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November, 1977

This paper was prepared for inclusion in the Proceedings of the
NATO Summer School Conference, October, 1977, held at Corfu, Greece.

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COMPUTER SIMULATION AT HIGH PRESSURE

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ABSTRACT. The use of either the Monte Carlo or molecular dynamics method to generate quantitative-of-state data for various materials at high pressure is discussed. Particular emphasis is given to phase diagrams such as the generation of various types of critical lines for mixtures, melting, structural and electronic transitions in solids, two phase ionic fluid systems or astrophysical interest as well as a brief aside of possible eutectic behavior in the interior of the earth. Then the application of the molecular dynamics method to predict transport coefficients and the neutron scattering function will be discussed with a view as to what special features high pressure brings out. Lastly, an analysis by those computational methods of the measured intensity and frequency spectrum of depolarized light and also of the deviation of the dielectric measurements from the constancy of the Clausius-Mosotti function is given that leads to predictions of how the electronic structure of an atom distorts with pressure.

1. INTRODUCTION

The computer simulation methods have no difficulty generating any pressure, however high. They only require an intermolecular potential, preferably pair-wise additive, although that is not necessary in principle. If that, however, is not the case, the computations are vastly more complex and no practical calculation exists as yet that overcomes this difficulty. Since all materials under sufficient pressure become metallic, where the pair-wise additive approximation is inadequate, one has to resort to approximate schemes such as effective pair-potentials; for example, the

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pseudopotential. These potentials, however, are now strongly density and temperature dependent. If one goes to still much higher pressures where the electrons are all stripped off the nuclei, the description of matter becomes simple again, namely by a pair-wise additive Coulomb potential between the nuclei neutralized by a uniform electron gas. In all these situations the computer simulation method can make a useful contribution. In the experimentally accessible range the calculations coupled to experiments can back-out an effective pair-potential that can be used to predict not as yet measured other properties or extend the range of measured ones. It is, however, in the experimentally inaccessible region that the computer method likely makes its most valuable contribution.

So far the above discussion had computer simulation methods in mind in which the particles obeyed classical mechanics. It is, of course, this limitation that led to the introduction of pair-potentials that in metals can be considered a stop-gap measure. To deal with at least the unbound electrons in a metal more accurately one needs to deal with them quantum mechanically and a few attempts of calculating the properties of an electron gas by computer simulation methods are under way but as yet too incomplete and complex to discuss here. Nevertheless they may ultimately provide a rather accurate description of matter under all pressures. Here we will confine ourselves to classical calculations but within that framework, in interpreting light scattering experiments, discuss in some detail how the electronic structure of an atom distorts as pressure is applied. This, after all, is the fundamental effect of all high pressure experiments.

2. PHASE DIAGRAMS

The computer methods can generate equations-of-state quite accurately with a few hundred particles, however phase transitions are disturbed because the large fluctuations necessarily associated with these transitions are limited by the finite system. A particular difficulty also occurs with reproducing crystal transformations because of the asymmetry imposed on the system by the shape of the cell to which the few hundred particles are confined. Thus with solid phases one is generally restricted to try out various crystal structures and determine the very small free energy difference between the various possibilities, a not very fruitful procedure. The distortion in fluid phase transitions is not serious unless one asks questions which are connected with long range correlations which is of not particular concern here.

2.1 Critical Line in Gas Mixtures

The computer results for the equation-of-state have shown the remarkable validity of the van der Waals model above the critical density.¹ That model consists of determining the thermodynamic properties and pair distribution function of a reference system, usually taken to be a purely repulsive potential. The attractive potential is then added as a perturbation utilizing the pair distribution of the unperturbed system. This theory depends on the observation that the structure of a fluid is primarily determined by the repulsive forces and one would guess increasingly so the higher the pressure. The only modification of the present procedure, which is utilized near normal conditions, that needs to be made involves the use of a hard sphere reference system. Under normal conditions the steep repulsive potential is usually replaced by an equivalent hard sphere potential to simplify matters. The choice of that hard sphere diameter is given by several recipes which makes that diameter temperature dependent.² This is likely to become an inappropriate procedure at higher pressure where the softness of the repulsive potential plays an increasingly dominant role. What needs to be done and has already been done to a considerable degree is to generate properties for soft repulsive potentials of the form r^{-n} , for example, or of the exponential type and then the task will be to find the power of n , which best reproduces experimental results after some reasonable attractive potential has been added on. That procedure is not significantly more difficult than the use of a hard sphere reference system since still a single reduced variable characterizes the properties of a r^{-n} system.

