively. Our model ignores all other short and long range effects. Yet it is not simple. It is more complex than most of conventional cooperative models currently much studied, e.g., the Heisenberg model. To make it tractable, we have applied a certain mathematical transformation to the model.

The process is equivalent to making the metal lattice rigid at the expense of introducing multi-atom scattering, e.g., 4-body interaction. The resultant model represents an ensemble of weakly interacting diffusons--quasiparticles of diffusion.

Although diffusons do not behave simply except in some special limits, the cooperative process of diffusion can be much better understood in terms of them. Still, usefulness of any model comes from its ability to explain observed behavior as well as its ability to make predictions, which can be independently verified. Our efforts in 1979-80 have been devoted to understanding of our model in order to test the usefulness of our model. Also, some unusual features of metal hydrides require separate studies to determine their importance to the overall goals of our project. Our progress made along these lines during the past year is briefly described below. For details, we refer to specific publications given in sec. III.

A. Our Diffusion Model--Examination and Exploration (See 1, 8, & 9)[+]

Our model has been applied to describe the A & B phases of metal hydrides, e.g., PdH. In particular, it is aimed at looking at the different behavior of the time correlation function in the two phases observed in some recent experiments. Our model assumes that the metal-hydride lattice is nonrigid and that the embedded protons are coupled pairwise via a phonon field. We find that the unitary-transformed Hamiltonian is expressible in terms of diffusons--certain quasiparticles--which can lead to a soluble situation in some suitable limits

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such as constant-coupling. Using our diffuson model and an RPA, we have obtained time-dependent autocorrelation function. The correlation function for the A phase is different from that for the B phase, but they are continuous at the second-order transition point. Our model indicates the existence of a tricritical point depending on the magnitude of the phonon-coupling parameter which enters into the original Hamiltonian. Our model also applies to metal deuterides. Within an RPA, it predicts that the time correlation functions are strongly isotope-mass-dependent, but that the phase transition temperatures T_c are only weakly isotope-mass-dependent, i.e., $T_c(\mathrm{PdH}) \simeq T_c(\mathrm{PdD})$. Our prediction on the transition temperature having essentially no mass dependence is remarkable in view of the strong mass dependence shown in the superconducting temperature in the same metal hydrides. Our conclusions, nevertheless, seem consistent with the known and extrapolated information on metal hydrides.

B. Connection between our Model and other Physical Models (See 3, 4, and 7)

In constructing our model, we have sought to incorporate only essential information. As pointed out already, our model still is more complex than most of conventional cooperative models currently in vogue. Hence, it seems prudent to look at our model under some suitable approximations such as the RPA which are physically reasonable. In so doing, we can obtain considerable qualitative information about our model. Also, if our model reduces to some known limits, we have at our disposal already existing knowledge which will be qualitatively correct.

For this purpose, our transformed Hamiltonian (i.e., an ensemble of weakly interacting diffusons) has an advantage over the original form since its lattice now is a rigid one as are the lattices for all conventional models. If we introduce constant-coupling in particular, our model becomes a generalized version of the van der Waals model of quantum spin. The ordinary van der Waals model has only two-spin interactions, but our model has 4-spin interactions.

The physics of the van der Waals model has been extensively studied recently by us [R. Dekeyser and M. H. Lee, Phys. Rev. B 19, 265 (1979)]. The model has second-order phase transition, whose critical behavior is all mean-field-like. From this study, it is evident that for temperature T greater than the critical temperature T_c our diffusion model behaves much like the van der Waals model. Thus, for the high temperature side, the space and time correlation functions for our diffusion model must have the same structure as those for the van der Waals model. But for $T < T_c$, there can be an important difference in ordering. The van der Waals model is unable to have first order transition, but our diffusion model can have a tricritical point depending on the strength of the 4-spin interaction.

C. Related Problems (See 2, 5, 6)

Using metal membranes ultimately as separation devices for light gases is the underlying motivation of our project. One special feature of hydrogen diffusion in palladium is that the physical process is cooperative. That is, hydrogen diffusivity is mediated by the metal lattice. Thus, the metal is not merely a static, sieve-like barrier but it acts as a dynamic agent. This role of metals appears rather similar to that played by biological membranes with respect to the permeation of nutrient molecules. For biological transport, biomembranes act as separation devices much as the transition metals do for light-gas diffusion. Hence, any progress made in one area can provide considerable insight into the other area. This possibility was noted in our original proposal of 1977.

In constructing our model of diffusion, we have in fact made use of cooperativity much utilized in biomembranes. Reciprocally, our recent advances in hydrogen diffusion in metals have enabled us to describe transport of neutral molecules in biomembranes in a manner of cooperative diffusion. For additional details we refer to our paper (second article in Sec. III).

Experimentalists have recently turned to the Mossbauer line shapes to investigate hydrogen diffusion in metals. The very narrow, well-defined lines of the Mossbauer spectra contain a wealth of information on the relaxation of the metal hydride systems, which is directly related to the time correlation function, hence also to the diffusion coefficient. In order to interpret these spectral lines, we have made studies of the relaxation phenomena. Our preliminary progress made is reported in our publications 5 and 6.

III. Publications[+]

A. Journal Articles

1. S. Banerjee and M. H. Lee, Diffusion Model for Hydrogen-Palladium System, J. Appl. Phys. 50, 1776 (1979).
2. M. H. Lee, et al., Binding Site Model of Membrane Transport, J. Memb. Biol. 50, 205 (1979).
3. S. K. Oh and M. H. Lee, High-Temperature Fluctuation Expansions, Phys. Rev. B 19, 5815 (1979).
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B. Contributed Papers at Conferences (Abstracts Published)

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IV. Scientific Personnel (Other than the Principal Investigator)

A. Postdoctoral Level

Dr. S. Banerjee joined the Project in December 1977 coming from Brookhaven National Laboratory. He holds a Ph.D. in Physics (1977) from SUNY at Stony Brook, where Professor M. Blume was his PhD supervisor. Dr. Banerjee is supported fully by the Project.

B. Predoctoral Level

Two predoctoral students, each supported by the project approximately on a half-time basis, and a third student supported by a University graduate fellowship, work on their thesis research as members of the Project. They are assigned to work on problems connected with the Project under the supervision of the Principal Investigator.

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