

THEORY OF LIQUIDS AND SOLUTIONS WITHOUT EQUATIONS

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When I was asked to give this talk, I was told that there would be a wide-ranging audience and therefore one should try and avoid equations if at all possible. I don't know quite what that reflects on the average chemist, but I thought that it would be quite a challenge to present a talk entitled "The Theory of Liquids Without Equations". I decided also that there was a moral to a title of that kind, and at the end of the talk I will reveal to you what the moral actually is.

At the outset I would like to consider what is essentially a map of a system that one wishes to study, namely, the phase diagram. The phase diagram tells you where you are and tells you something about what you're doing. I would like initially to put emphasis on phase diagrams because many people do experiments on systems (that is, on solutions) for which the phase diagram is either not known or very poorly known, and this always annoys me. If I am listening to a talk I often ask the question "Well, what was the phase diagram for your system?" and find nine people out of ten are unable to answer that question, simply because the phase diagrams are unknown. And of course, when one is dealing with solutions these diagrams can be exceedingly complex.

I will take a very simple case of a solution, the case of neon mixed with argon. Fig. 1 is taken from a paper by Streett & Hill and is perhaps the simplest phase diagram for a solution that you can have, and already it is to me an exceedingly complex diagram (1). The lines EA and EH represent the coexistence lines for pure liquid argon between liquid and gas, and liquid and solid, and the region in the PT plane between these lines corresponds to pure liquid argon. The third axis denotes the composition of neon, and the heavy solid lines represent isotherms that were measured by Streett & Hill. So, for example, if you take a certain concentration of neon (W) and a certain temperature (T_4) then you will find that for a wide range of pressures a box of the material of this composition will divide into two phases, a liquid-like and a gas-like phase each of which has a different composition or ratio between neon and argon. What one tends to do when one takes a solution is to think of a section of the phase diagram at constant pressure so that one tends to think of a horizontal section to this diagram, and one tends to plot a curve at constant pressure as a function of composition and temperature; in this way you get a phase boundary line of a certain shape with a critical point at the top of such a line. The line of critical points that you then get for all possible cases is represented by the dotted curve, A through to B. Most people, I think, do their experiments in a region which is above this line of critical points where the solution exists for all possible compositions.

So I think the first point I wish to make is simply that, in order to understand your substance, you need to measure this whole phase diagram first of all and to figure out where you are, and if you are going to explain the properties of the solution in terms of a theory you would like a theory which will cover this entire function. Very frequently you will find that both experiments and theories are confined to a limited region of such a function. It may be a region at a low temperature and relatively high densities, as at the upper rear part of this three-dimensional diagram, or it may be a region near the lower front part where the temperature is higher and the density lower. You tend to find that experiments are done in a very confined part of this space, and models are developed which apply in a confined part of this space also, and on the whole that is a very unsatisfactory feature. To really understand the system one has to look over the whole function and explain it all. And, of course, from the formal point of view there are ways of writing problems down in such a way that they are general enough to cover everything.

One of the conventional ways of doing that is to discuss the interactions between the molecules forming this solution in terms of pair potentials and three-body potentials and four-body potentials, and a similar series of correlation functions. So I would like now to look at that formal structure and to see just what it entails. I will simplify the problem and discuss these functions for the case of rigid linear molecules; this is obviously a substantial simplification. So what one is really saying is that one could discuss all the properties throughout the entire phase diagram if one knew everything represented in Fig. 2.

