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PROGRESS REPORT

THEORETICAL PHONON PHYSICS

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Progress Report
Theoretical Phonon Physics

J. A. Krumhansl

The period 1971-72 has been one of the most productive in the history of this contract, as measured both by publications and by participation in conference reports on the work.

The main topics studied include: Theory of random lattice excitations (Nickel and Krumhansl); The structure of liquids--both classical and quantum (Pollock, Hansen, Wang, Krumhansl); The equation of state of condensed solid gases at high density (Pollock, Krumhansl--with G. V. Chester and E. Salpeter); Topics in alloy theory (Stroud--with Ashcroft); Topics in transport theory (Nickel--with Wilkins); Collective motion of interacting dipoles (Mandell, Krumhansl); Miscellaneous studies of vibrations of biopolymers (Stare, Krumhansl).

These topics relate to the following applications: general experimental results on the electrical and thermal properties of disordered alloys, as studied experimentally by R. Pohl in a companion program here; experimental properties of the physical properties of liquids, as determined both by physical-chemical measurements and by neutron scattering; applications to both astrophysical questions (terrestrial and Jovian planets) and to materials under extreme structural conditions; basic

thermal and electrical properties of crystals with defects.

Titles and abstracts of work done in 1971-72 either published or in process of publication is as follows:

"Pair Effects in Random Lattices; A Generalized C.P.A. and its Equivalence to Diagrammatic Expansions", B. G. Nickel and J. A. Krumhansl, Physics Letters, 36A, 111(1971): A generalization of the coherent potential approximation that is exactly equivalent to self-consistent diagrammatic summation techniques is discussed. Explicit expressions for the pair case are given.

"Self-Consistent Average Green's Function in Random Lattices: A Generalized Coherent-Potential Approximation (n) and its Diagrammatic Equivalents", B. G. Nickel and J. A. Krumhansl, Physical Rev. B, 4, 4354(1971): We describe a simple generalization of the coherent-potential approximation that is exactly equivalent to the self-contained cumulant expansions and the self-consistent diagrammatic-resummation techniques. A detailed analysis of these different methods for the pair case is given.

"A Note on the Two-Dipole Problem", M. J. Mandell, Solid State Communications, 9, 1323(1971); The problem of two free-rotor quantum dipoles with fixed interparticle distance is considered. For various values of interaction strength, the

correlation and the parallel and perpendicular susceptibilities are calculated as a function of temperature, and the zero-temperature polarization is calculated as a function of electric field. We discuss the nature of the elementary excitations of a lattice of electric dipoles. These results are applicable to understanding the observed susceptibility maximum in doped alkali halides, and the properties of such molecular crystals as the hydrogen halides.

"The Superposition Assumption I: Low Density Fluid Argon", J. A. Krumhansl and Shein-shion Wang, to be published J. Chem. Phys. March 1972: The accuracy of the superposition assumption is checked by calculating the pair potential and its derivative from the Born-Green equation using the SA triplet function. These values are then compared with those for which the Monte Carlo triplet function was used. It is found that the SA results are poor.

"The Superposition Assumption II: High Density Fluid Argon", Shein-shion Wang and J. A. Krumhansl, to be published J. Chem. Phys. March 1972: The triplet correlation function for high density fluid argon was calculated by the Monte Carlo method with a truncated cube as the basic box. This new box provides us a longer range for the triplet function than the conventional cubic box using the same number of particles; it also provides us better statistics for the same computing time.

The MC $g^{(3)}$ at $\rho^* = .80$ was found to be very different from the SA prediction. Upon substituting both MC $g^{(3)}$ and SA $g^{(3)}$ into the Born-Green equation, it is found that the result is fair for MC $g^{(3)}$ but very poor for the SA one. We conclude that the Superposition Assumption is poor at high density.

"Triplet Correlation in Liquid Argon by Monte Carlo Method", J. A. Krumhansl and Shein-shion Wang, to be published J. Chem Phys.: The triplet correlation function for low density fluid argon was obtained by Monte Carlo method for three different temperatures, assuming a Lennard-Jones type potential. The agreement with the prediction of the Kirkwood superposition assumption was found to be better than 10% for most values. The main difference between the two was found to be at small distances, where the SA gives unreliable estimates; and at the peaks of the triplet function, where the SA predictions are too strong.

