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A STUDY OF MECHANISMS OF HYDROGEN DIFFUSION IN SEPARATION DEVICES

MASTER

Annual Progress Report
1980-81

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Abstract

The progress made during the period of 1980-81 under the auspices of a Department of Energy contract (DE-AS09-77-ER01023) is summarized in this annual progress report. Our progress is described in detail in 9 scientific articles, listed under Publications in sec. III. Our main results are in the following 3 areas: 1. Static and Dynamic Properties of the Hydrogen Diffusion model. 2. Exact Asymptotic Solutions of the Model. 3. New Physics of the Lattice Hydrogen. The progress made during this period has been particularly significant. Our hydrogen diffusion model has brought to light a number of puzzling features of hydrogen metal systems. Our advances have made it possible now to begin to study some of our long-range objectives put forth in our initial proposal.

I. Overall Objectives

The diffusion of light gases, e.g., hydrogen isotopes, in transition metals such as Pd is now well established to be highly selective. Hence, membranes made of these metals can serve as an isotope separation device in heavy-water enrichment, in the nuclear fusion reactors. The nature of light-gas diffusion in transition metals is rather poorly understood, but currently is receiving some attention from a number of different interdisciplinary directions. Recent investigations show that the dynamical processes cannot be explained in terms of a classical picture such as the Arrhenius theory. They suggest a quantum statistical description. To realize possibly rich applications of the hydrogen diffusion mentioned above, we need to know the detailed mechanisms involved. For this purpose, a study of transport mechanisms has been initiated under the auspices of a DOE contract. For further details, see our original proposal.

II. Progress made in 1980-81

Previously, we constructed a quantum statistical mechanical model of hydrogen diffusion in a transition metal. (See J. Appl. Phys., 1979, Vol. 50(3), pp. 1776-1778.) The model represents a preliminary picture of hydrogen transition mechanisms from the point of view of quantum statistical mechanics. The needs for such a description and the basic features of our model are already given in our previous reports to the DOE, also recently published in J. Separation Sci. & Tech., 1980, Vol. 15(3), 457-474.

During the period of 1980-81, we have carried out a detailed analysis of our model in the following 3 main areas for the purpose of ultimately achieving our overall goal of sec. I.

A. Deduce static and dynamic properties of the Model (2,3,4,5).

B. Obtain exact solutions of the Model in some limiting regimes (1,6,7).

C. Interpret our Model to provide an understanding of the complex physics of hydrogen in a metal (8,9).

Here the numbers in a parenthesis denote our publications listed in sec. III. These 3 areas of our progress will be separately described in this section.

As may be inferred from our output (see sec. III), considerable progress was made during this period, following the impetus of the last year's efforts. One important result is that a new picture of the lattice hydrogen (i.e., hydrogen in a metal, after Alefeld) has emerged, completely different from the existing accepted one due to Alefeld, which we have long felt was incorrect. This new picture comes from a slightly modified version of our Model. It can explain much of the physics of the lattice hydrogen unambiguously, whereas the Alefeld picture leaves several important points unclear. Our work was culminated by an invitation received to address at an international symposium on metal hydrogen systems in April 1981. This symposium was attended by people interested in energy and energy-related problems, more than 2/3 of the participants coming from outside the U.S.

A. Static and Dynamic Properties

Hydrogen-Metal Systems exhibit phase transitions of both first and second order. The phase transitions are reminiscent of those of a one-component ordinary gas-liquid system, but with one important difference. The second-order transition in metal-hydrogen systems has been experimentally observed to be classical or mean-field-like (as demonstrated recently by F. D. Manchester and his co-workers), whereas the gas-liquid transition is nonclassical. Thus, the validity of any theoretical model for metal-hydrogen systems can be judged by the critical behavior which it produces. In addition, it is an advantage to illustrate static and dynamic properties of the model in the neighborhood of the critical point, where many of irrelevant details can be suppressed by critical fluctuations.

A careful examination of the Alefeld picture, in the vicinity of the critical point, shows that the gas-liquid analogy breaks down completely. The ordering in the B-phase of the H/Pd system, for example, is not in the coordinate space in the usual sense. It seems more analogous to the Bose Einstein condensation. In particular, at the A-B transition of the H/Pd, one finds no structural anomaly The coexistence of the two phases is not one of phase separation, but one of interpenetration of the two phases (similar to the coexistence of the normal and superfluid components of liquid ^{4}He below the lambda temperature). Hence, the traditional intepretation of the A phase as gas-like and the B phase as liquid-like is untenable. This difficulty casts a doubt on the existing understanding of hydrogen-metal systems. Our model completely removes this difficulty and provides a new understanding of hydrogen-metal systems.