Near critical densities, however, the choice of the form of the repulsive potential is unimportant since the density is low. Thus, one can, for example, easily predict the behavior of the critical lines in a mixture of gases by the van der Waals model. Indeed, van der Waals himself already used his theory to make such predictions. The only difference now is that it is possible to be more quantitative, since the properties of the reference system can be much more accurately represented than by means of the equivalent, b . Furthermore, the attractive forces need no longer be represented by a constant value of the cohesive energy density but can be calculated accurately by the perturbation theory. This modified or augmented van der Waals theory can then be used to predict quantitatively the behavior of critical lines in mixtures provided the various pair interaction potentials are known.³ It can thus be established under what conditions of differences in repulsive potentials and in strengths of attractive potentials the two critical points of the pure components are connected. As the two pure components differ more in their interaction potentials the two critical points not only become disconnected, but the critical temperature of the mixture becomes

from the combined effect of zero point energy and thermal energy. The surprising prediction⁶ is that for protons the maximum temperature in this closed region is about 3000°K above which a solid cannot exist at any pressure. Thus most protonic stars can be predicted to have fluid interiors.

2.3 Electronic Transitions

Certain substances, in particular cerium, have a solid-solid critical point in apparent contradiction to the above general statement which does not allow continuous transitions from one symmetry to another. That difficulty is easily resolved since it was found that both crystal structures were the same on either side of the phase line below the critical point. Closely associated with this critical point is a melting extremum in cerium. Similarly in cerium a solid-solid phase transition has been observed between two identical crystal structures which however does not end in a critical point but instead intersects the melting line and again at a melting minimum. These phenomena can be explained in terms of an electronic transition that the atom undergoes as it is compressed. The effect of pressure is to stabilize electronic energy levels of higher angular momentum but lower electronic quantum number. At the density at which this electronic shift occurs the size of the atom suddenly shrinks and one might think that this effect could be well modelled by a repulsive step potential by which is meant that to a hard sphere core a repulsive mound or repulsive square-well of certain height and width has been added on. These systems can be investigated by computer simulation and indeed some of the qualitative features of these phase diagrams are reproduced.⁸

A solid-solid critical point is obtained if the width of the added mound is not too large. Of course, after the electronic phase transition has taken place the new phase does not have to have the same crystal structure as the previous one and if not, no critical point would be observed. The computer calculation, for reasons previously mentioned, has excluded that possibility. Also observed is a melting maximum with this square-mound potential that can be qualitatively understood in terms of larger freedom of motions in a fluid which allows fluid configuration to sample the smaller diameter before the solid can. The fluid then becomes denser in the mean than the solid for some density range because the solid is constrained to maintain its lattice structure, and, so to speak, all the lattice spacings have to shrink simultaneously when the appropriate pressure is reached. Unrealistic in these calculations is that the solid-solid phase transformation does not intersect the melting curve near its extremum and that the width of the mound is unrealistically large before these two

The mixture becomes eventually stable, that is the critical temperature goes to 0°K, at the enormous pressure of 10^8 Mbars because then the electron gas pressure dominates and the mixture becomes nearly ideal.

More realistic calculations applicable to the center of Jupiter would allow for the electron gas to distort, that is to increase its density in the neighborhood of the nuclei. This can be done through linear response by perturbation theory if this distortion is small. Since this is not the case one crude approximation would be to place effective partial charges on the helium nuclei. As can be readily seen, this reduces the charge difference between hydrogen and helium and since in the unscreened case the critical temperature was already close to center of Jupiter conditions any lowering would predict miscibility.