"Liquid Helium Configuration Around a Metastable Excited Helium Atom", J. P. Hansen and E. L. Pollock, to be published Phys. Rev. May 1972: The pair distribution for normal He atoms in the vicinity of a metastable 2^3S He atom is calculated in the zero temperature limit, from first principles, using a variational Jastrow wave function and the Percus-Yevick integral equations for fluid mixtures. From this pair function, the

"bubble radius", coordination number, and energy per metastable atom are calculated.

"Ground State Properties and Low Excited States of Solid Helium-4 and -3", J. P. Hansen and E. L. Pollock, To be published Phys. Rev. May 1972: Previous Monte Carlo computations of ground-state properties of solid Helium using a correlated trial wave function are extended in several directions. A generalized wave-function which includes a simple model for "phonon" correlations is tested; no significant lowering of ground-state energies is obtained. Detailed results for BCC He³ and HCP He⁴ are tabulated in the low density region. The extension of the variational computations to considerably higher densities (10 cc/mole) stresses the need for inclusion of short-range correlations over a wide density range and clearly reveals the inadequacy of the commonly used Lennard-Jones 12-6 potential with the deBoer parameters. Various other recently proposed interaction potentials are investigated in conjunction with known three-body forces. Reasonable agreement with experimental energies, pressures, and compressibilities follows from the use of a potential due to Beck. The relation between the melting properties of Helium and two "hard-core" models is discussed and the possibility of Bose-Einstein condensation in the solid is investigated in conjunction with a theorem due to Reatto. A possible extension of the computer "experiments" to

the study of low excited states in the solid is presented and the limitations of this formalism are clearly stressed.

"Note on the Band Gaps of Semiconductor Alloys", David Stroud, AT(30-1)-3699, AEC Report NYO-3699-61, (1971): It is shown, on the basis of perturbation theory and a simple assumption about the matrix elements of the scattering potential, that the effect of alloy disorder is inevitably to reduce the band gap of a semiconductor alloy below its virtual-crystal value. The conclusion is found to be in agreement with existing experiment and calculation.

"Theory of the Melting of Simple Metals: Application to Na", D. Stroud and N. W. Ashcroft, Phys. Rev. B, 5, 371 (1972): The melting curves of the simple metals may be calculated by a method which involves no adjustable parameters whatsoever if the electron-ion pseudopotential is known. This simplicity is made possible by the use of variational principles to determine the free energies of the solid and liquid states. The approach yields a volume-and temperature-dependent effective Debye temperature for the solid, and an effective volume-and temperature-dependent hardsphere packing fraction for the liquid. As applied to Na, the method gives a melting curve in good agreement with experiment up to at least 40 kbar. The long-wavelength limit of the pseudopotential, which is not well known

for most metals, is eliminated via the correct equilibrium density at 0°K. (The melting curve is not, however, sensitive to the choice of this parameter.) Additional thermodynamic quantities are computed for both phases and along the melting curves in good agreement with available experiment. Lindemann's law is fairly well obeyed in the solid phase, although not perfectly, and its analog (i.e., constant hard-sphere packing fraction along the melting curve) holds in the liquid. The Lindemann ratio varies between 0.013 and 0.015 along the melting curve; the packing fraction is about 0.42. Above certain temperatures, there exist no Debye temperatures for which the free energy of the solid phase is stationary; following previous workers we interpret such temperatures as forming a line of mechanical instability which, however, lies far above the actual melting curve.

"Validity of the Boltzmann Equation for Systems with both Electron-Phonon and Impurity Scattering", B. G. Nickel and J. W. Wilkins, Cornell University, AEC Report NYO-3699-56, (1971): A recent calculation of Mills⁽¹⁾ indicating large deviations from Mathiessen's rule are shown to be in error because of the neglect of terms of the same order in perturbation theory which remove the reported divergency and leave only very small corrections to the Boltzmann equation. In addition it is suggested that the experimental basis for these large

deviations may be capable of a different explanation.