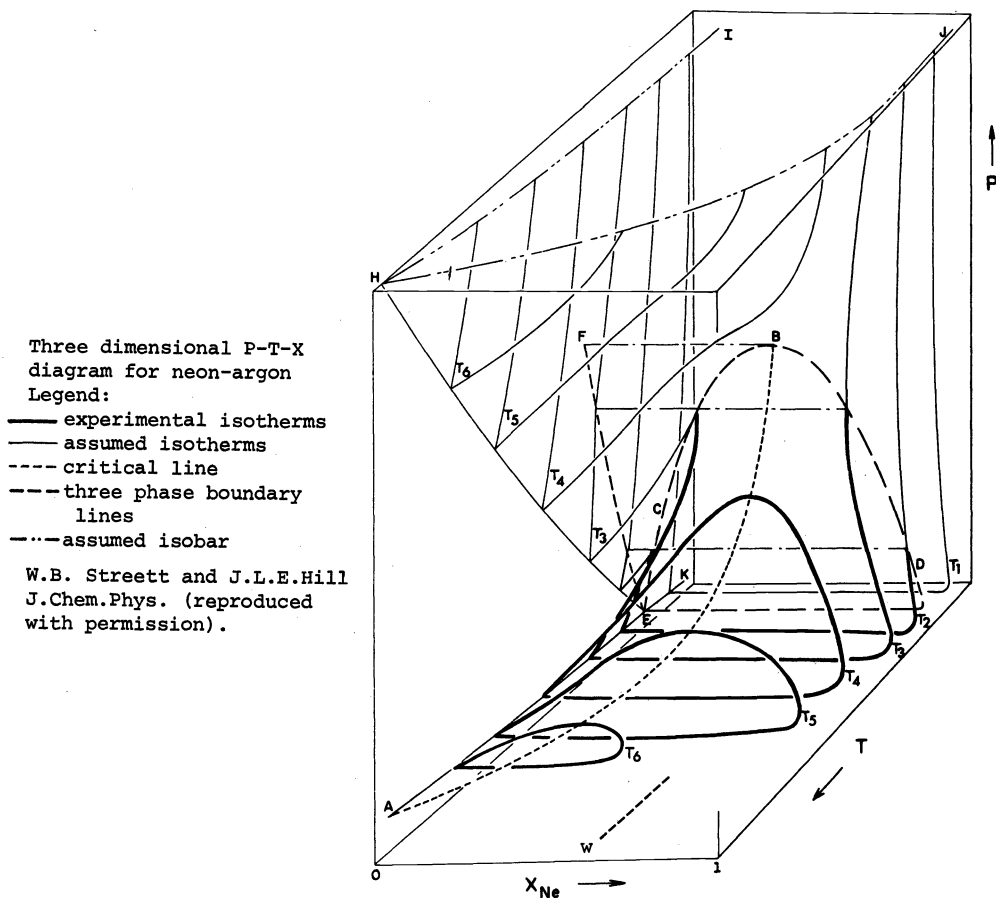
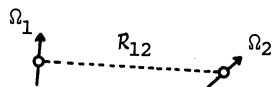
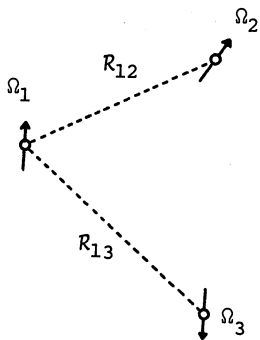


Fig. 1. Phase equilibria in neon-argon.



$$U_2(R_{12}; \Omega_1; \Omega_2)$$

$$g_2(R_{12}; \Omega_1; \Omega_2)$$



$$U_3(R_{12}; R_{13}; \Omega_1; \Omega_2; \Omega_3)$$

$$g_3(R_{12}; R_{13}; \Omega_1; \Omega_2; \Omega_3)$$

$$U_N(R_{12} \cdots R_{IN}; \Omega_1 \cdots \Omega_N) \quad g_N(R_{12} \cdots R_{IN}; \Omega_1 \cdots \Omega_N)$$

Fig. 2. Configurations and energies for N rigid linear molecules.

The lowest-order function of interest is the pair function. What we imagine here is that we have a molecule denoted by an arrow which is oriented in the direction Ω_1 and we place our origin at its centre of mass and we ask questions about another molecule, number 2, which is a distance R_{12} from the first one and oriented in the direction Ω_2 . Well then, first of all we'll have a potential energy U_2 between these two molecules in this configuration, and then we'll have a probability g_2 of finding this second molecule at the distance given and orientation Ω_2 . So these are the two simplest, lowest-order functions which we would like to know. And in fact most theories today tend to cut this whole set off at this point and work only with these, and suggest that the remaining functions -- the remaining potentials in particular -- may be neglected. However, that is not so in reality because molecules are polarizable and deformable in various ways, and therefore when you bring a third particle up, the first two can be slightly deformed and additional energy is developed, the so-called three-body energy. So what we show next in Fig. 2 is our molecule 1 and our molecule 2 and then we have a third molecule number 3 at the position and orientation shown, and an additional energy that is beyond the simple sum of the pair energies for this combination, additional energy U_3 . An then of course, we will have a three-body correlation function, g_3 , to describe the probability of finding three molecules in this configuration. And if we wish to describe the entire system we will have to carry on this scheme of things up to a number N , being the total number of molecules that we have in our box. So the first problem facing the theorist is that there is this huge number of functions we would really like to know to understand the full system.