2.5 Interior of the Sun

The phase separation of stripped helium and hydrogen opens up the possibility of much higher temperature phase separation for highly charged nuclei in a hydrogen plasma. For example, completely stripped iron of charge $Z=26$ might separate in hydrogen below a temperature of 10^7 degrees or 1 kev since the potential energy scales as Z^2 . Thus, the possibility exists that the small amount of iron which is believed to be distributed in the sun according to cosmic abundance values might be insoluble. If iron were less soluble at temperatures of about 1.5 kev than one part in 10^6 , the cosmic abundance value being one part in 10^5 , one could very well resolve the neutrino dilemma. That dilemma consists of not finding experimentally any neutrinos while stellar evolution models demand that they should be observed. These neutrinos are essentially a measurement of the temperature in the interior of the sun, because they are generated only by an extremely energetic reaction of two α particles so that they fuse into another nuclei that decays by giving off the searched for neutrinos. At 1.5 kev, the fusion will not take place unless the kinetic energy of collision corresponds to about 10 times the mean since otherwise the coulombic repulsion barrier cannot be overcome. Thus a small overestimate of the temperature would cut out the reaction since the number of particles in the high energy tail of the Maxwell-Boltzmann distribution would be drastically affected.

Such a lowering of the temperature could be achieved by removing the small amount of iron, since it contributes about 30% to the opacity in the interior of the sun. The reason for this small amount contributing so much is that this element is the only one of high Z value present in significant amount. Because this element at the temperature in the interior of the sun still has bound electrons it contributes through the bound-free transition significantly to the opacity. Iron has two inner electrons which

iron silicide the possibility of eutectic behavior is large since they do so under normal conditions and under as high a static pressure (180 Kbars) as has been reached. Furthermore, the concentration required to keep the sound speed constant is in reasonable agreement with the observed nearly pressure independent liquidus. The proposal has two further consequences. One is that only is the sound speed nearly constant in that region, but, as might be expected, the density is also nearly constant. This could lead to hydrodynamic instabilities in that region. The other consequence is that the eutectic melting temperature is considerable (about 30%) lower than that of pure iron. As a result the application of Lindemann's melting law to the eutectic would lower the temperature in the center of the earth by about 30% and those temperatures would then be in better agreement with other temperature estimates that have been proposed.

3. TRANSPORT PROPERTIES

The computer method of molecular dynamics is capable of generating any transport property under any desirable conditions given again an intermolecular pair-potential. There are, however, a few differences with respect to equilibrium properties that are worth emphasizing. Furthermore, it is interesting to point out what special features of transport behavior is brought out in high pressure studies.

The van der Waals model for transport properties reduces to that of hard spheres, since a mean attractive field does not exert any force on the particles. Indeed hard spheres give a very good account of transport properties, if again a suitable choice of the temperature dependent hard sphere diameter is made.¹³ Should that be inadequate at very high density again a soft repulsive potential must be investigated directly. However, the perturbation methods, so successful in equilibrium, fail for non-equilibrium and that is because a small attractive potential can vastly change the trajectory of a particle.¹⁴ That occurs when a perturbation potential can change a glancing collision to a bound trajectory. In fact, there exists as yet no fundamental theory which can deal practically with anything but a hard sphere system. For the hard sphere system, the Boltzmann equation is used at low density, and the collision rate scaling suggested by Enskog is used to boost the low density results to high density. The molecular dynamic calculations have shown this to be a good approximation except at densities near the melting point.

The correction near the normal melting point boosts the viscosity by a factor of about 2 above the Enskog value and similarly the diffusion coefficient is reduced by about a factor of 2.¹⁵ The

theory, this is, however, easily taken care of by the viscoelastic theory, and indeed a crude introduction of that effect led to quantitative predictions of the neutron scattering function also at high density.

