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Thermal Neutron Scattering Studies of Molecular
Dynamics and Critical Phenomena in Fluids and Solids

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Neutron Spectroscopy and Materials Research Group
Massachusetts Institute of Technology

Principal Investigator
Associate Investigator
DSR Staff
Research Assistants

Professor S.H. Chen
Professor S. Yip
Dr. H.C. Teh
T.A. Postol
P.A. Walsh

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I. Introduction

From the beginning of this project our experimental program has always been closely tied to our general theoretical interests and capabilities. Because of this we are more limited in the type of measurements we make, but on the other hand we feel that we can provide a more complete analysis of the data we do obtain. Since our strongest theoretical activity is in the area of non-equilibrium statistical mechanics in fluids, it follows that experimentally we should concentrate on neutron and light scattering measurements of dynamic structure factors. In Neutron scattering we are somewhat handicapped by the fact that the MIT Research Reactor is not a high flux reactor. This means that we have to direct our efforts to intensive rather than extensive studies. However, in the field of "Photon Correlation Spectroscopy" our position is at the forefront of instrumentation development, and during the past few years we have acquired considerable equipment for laser experiments.

During the current grant period we have continued our study of quasielastic scattering in dense gases and dynamic structure factor in liquid metals. Measurements on hydrogen gas at high pressures and liquid gallium at small wave number transfers are in progress. These investigations will

continue into the next grant period and will form the basis for additional experiments in gas mixtures and liquid bismuth.

Our experimental program encountered a difficulty this year which resulted in the loss of data taken over a three month period. Because of manpower shortage we have had to rely on rather inexperienced graduate students to run the three-axis spectrometer. Over the years this has led to insufficient maintenance and consequently degradation of the long-term reliability of the spectrometer. Earlier in the year we discovered that our room temperature data on hydrogen at high pressures had to be discarded and it was necessary to rebuild parts of the spectrometer and its computer control. We were able to get an experienced postdoctoral fellow, Dr. H.C. Teh from the laboratory of Professor B.N. Brockhouse, to join our project in June. Dr. Teh worked with S.H. Chen on rebuilding and recalibration of the spectrometer and its computer control. In October the spectrometer system was put back into operation.

The beam port charge in the present budget does not cover the entire 12-month period. Professor R. Wilson of Harvard University used our beam port to carry out an experiment on the determination of parahydrogen cross section. During this period which covered approximately three months our project did not pay for any beam port cost.

II. Research Performed

A. Pressure Dependence of Incoherent Scattering in Gases

By measuring the quasielastic scattering of neutrons in pressurized hydrogen gas we have investigated the effects of intermolecular collisions on the spectrum of single-particle density fluctuations^[10]. Our experiments provided the first observation of the phenomenon of collisional narrowing by neutron scattering. Recent kinetic theory calculations predicted a certain variation of the quasielastic line width with gas density and wave number transfer. The experimental results confirmed such a behavior and therefore constitute a "first" demonstration that the Boltzmann-Lorentz transport equation with Enskog modification is valid over a wide range of densities and wavelengths.

A basic motivation for the present lineshape study in dense gases comes from theoretical investigation of molecular-level descriptions of thermal fluctuations in fluids which are valid at arbitrary wavelengths and frequencies. It is believed that kinetic equation at the level of the linearized Boltzmann equation cannot adequately describe the behavior of short wavelength fluctuations since such equations are valid only for wavelengths long compared to the molecular diameter. On the other hand, for incoherent scattering the appropriate equation to use is the Boltzmann-Lorentz equation to which this restriction does not apply. Furthermore, the extension of the Boltzmann-Lorentz equation to higher densities involves simply a rescaling of the

collision frequency if the Enskog modification is considered reasonable. The hydrogen gas data provided a confirmation of these theoretical ideas concerning single-particle density fluctuations. However, it still remains to show that coherent lineshape measurements can not be equally well explained by the linearized Boltzmann equation with Enskog modification. In that case one would be in a position to test the recently derived generalized Boltzmann equation. We have also investigated the sensitivity of the Boltzmann-Lorentz solutions to the intermolecular interaction potential^[8]. Although the density fluctuation spectrum at one temperature does not seem to vary with different potentials, we feel that the effects of the potential will be much more pronounced if measurements are made at different gas temperatures.

It has been pointed out recently by Egelstaff et al that there is a simple relation between the isothermal pressure derivative of $S_s(Q, \omega)$ and the Fourier integral of a certain time-dependent three-particle self correlation function. We were able to measure the pressure derivative of $S_s(Q, \omega)$ for hydrogen around 145 atm. for various values of Q ^[9]. We also formulated a method^[9] to calculate the pressure derivative starting from a rigorous kinetic theory formulation and showed that the best way of testing various kinetic models is to measure the pressure derivative of the dynamic structure factor.

As an extension of the work in [10], we are now measuring $S_s(Q, \omega=0)$ for hydrogen gas at 1000 atm. and above.

By measuring this quantity by differential methods we are trying to verify the density dependence of the self-diffusion coefficient as predicted by the computer molecular dynamics calculations of Alder and co-workers.