Let's go back to the beginning and ask a very simple question. Let's just think of this energy U_2 and ask: can we understand U_2 , and secondly, can we actually measure it in any given case? Well, I have drawn a simple example in Fig. 3, with which most of you will be familiar, to show how this function will vary. I am thinking now of a rather simple case -- again a rigid molecule -- with the potential energy between two such molecules in particular orientations Ω_1 and Ω_2 , and we could pick some orientation. If this were a polar molecule, so we could essentially treat it as a positive and a negative charge with some separation, then if we brought like signs together we'd have a repulsive system and the pair potential would look something like that illustrated, and if we brought unlike charges together, we would then have a potential like the lower illustration, with an attractive part to it. But these would be extreme situations, and there would be an average potential in the middle as shown. So that all cases of all possible orientations of the molecules will produce values of this function which lie between these two extremes, and we could therefore think of theoretical models of treating this system on the basis that this amount of variation was all that was allowed. Well, as I say, one can dream up models of that kind, and I will discuss what one might do with those models later.

I think it is useful to think of how the experimentalist would approach this problem, saying "well, we have this great sequence to measure; let's start with the first member U_2 and try and measure it", and what I've put in Fig. 4 is the ideal experiment one would like to conduct in order to measure that lowest function. What one would have to do would be to take a beam of molecules, and align the molecules in the beam (as I've drawn all the arrows parallel to represent an aligned beam). One would define the wave vector; that is, one would define the direction the beam was going and the velocity of the molecules, and one would fire them at a target of similarly aligned molecules. That is you would have to take a target and somehow align all the molecules in this target, getting them to point in a certain direction. And of course if you want to have single scattering events that you are going to observe beyond the target, the target will have to be very thin; you might think of somehow aligning them in a crystal, but in that case you would have to have a very thin crystal. And then beyond the target, as shown, at certain angles of scatter you would try to observe the scattered molecules, and you would have to measure the direction and the velocity with a detecting system. You'd also have to measure the change in orientation of the molecule on scattering and I've drawn a number of different orientations for these scattered molecules in the figure. And if you measure all that, you could then invert the data and find the pair potential between two molecules. There is a list at the side in Fig. 4 of all the things that will be required for that purpose. When I put the problem in that way you can see immediately that it is an impossible problem to the experimentalist, not only impossible now, but likely to be impossible for a very, very long time into the future. This applies to even the simplest of all possible cases that one could pick, simply because of the difficulty of defining these directions. The corresponding case for an atom such as argon or neon is of course soluble in principle, although very difficult in practice, because for an atom we don't have to worry about these directions, and we only worry about the angles and the velocity. But once you add the directions, which you obviously need as soon as you go to the molecule problem, then you make the whole situation quite impossible to the experimentalist. Therefore, even the lowest order function of that list I had is not accessible experimentally, and the best one can do is to make some intelligent guess about it and try and evaluate the consequences.