4. LIGHT SCATTERING AND DIELECTRIC BEHAVIOR

Much can be learned from the theoretical interpretation of spectral line shapes and intensities about the distortion of atoms and molecules under pressure. The theory is rather complex and still being worked on and so we shall here confine ourselves to the simplest possible situation, namely depolarized light scattering from rare gases at various pressures. Since the theory for deviations of the dielectric behavior from the constancy of the Clausius-Mosotti function is very similar to that of the depolarized light scattering we shall also discuss the complementary information obtained from these experiments.

For spherical atoms depolarization of light can only come about because of a temporary asymmetry in the polarization of a collection of rare gas atoms. Such an asymmetry results from an asymmetric density fluctuation in which in some arbitrary region of the fluid more atoms are temporarily packed. This higher density region is necessarily accompanied by another region that is less packed, since the average density must remain constant. On the average, of course, each separate region must also be of the mean density, but the temporary density fluctuation leads to an asymmetry in the polarization merely because more polarizable material is located in one region and less in another, the two regions defining a direction that can rotate the polarization of the laser light. Computer simulation can readily calculate this depolarization as the autocorrelation function of the induced-dipole tensor. The Fourier transform of this autocorrelation function gives the frequency spectrum of the depolarized light, while the initial value of the autocorrelation function gives the intensity of the line.

Comparing the theoretical results with experimental observations showed that the frequency spectrum under all conditions of temperature and pressure and a number of different rare gases was well reproduced while the intensity showed increasing deviation from experimental results at higher density.¹⁷ At liquid densities the experimental intensity was a factor of about 8 less than the calculated one. What this meant is that accompanying the density fluctuation is an electronic distortion of the atom that nearly instantaneously responds to the density fluctuation, and that reduces the polarization caused by the density asymmetry. If the slow process in the polarization were the relaxation of the density asymmetry, then it is clear that the calculation which

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higher than that of either component; circumstances leading to so-called two-gas phase equilibrium.

2.2 Melting

The single most important result of the computer simulation method for equilibrium properties is that melting occurs in purely repulsive systems such as hard spheres.⁴ Since all systems have rather steep repulsive potentials one can understand the universality of the phenomenon. At the same time there is still no *a priori* theory that can deal with melting and it remains the outstanding theoretical problem in equilibrium statistical mechanics. Nevertheless, there exists an old empirical observation based on geometric considerations and consistent with the fact that only a repulsive potential is required, that predicts melting very well in all known cases. This is Lindemann's rule which says that melting occurs when the root mean square excursion of a particle from its lattice site (the Debye-Waller factor) is about ten percent of its lattice spacing or roughly the substance is thirty percent expanded from close-packing.⁵ Given the universality of this rule, it is hard to understand why geophysicists predicting melting under pressure widely use some other, empirical procedure based on extrapolating low pressure data that leads to rather different predictions than Lindemann's rule.

The question of what ultimately happens to the melting line as pressure increases can be answered quite definitively.⁶ These considerations must take into account the argument that there cannot be a solid-fluid critical point because it is impossible to go continuously from an ordered system to a disordered one or from some symmetry to no symmetry. As was previously pointed out compressing materials turns them metallic, weakening the repulsive forces till ultimately the potential becomes coulombic between the bare nuclei neutralized by an electron gas background. However, it was found by computer simulation that such a coulombic repulsive system called a one component plasma also has a solid-fluid phase transition which incidentally conforms quite well to Lindemann's criterion.⁷ This state of affairs lasts till enormous pressures are reached where the density is so high that the nuclei have to be treated quantum mechanically. It is then easy to show that the lattice must melt even at the absolute zero because the zero point energy rises faster, namely as the reciprocal square of the lattice spacing than the potential energy which increases for coulombic potentials linearly with reciprocal lattice spacing as the density increases. These considerations, nevertheless, do not contradict the impossibility of a critical point because they predict a closed region in pressure and temperature below which a solid exists. Melting is always first order resulting

phase lines intersect. The mound model seems to be too simplistic to represent these details well.