This new understanding, described more fully in our publication No. 4, has emerged from a careful analysis of our model. Our progress will be briefly summarized here, referring to our publication for full detail. Our cooperative hydrogen diffusion model is isomorphic to a model of magnetism for biquadratic exchange spin interaction.

See our publication No. 2. (Generally, ordering is much more easily analyzed in magnetic systems than in any other physical systems. Thus it is a common practice in many-body problems to look for isomorphic magnetic models). The biquadratic exchange model has two kinds of ordering: dipolar and quadrupolar. Our analysis shows that the A and B phases of H/Pd are closely related to quadrupolar ordering, rather than to dipolar ordering, from which the gas-liquid analogy was erroneously derived by Alefeld. Unlike the dipolar ordering, the quadrupolar ordering does not exhibit a simple spatial geometric distribution. This is consistent with the lack of structural anomaly observed in the A-B transition of H/Pd, i.e., no phase separation. Our analysis shows furthermore that the observed critical point really is a tricritical point. It is known that the critical behavior about a tricritical point is mean-field-like. The experimental finding of Manchester et al is indeed that the critical behavior in H/Pd is entirely mean-field-like. Thus, our analysis clears up the long-standing mystery that the critical behavior of H/Pd is mean-field-like or classical whereas the critical behavior of ordinary fluids, after which Alefeld constructed his model, is nonclassical.

Our model describes other physical properties. Some of the more important ones are briefly discussed below. It divides the system into high and low temperature regions, determined by the critical temperature T_c. This division is not trivial as T_c is not a simple number. The critical temperature is found to depend on the relative magnitudes of J vs K, delocalizing and localizing tendencies of the lattice hydrogen, roughly proportional to the lattice cell dimensions and the elasticity of the lattice, respectively. For $K < K_c$, where

$K_c = 2J/3$, T_c is independent of K for fixed J, so that one can absolutely assign the two temperature regions. For $T > T_c$, the static and dynamic behavior is entirely classical, i.e., the free energy is dominated by the entropy, not by the cooperative interaction. Thus, the diffusive mode, for example, must follow the Arrhenius pattern. For $K > K_c$, the critical temperature is a function of K in such a way that the high temperature region is reduced. That is, the classical domain is diminished and the quantum domain is enhanced. The tricritical point is given by $K = K_c$ and $T = T_c$ for fixed J. For $T < T_c$, there are dipolar and quadrupolar regions separated by a mixed phase region. The dipolar region bounded by $0 < K < K_c$ and $0 < T < T_c$, and the quadrupolar region by $K >> Kc$ and $0 < T < T_c$. In the dipolar domain, the critical temperature is a constant number, meaning that T_c is isotopic-mass independent, i.e., H/Pd and D/Pd have the same value for T_c. Recently, the Soviet group, headed by V. A. Somenkov, has found such a result. These properties of our model lend a strong support for its validity in describing hydrogen in the Pd metal.

B. Exact Solutions of the Model

The cooperative hydrogen diffusion model of ours is a complicated model and it will not yield exact analytic solutions in its original form. (One cannot solve, e.g., the partition function analytically.) Exact solutions are obtainable, however, if the model is taken to some limiting domains. These asymptotic exact solutions are important because they provide guidance to approximate solutions and suggest clues to the true behavior of the model.

In our publications (Nos. 1, 6 and 7), we have studied appropriate limiting cases of the model. At these limits the model still retains its essential character. The first limiting case involves a modification of the cooperative interaction in the lattice hydrogen. Under a constant coupling limit, the range of the cooperative interaction is made infinite which makes the model soluble. This case turns out to correspond very closely to the spin van der Waals model of Dekeyser and Lee. The time correlation function for the van der Waals model is completely determined so that, via the correspondence, we know the diffusive mode of the lattice hydrogen. In fact, the time correlation function in the high temperature region is Gaussian, i.e., correlated in short times only. It is consistent with the observed classical transport behavior of the lattice hydrogen. Our asymptotic exact solution indicates, thus, that the range of the cooperative interaction (as yet not established experimentally) involves more than near neighbors. This information is useful since it implies that the long-range nature of interaction can come about only through the lattice distortion and it is in the lattice distortion (i.e., nonrigidity of the lattice) that the controls for transport mechanisms are contained. These are in fact the basic premises of our original model.

The second limiting case aims more at mathematical simplification than at physical understanding. If we were to look for the relaxation function of our model via Mori, we would be faced with infinite continued fractions. It would be a mathematically untenable situation. Our modification is to smoothen the model, i.e., replace the fields due to near neighbors with a uniform field. Then, the continued fraction terminates naturally and we can obtain an exact relaxation function. Owing to the truncation of the continued fraction, the relaxation function is nondiffusive. But this procedure teaches us how to systematically improve the nondiffusive solution by successively pushing the order of the continued fraction. An illustrative case is treated in detail in our publication No. 7.