"Evaporation of Cold Metallic Hydrogen", E. E. Salpeter, Phys. Rev. Letters 28, 560(1972): Solid metallic hydrogen is only metastable at low pressures, but the transition to the molecular form may require surface phenomena. The "evaporation" of pairs of adjacent surface atoms (forming free H_2 molecules) is discussed. A monolayer of surface atoms is lost in e^G times a lattice vibration period, where $G \lesssim 20$ at zero pressure and temperature. G increases with pressure and decreases with temperature above $T_c \sim 150^\circ K$.

In addition to the above, earlier work done on solid molecular hydrogen and related questions will appear in Physical Review, April 1972 as follows:

"Quantum Theory of the Equation of State for Solid Hydrogen", J. A. Krumhansl and S. Y. Wu: A variational calculation of the ground-state energy of molecular crystalline hydrogen has been carried out, including the effect of correlation between the motions of the particles. The principal purpose was to obtain the equation of state for solid hydrogen at absolute-zero temperature over a wide range of densities. We are concerned with energies on a scale appropriate to high-pressure phenomena, and therefore approximated the molecular rotational

behavior, so that the very low-temperature phase transitions are not descriptably in the present model. The variational form of the energy was obtained by truncating the cluster expansion of the ground-state energy. The effect of short-range dynamic correlation is taken into consideration through a Jastrow-type pair-correlation function in the trial wave function. To facilitate the fast convergence of the cluster expansion, a model correlation function with an explicit hard-core exclusion effect was employed. With this pair-correlation function, the truncation approximation was extended into the high-density region where previous functional forms for pair correlation had not been satisfactory. Numerical computations were done for a Lennard-Jones potential, a Buckingham exp-6-type potential, and a nonspherical molecular interaction due to Wang Chang. The results compare favorably with experiment, although there is a systematic difference at high density; either all of the assumed potentials are inadequate or the experimental data are in error.

"An Equation of State for Solid Hydrogen", Thomas A. Bruce:
An equation of state for solid hydrogen is obtained from variational calculations for pressures up to 112 K-bars. The Lennard-Jones potential is assumed and a brief investigation of

the Buckingham Exp-6 potential is also made. It is suggested that for high densities, quantum crystals may become harmonic and that Monte Carlo variational calculations for these high density regions may not be necessary.

"The High Pressure Behavior of Solid H_2 , D_2 , He^3 , He^4 , and Ne^{20} ", E. L. Pollock, T. A. Bruce, G. V. Chester, J. A. Krumhansl: The failure of the harmonic approximation for the lattice dynamics of solid H_2 , D_2 , He^3 , and He^4 at densities corresponding to pressures below the order of 10^3 atmospheres is well known. We present evidence that the equation of state for solid H_2 , D_2 , He^3 , He^4 , and Ne^{20} at high densities may, however, be calculated successfully in the harmonic approximation. Equation of state curves at high density for H_2 , D_2 , He^3 , He^4 , and Ne^{20} (all for the fcc phase at $T = 0^\circ K$) are given and compare well with results from Monte Carlo or cluster expansion treatments using a Jastrow wave function. The comparison with experiment shows good agreement with experiment in the high density range for He^3 , He^4 , and Ne^{20} . For D_2 and H_2 the theoretical methods agree closely with each other at high densities, but not so well with the experimental data of Stewart in that region, suggesting either inadequacy of potential or of experimental data. For the Lennard-Jones and Buckingham potentials used for pressures ranging from a few thousand to several million bars the Domb-Salter approximation

gives an accurate result for the zero point energy of the harmonic crystal. Our results lead us to conclude that good high density computations are not critically dependent upon short range correlation effects.

Personnel Activities

The principal investigator, J. A. Krumhansl, devoted 15% of his time during the academic year and one month in summer 1971 to the research program under this contract, and expects to continue the same distribution during the next contract period. In September Dr. D. Stroud left Cornell to assume duties as Assistant Professor of Physics at Ohio State University; and at the same time Dr. J. P. Hansen returned to his position at Orsay, France. Graduate students Pollock, Mandell, and Stare received support from this contract.