One would expect these electronic phase transitions to be quite a common phenomena, since many heavy elements, for example, all the rare earths, have their 4 f orbitals empty and some 5 shells filled under normal conditions. Indeed there is evidence from shock wave data on rare earth elements that there is a sharp break in the shock versus particle velocity plot at or below the melting point that leads into a more compressible phase.⁹ This would be consistent with an electronic phase transition at a melting maximum or, if below melting with crossing a critical line in a solid that leads to a more compressible liquid phase. The sharpness of the break indicates that the fluid is denser than the solid. Such a first order electronic phase transition cannot occur in a fluid phase basically because a fluid is so flexible that it can sample or average over at least all ranges of distances less than a diameter of a particle. In the solid, as Lindemann's rule indicates, it is only possible by thermal fluctuation to average over structures in the potential which are less than 10% of the size of an atom. One would expect many of the effective size changes accompanying electronic transition to be of that order or less.

2.4 Interior of Jupiter

It has been suggested that under the pressure and temperature conditions in the interior of Jupiter, helium may not be completely soluble in hydrogen. In the interior the pressure is estimated to be about 40 Mbars and the temperature about 10,000°K or 1 e.v. Under those conditions hydrogen is certainly completely stripped of electrons, but for helium an estimated 100 Mbars is required so that it is only partially pressure and temperature ionized. Nevertheless, as our first attempt to predict the possibility of phase separation it shall be assumed that all electrons form a uniform background in which α particles and protons interact via their unscreened coulomb potential. Since these nuclei under these conditions are still well described by classical mechanics, the problem is easily studied by computer simulation.¹⁰

These calculations indeed show phase separation below a critical temperature of about 1 e.v. over a wide region of pressure. The qualitative reason for phase separation comes from potential energy considerations, namely that local charge neutralization is more effective in the pure phases than the mixture, given the constraint of uniform electron charge distribution. So to speak, in the mixture of uniform charge distribution the different species cannot each be surrounded by a charge neutralizing sphere radius that in an effective as in the pure species separately.

are bound by 8 kev and the next 6 ones would be partially bound because they require about 2 kev to be ionized.

Calculations using dilute electrolyte theory, since iron is present in such small concentrations and at high temperature, show indeed that iron even if only of charge 20 would be soluble by less than one tenth cosmic abundance.¹¹ The proposal is hence that iron precipitates out into the center of the sun. The calculations cannot, however, be entirely trusted as yet. First of all, though the iron poor phase is indeed very dilute, the iron-rich phase that precipitates can by no means be adequately described by the dilute Debye-Hückel theory. One thus needs to introduce higher density corrections and once these were made they led to significant changes in the phase diagram. The next model to be investigated is to calculate for an effective Z of 24 the phase diagram over a wide range of iron concentration through an approximate integral equation which, however, has proved reliable for long range potentials, the so-called hypernetted-chain equations. These can be used at all densities of iron and the validity of the results can be checked at selected points by machine simulation methods. Once the reliability of that equation has been established, the further screening of electrons can be taken care of by perturbation theory as discussed in the case of Jupiter. By this procedure, it might thus be made theoretically plausible that the solubility of iron is significantly less than cosmic abundances.

2.6 Interior of the Earth

There appears to be another possible type of phase transition in the core of the earth that is, however, not well simulated by computer methods. It stems from the observation of sound propagation in the deep interior of the earth from which it can be concluded that there appears to be a region of some 500 km sandwiched between the solid and liquid core where the sound speed is nearly independent of pressure over some 500 Kbars. Since no known pure substance is expected to behave this way, it seems reasonable to ascribe this observation with the phase transition, in particular eutectic behavior.¹² The argument would be that going into that region as pressure and temperature increase, the iron would precipitate out and settle eventually in the core while the fluid follows the liquidus branch of the eutectic. The consequence would be that the concentration of presumably a lighter and hence smaller sound speed component would increase. The concentration increase would then compensate the usual pressure increase of the sound speed leading to a nearly constant value in this region.