B. Dynamic Structure Factor of Liquid Gallium

We have maintained an active interest in the dynamic structure factor measurements on liquid metals. We have analyzed our data on liquid Ga using the generalized hydrodynamics approach [6,7]. The $S(Q,\omega)$ data cover Q values mainly in the vicinity of the first diffraction maximum, and it was found that the results could be explained by wavelength- and frequency-dependent transport coefficients characterized by a single relaxation time. Recent computer calculations and neutron data on liquid Rb obtained at Argonne National Laboratory indicate that another relaxation time is needed to explain the behavior of the dynamic structure factor over the whole range of Q values. We are in the process of measuring $S(Q,\omega)$ of Ga in the Q range $0.2 - 1.8 \text{ \AA}^{-1}$. We feel that by studying the linewidth variation with Q in this range we can help to clarify the possible existence of a relaxation time associated with the dynamics of small clusters (10 - 20) of particles.

C. Photon Correlation Spectroscopy

Since 1969 S.H. Chen has been active in developing a method of high resolution light scattering spectroscopy called "Photon Correlation Spectroscopy". The technique combines single-photon counting with a multichannel digital autocorrelation analysis similar to the statistical chopper system in the neutron time-of-flight spectrometer. We constructed the first spectrometer of this kind in this country and since then have carried out studies of critical fluctuations in fluid and measurements of bacteria motility in solution. The project was originally supported by the Sloan Fund for Basic Research and a NIH contract, but this support ended in June 1973. There is a plan to submit a research proposal to NIH on the biophysical aspects of this research. We feel that it is more appropriate to transfer the critical phenomena portion of the research to the present AEC grant. A total of 15 publications have come out of this activity in the last five years and three of them have acknowledged AEC support. Besides several review articles on applications of this technique, S.H. Chen is also preparing a monograph on "Photon Correlation Spectroscopy and Its Applications" to be published by Academic Press.

Since September 1973 we were able to use part of the left over fund from previous years to purchase a data analysis system which, combined with our present spectrometer

system, should bring our capability in instrumentation up to its fullest extent.

D. Related Activities

Both the Principal and Associate Investigators have devoted significant fractions of their efforts to writing review articles in the general areas of neutron and light scattering spectroscopy. We feel that this activity is an integral part of overall research objective. The review articles are listed in Section III.

During the academic year 1972-73, S. Yip was on sabbatical leave from MIT. Although he maintained contact with grant activities, he was officially not part of the project and there was no salary charge for him during this period.

III List of Publications during 1973

A. Review Articles

1. S.H. Chen, "Introduction to Neutron, X-ray and Laser Spectroscopy" Chapter 1, in Neutron, X-ray and Laser Spectroscopy in Biology and Chemistry, Ed. by S.H. Chen and S. Yip, Academic Press (1974).
2. S.H. Chen, "Application of Photon Correlation Spectroscopy to Chemical and Biological Problems", Chapter 12, in Neutron, X-ray and Laser Spectroscopy in Biology and Chemistry, Ed. by S.H. Chen and S. Yip, Academic Press (1974).
3. S. Yip, "Quasielastic Scattering in Neutron and Laser Spectroscopy" Chapter 2, in Neutron, X-ray and Laser Spectroscopy in Biology and Chemistry, Ed. by S.H. Chen and S. Yip, Academic Press (1974).
4. S. Yip, "Spectral Distributions of Density Fluctuations in Fluids", a chapter in Thermodynamic and Statistical Physics, Ed. by M.G. Velarde and L. Conlin-Garcia, Madrid, Spain (1973).

B. Thesis

5. P.W. Walsh, "Thermal Neutron Scattering Studies in Gaseous Hydrogen at High Pressures", M.S. Thesis, MIT (1973).

C. Published Papers

6. S.H. Chen, Y. Lefevre and S. Yip, "Dynamics of Liquid Gallium in the Supercooled State", in The Properties of Liquid Metals p.119, Ed. by S. Takeuchi, Proceedings of the Second International Conference, Taylor and Francis Ltd. (1973).
7. C.H. Chung, S.Yip and P.A. Egelstaff, "Dynamic Structure Factor Calculations and Neutron Inelastic Scattering", in The Properties of Liquid Metals, p. 125, Ed. by S. Takeuchi, Proceedings of the Second International Conference, Taylor and Francis Ltd. (1973).
8. O.L. Deutsch and S. Yip, "Van Hove Self Correlations in a Maxwell Gas", Phys. Fluid (to appear in Jan. 1974).
9. S.H. Chen, Y. Lefevre, G. Mazenko and P.A. Egelstaff, "Pressure Dependence of the Incoherent Scattering Law and the Time-Dependent Triplet Correlation Function in Dense Hydrogen Gas", Paper Presented at the Conference on "Molecular Motions in Liquids", Paris, July (1973), Proceeding to appear (1974).
10. S.H. Chen, Y. Lefevre and S. Yip, "Kinetic Theory of Collisional Line Narrowing in Pressurized Hydrogen Gas", Phys. Rev. A, Dec. (1973).
11. P. Tartaglia and S.H. Chen, "Intensity Correlation of Light Scattered from Hydrodynamic Fluctuations", J. Chem. Phys. 58, 4389 (1973).

12. P. Tartaglia and S.H. Chen, "The Spatial Coherence Factor in Light Scattering from a System of Independent Particles", Optics Comm. 1, 379 (1973).
13. P. Tartaglia, T. Postol and S.H. Chen, "Comment on the Letter by Jakeman et al, Correlation of Scaled Photon-Counting Fluctuations" J. Phys. A6L35 (1973).