C. The Physics of Lattice Hydrogen

A signal progress made during the current period concerns our discovery of a certain peculiar property of the A phase of H/Pd. We expect much of our next year's work to continue to center on our finding of this special property of the A phase and its far-reaching implications. The physics of the A phase has enormous practical implications also since most of the transport processes mentioned in sec. I are likely to take place in the A phase.

The A phase has been hitherto regarded simply as the dilute hydrogen phase. Here the hydrogen concentration is measured relative to the metal atoms. For example, the critical concentration (according to the recent measurements by Manchester and his co-workers in Canada) is $x \approx 0.3$, where x denotes the number ratio of the absorbed hydrogen atoms to the Pd atoms in the metal. It would actually be more appropriate to measure the number of hydrogen atoms with respect to the number of total octahedral interstitial sites of the fcc Pd lattice, say y. This is because the Pd atoms mediate hydrogen-hydrogen interaction, but otherwise they play no other roles. Hence, it is more useful to measure the hydrogen number with respect to the octahedral interstitial number provided that the tetrahedral interstitial sites are energetically forbidden. As long as x is less than unity, one can disregard the tetrahedral interstitial sites. At $x \approx 0.5$, the distinction between x and y is not important; but as x becomes smaller, the difference becomes significant. In fact it is only through y one can understand one very subtle but important experimental fact--

the existence of a miscibility gap in H/Pd at the dilute end. That is the A phase persists for temperatures below $T_c \approx 566K$ with very minute amounts of the lattice hydrogen. Thus, one is led to question the very meaning of the A-phase itself.

Our important progress here is in finding an answer through another physical problem where there also exists a similar miscibility gap---3He/4He liquid mixtures at very low temperatures. In these He mixtures there is phase separation of the 3He-poor superfluid 4He phase and the pure 3He normal fluid phase. The 3He-poor phase has a 6% 3He molar concentration in liquid 4He. Clearly, the A phase of H/pd has the appearance of the 3He-poor superfluid 4He phase. In light of this discovery, we see that the A phase of H/Pd is not a dilute hydrogen phase, it is a hydrogen-poor octahedral interstitial phase. The octahedral interstitial sites may be thought of as quasiparticles, previously identified as diffusons but derived entirely independently. See our work, J. Appl. Phys., 1979, Vol. 50(3), pp. 1776-8. This connection establishes the A phase of H/Pd. We shall pursue other consequences of our discovery next year.

III. Publications†

A. Journal and Book Articles

1. S. Banerjee, R. Dekeyser, and M. H. Lee, Statics and Dynamics of Constant-Coupling Hamiltonian, J. Magn. & Mag. Mats. 15-18, 428 (1980).

2. M. H. Lee, Nonrigid Lattice Model of Hydrogen Diffusion in a Transitional Metal: A Statistical Mechanical Approach, J. Sep. Sci. and Techn. 15(3), 457 (1980).

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3. M. H. Lee and S. Banerjee, Time Correlation Functions in the A and B phases and Possible Existence of a Tricritical point in a Cooperative Model for Metal Hydrides, J. Less Common Metals 74, 244 (1980).

4. M. H. Lee and S. Banerjee, Analysis of a Cooperative Model of Hydrogen Diffusion in a Transition Metal, in Metal-Hydrogen Systems, edited by T. N. Veziroglu. (Pergamon Press, Oxford, 1981).

5. M. H. Lee and S. Banerjee, Low-Temperature Behavior of Biquadratic Exchange Model, (submitted to Physica, B+C, 1981).

6. M. H. Lee and I. M. Kim, The Bounds of Falk and Bruch in the Low Temperature van der Waals Model, (submitted to Physica, B+C, 1981).

7. M. H. Lee, Time Evolution, Relaxation Function, and Random Force for a Single-Spin Model, (submitted to Phys. Rev. B1, 1981).

8. I. M. Kim and M. H. Lee, Fluctuation and Susceptibility for the spin van der Waals Model and The Bounds of Falk and Bruch, (submitted to Phys. Rev. B1, 1981).

9. M. H. Lee, Long Range Order in the spin van der Waals Model, (submitted to J. Statistical Phys., 1981).

B. Contributed Papers at Conferences (Abstracts Published)

1. M. H. Lee, S. Banerjee, Time Correlation Functions in the A-B Phases of metal Hydrogen Systems International Symposium on the Properties and Applications of Metal Hydrides, Colorado Springs, Colorado, April 7-11, 1980.

2. M. H. Lee, Analysis of a Cooperative Model of Hydrogen Diffusion, International Symposium on Metal Hydrogen Systems, Miami Beach, Florida, April 13-15, 1981, (invited talk).

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 Ph.D. 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.