This suggestion is supported, however weakly, by both static and dynamic data. If the component is either iron sulfide or

origin of this discrepancy is that the Enskog theory leaves out the effects of backscattering, that is the high probability of the reversal of a particle's velocity in dense media by the neighboring particles. In hydrodynamic language the medium acts viscoelastically on a short time and distance scale. It is clear that at higher pressures this effect will become even more important. It is proposed that this effect will probably be adequately dealt with by introducing a space and time dependent viscosity in the hydrodynamic or Navier-Stokes equation. This generalization of hydrodynamics is fairly easy to execute and will make the predictions of transport coefficients at high pressure more reliable. Since this theory is not confined to hard spheres, it is hoped that it will also be useful for other systems. In the meantime, the hard sphere model has been successfully used to predict the experimental viscosities and diffusion coefficients of various materials including metals under pressure. It has, for example, been used to predict the viscosity of liquid iron in the core of the earth.

The hard sphere calculations of the viscosity and the diffusion coefficient have shown that even when there are deviations from the Enskog theory, that the product of these two transport coefficients is remarkably constant since they deviate in opposite directions. The product of the viscosity and the diffusion coefficient is, furthermore, very well given by the macroscopic hydrodynamic calculations of Stokes, if slip boundary conditions are employed between the moving sphere and the viscous medium.¹⁵ The surprising nearly quantitative validity of hydrodynamics on a microscopic scale is the central result of the computer simulation studies. It is this observation that leads to the above suggestion of generalizing hydrodynamics by introducing non-constant transport coefficients to make hydrodynamics even more quantitative on a molecular scale. As far as the validity of the Stokes-Einstein relation is concerned, it can be made use of under high pressure conditions by measuring only one of the transport coefficients, namely the one that is easier to measure, to predict the other.

The remarkable validity of hydrodynamics is also evident in its prediction of the neutron scattering function. A recent calculation of the neutron scattering function for hard spheres by computer simulation shows that both kinetic theory and hydrodynamics can predict the function very well.¹⁶ This shows, first of all, that the neutron scattering function is very insensitive to the detailed molecular motions that go on in a fluid. Significant differences between the two theories and the calculation occur only at the highest densities, and these are, of course, of interest at high pressure. Both of the theories fail to take into account the backscattering effect, spoken of earlier. In the hydrodynamic

neglected the electronic distortions would still give the correct spectra. The electronic distortion would surely oppose the density fluctuation in that the electrons would, so to speak, flow from the high density region to the low density region in order to minimize their mutual repulsive potential energy, and increasingly so at higher density. Thus, the intensity would be very much reduced at the higher density due to the opposing effect of the electronic polarization. The intensity thus represents a very sensitive measure of the distortion of the wave function of an atom with pressure.

To quantitatively account for this electronic distortion a polarizability of a pair of atoms (over and above that of the two isolated atoms) as a function of their separation is introduced. This pair-wise electronic distortion polarizability is as important to optical and electrical properties as the pair potential of interaction is to thermodynamic properties. It is also as difficult to calculate from quantum mechanical considerations as the pair potential. Hence one must resort to similar procedures in backing it out empirically from experiments as for the pair potential, leading to an inverted Lennard-Jones form for this function. One can also ask similar questions about the pair distortion polarizability as the pair potential, namely is it pair-wise additive and does it obey corresponding states. Preliminary investigations lead to positive answers to the last two questions.

A very similar induced dipole tensor autocorrelation function is involved in calculating the deviations from the Clausius-Monott dielectric function for the rare gases.¹⁸ If the electronic distortion is again ignored, it can be shown that these deviations must necessarily be positive, contradicting experiments at high density. Introducing electronic distortions, but this time of the diagonal elements of the induced dipole tensor, rectifies that situation. Combining these results with the light scattering results which involve the difference in the pair polarizability distortion parallel and perpendicular to the axis connecting two rare gas atoms, the electronic distortion in the two different directions can be separately extracted. Thus much can be learned from these experiments, coupled with an interpretation that requires computer simulation, about electronic distortion under pressure.