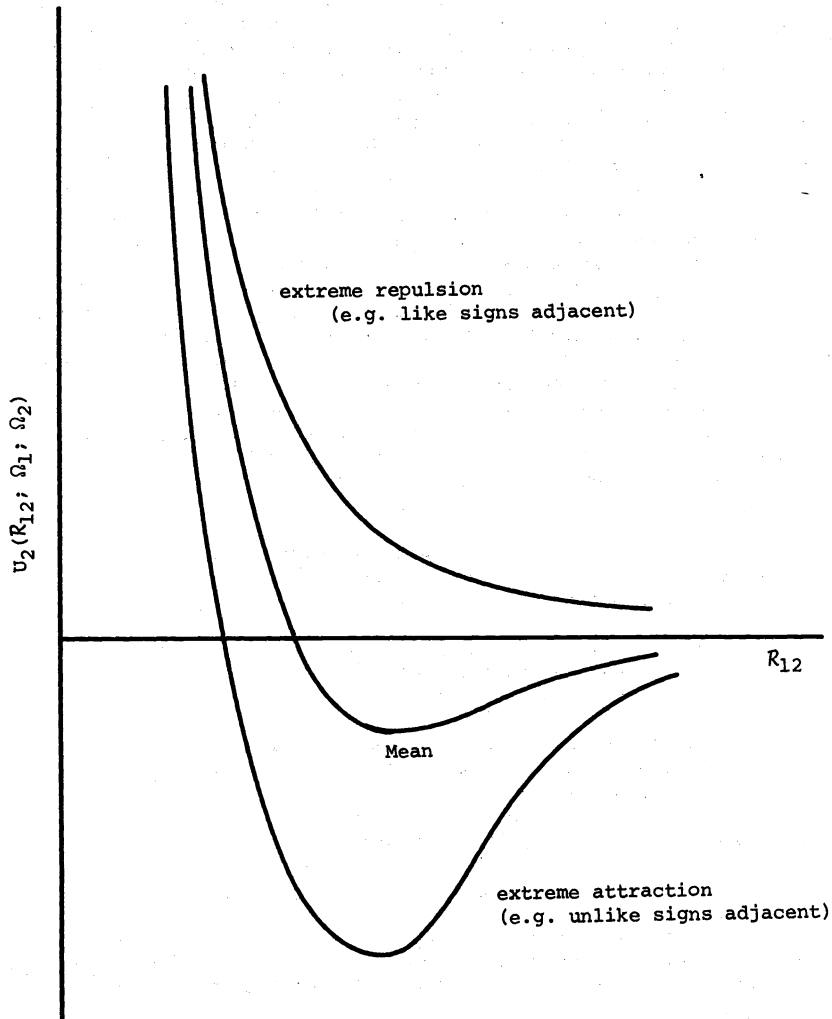


Fig. 3. Sketch of intermolecular potentials for simple rigid molecule (e.g. $^+AB^-$)

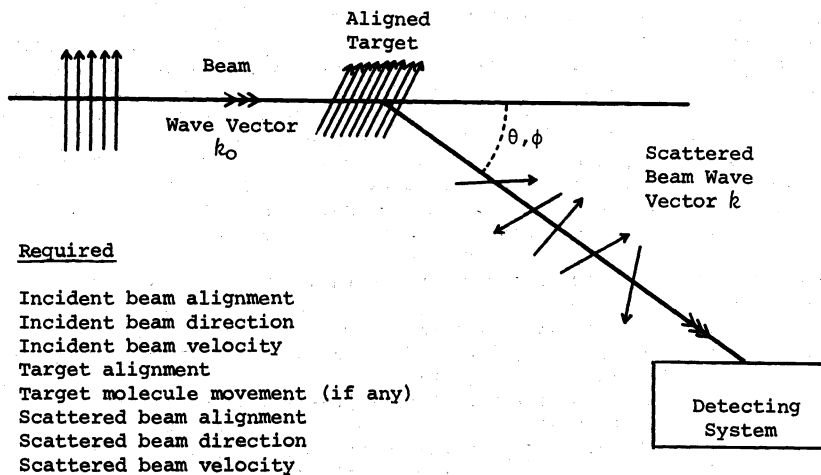


Fig. 4. Ideal molecule-molecule scattering experiment.

Well, how do theorists do that? Let us look at one of the methods by which that is done, and I think this kind of method was discussed in the theoretical section where all the equations will have been given, so I need only to sketch out the main steps that are used. But I do wish to emphasize really the very large number of severe approximations which are made here. First of all, we are going to assume that no potentials higher than the second matter. Then we are going to say that we cannot measure that potential. There is no technique known to people to measure it, so we are going to guess it. So we guess the potential. Now there are two kinds of guesses as I have outlined in the scheme of Fig. 5 but when we have made the guess we still can't proceed, so we are going to make some theoretical approximations using perturbation theory. In the first guess we'll assume that the largest, most significant part of the potential is spherical, and that we can initially therefore start with the hard-sphere system, for which we have some results, and we can modify the hard-sphere system by introducing a small change to steepness of the hard core, and work out the effect of that small change via perturbation theory. Then we can add on a small attractive part, and we can perturb that combination with an angular-dependent part to introduce the anisotropy. So there are three perturbations added to that hard core. That, number 1, is the simplest version. Or secondly, we can start off in a more complicated way with a different model potential and say that, instead of having a spherical core, we will have a core of some shape, a shape corresponding roughly to the shape of the molecule, and by some means we discover the properties of a fluid made of those hard objects. Then we do the same thing: we modify the steepness and add attractive parts and anisotropic parts. And this form of the theory is considerably more complicated than the first form because you are starting with a more complicated system. And these results are to be used for various calculations.

- (1) Assume a model potential with spherical core:
 Know properties of hard sphere fluid:
 Use perturbation theory:

Hard sphere + small change to steepness
 + small attractive part
 + small anisotropic part

OR

- (2) Assume a model potential with hard shaped core:
 Know properties of hard shape fluid:
 Use perturbation theory:

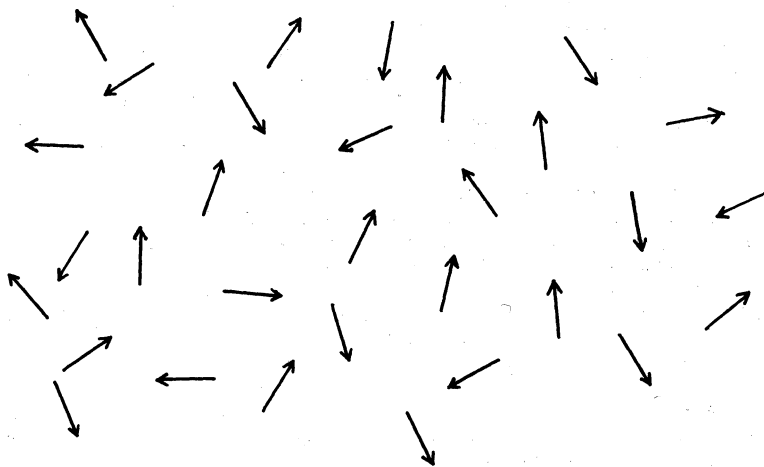
Hard shape + small change to steepness
 + small attractive part
 + small anisotropic part

- (3) Calculate (e.g.) thermodynamic properties
 Adjust model parameters to fit measured properties of real fluid or
 compare to computer simulated properties of the model fluid.

Fig. 5. Theory using pair potential alone.

The most common application is to calculate the thermodynamic properties of the system, and, having calculated the thermodynamic properties, there are two objectives. One is to look at some real fluids that you might think will correspond to your theoretical model and adjust the parameters in the model to get a reasonable fit to the properties of the real system. Now that is quite a good thing to do, because it gives you a way of describing and correlating the properties of the real system over some range, or some part of that phase diagram I showed initially. I think what you are trying to do there is to produce what I call an engineering recipe for the system. You are producing a recipe by means of which you can condense a large amount of information into a smaller and more basic set of quantities, namely, these model parameters. So that is useful but not necessarily fundamental, because these model parameters may not correspond too well to the real system.

Now the second objective is to try and develop the theory itself, and for this purpose what you would like to know are the real properties of a system which interacts with this pair potential alone. So that's an artificial fluid, a man-made fluid if you like, rather than a nature-made fluid. And you'd like somehow to discover the properties of this artificial fluid, and then compare that with the properties you calculated by this theoretical procedure. In that case you would be able to test your theoretical procedure and perhaps develop it further, and of course the method which one uses for that purpose is the method of computer simulation, and I will now briefly outline that method and make one or two comments on it. Again I think you will have heard of some examples of the use of this method previously. So I need only sketch through it briefly (Fig. 6).



1. Box of N molecules; $N = 256$ perhaps.
2. Given pair potential find probability of this configuration.
3. Move a molecule - find new probability
- repeat many times
4. Evaluate weighted average for property of interest.
5. Correct for quantum effects.

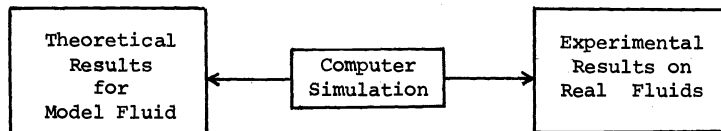


Fig. 6. Computer simulation of a fluid.

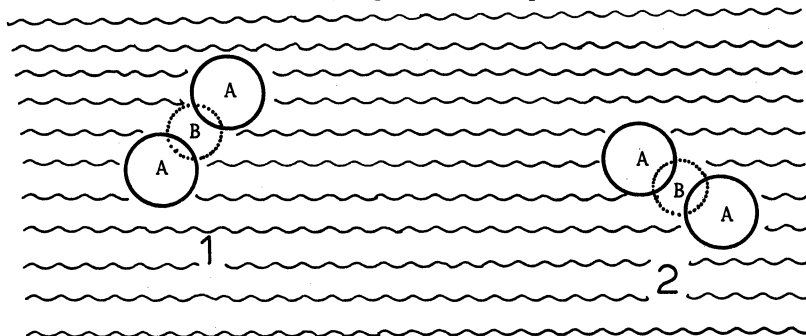
What one does is to take a number of molecules -- it might be 256 -- and place them in a box at convenient positions and with convenient orientations. Then you assume that a certain pair-potential exists between any pair of these molecules, and you figure out from that the energy of the total system, and hence the probability of finding that configuration. Then, if you are using the Monte Carlo method, you would move one of the molecules. That gives you a new configuration and you find the new probability, and then you repeat that many times to find the thermodynamic probability for the system at that temperature and density. And then you can evaluate a weighted average for any property to find the predicted value for that property. If you're going to make a comparison with a real system you would need to do step 5, correct for quantum effects. That can be quite a serious correction in some cases, but if you are just going to make a comparison with your theory, it may be sufficient to work through steps 1 to 4 in a normal classical calculation, so you are treating this purely as a classical system.

Computer simulation results are therefore used for two independent purposes. On the one hand they can be used for comparison with theoretical results for your artificial model fluids in order to develop theoretical techniques; and on the other hand they can be used to compare with experimental results on real fluids, simply because computer simulation represents the only satisfactory method to date of finding the consequences of a model potential and of making sensible predictions which may be compared with real experiments. So you can see from this that one faces a dual difficulty in studying molecular liquids, and especially in studying molecular solutions, the dual difficulty being first of all that one doesn't know how the molecules interact (and there is no way of finding that out), and secondly, one doesn't know how to do the theory. Thus the only way that is really open is that of computer simulation, which suffers from two defects. One is that it is a classical method, and secondly, that it is very difficult to use that method generally because of limitations in the range that can be covered on a conventional computer. That doesn't mean we should despair. Let's look at what has been done to date; an enormous amount of useful work has been done. You might think from what I say "well, everybody's crazy; they must all be barking up the wrong tree, going in the wrong directions". That may be true, of course but, however, obviously a lot of good has come out of the investigations and a lot of good could come out of further investigations. I'm just trying to put things in a framework which makes it possible to see the limitations and hence how limited are the things that we can really accomplish.

Because the things we can really accomplish are limited, it's nice to think about the way things should be done. What are the most sensitive things that one could do, and what are the ways in which one could construct information that would tell you the right model to use? I'd like rather briefly to consider questions of that kind. Now, with these models and with these theories I've been mentioning, one of the things frequently worked out is an atom-atom correlation function. These are worked out because they are, after all, fairly fundamental to the structure of the fluids. So I would like now to refer to Fig. 7 which will help to define what a partial correlation function is. What I've drawn here are first of all some wavy lines which in both parts of my diagram represent the fluid. They represent the bulk of the fluid, and then I've drawn here and there particular molecules which I wish to pick out of the whole mass of molecules in the fluid. In the upper part I have a linear rigid triatomic molecule ABA, which is molecule number 1 as far as our correlation function goes, and to the right of that is placed a similar molecule, number 2. And as this is a pure fluid made up just of those molecules, we can have then three partial correlation functions. We can start with A and we can look out from A and we can say "what is the chance of seeing an A on another molecule?" That would be from one A in molecule 1 to one or other A in molecule 2. That is the AA correlation function, the chance of finding another A on another molecule if your origin is on the first A. And then we can sit on a B and we can look out to other molecules and ask "what's the chance of finding another B?" It will be one of the illustrated B's looking at the other one. That gives you a second function; and then of course there is a third function looking from a B to find an A on a neighbouring molecule, or looking from the A to find a B. Those last two functions are the same. They give you a single cross correlation function. So in the case of this linear triatomic there are three correlation functions which one could consider. If one goes to a solution, and I have drawn a solution in lower Fig. 7, with positive and negative ions in it and some solvent molecules, then of course you can have a correlation function, for example a particular ion looking out at the solvent molecules, or an ion of opposite charge looking out at the solvent molecules, and many, many others. In general you will have a much larger number of correlation functions for the case of a solution than for a simple fluid.

PARTIAL (ATOM-ATOM) CORRELATION FUNCTIONS

A-B-A rigid molecule pure fluid



PARTIAL CORRELATION FUNCTIONS IN SOLUTIONS

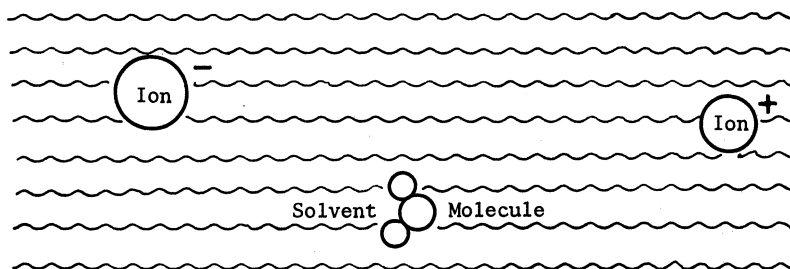


Fig. 7.

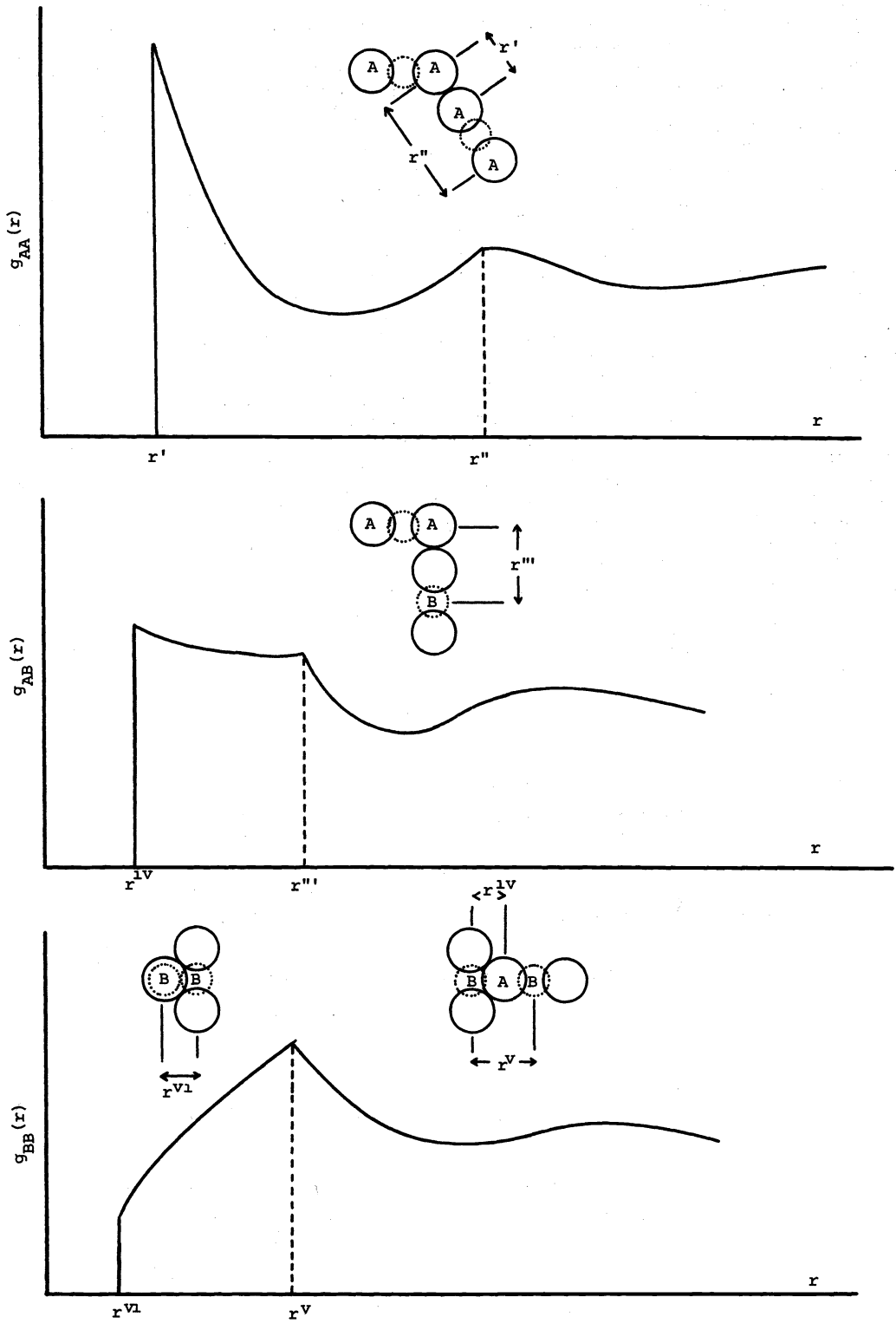
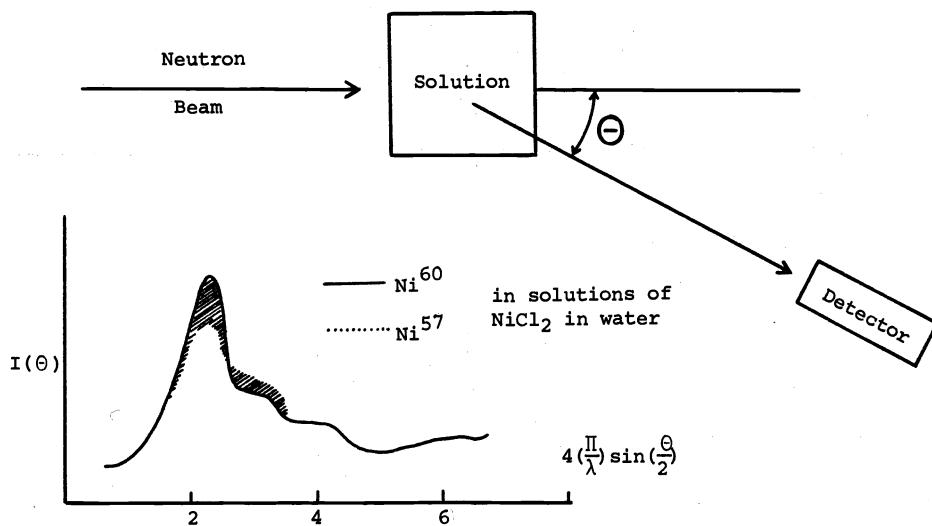


Fig. 8. Liquid.

So let's come back to the case of the triatomic molecule and look at the kind of function we would obtain in a liquid composed of those molecules. And what I have sketched in Fig. 8 are examples of the results obtained by using theoretical methods. In particular the RISM theory

of Chandler and co-workers has been used to produce results of this kind, and also there have been molecular dynamic calculations on the computer by Streett and Tildesley for this case (2,3). They have given us the form of these functions for a model in which the linear triatomic is treated as a set of fused hard spheres. So we have a hard sphere representing A; overlapping it a smaller hard sphere representing B; and then another overlapping hard sphere of A at the end of the molecule. Then the AA correlation function has the form illustrated, starting off with a step as the two hard objects strike one another. I have drawn in the little insert a molecule 1 and a molecule 2 in contact; the distance r' is the contact distance from A to A, as shown. In addition to this step, there is a cusp at r'' corresponding to the other distance shown across the two molecules. The cross correlation, g_{AB} has a similar step initially and also a cusp, and these arise at distances which can be related to the molecules in contact as drawn. Finally, g_{BB} has a similar shape with a step and a cusp, and the distance r^{VI} is produced when the molecules are in the configuration shown in which one molecule is viewed end-on (lower left). So to describe just the most elementary partial correlation functions for a fluid composed of these simple triatomic molecules, you need these three different functions. They look quite different and they are quite different, and for the initial phase of your perturbation theory you have functions of exactly this kind with these cusps in. Then as you develop the different stages of your perturbation theory, you'd obviously blur out all these sharp things, and you'd end up with a rather smooth function for the final real case.

Well, obviously those functions, while insufficient to describe the system, are nevertheless very illuminating concerning what is actually happening. Now I would like to turn to the question of solutions rather than pure fluids, and describe some of the ways those functions have been studied for solutions. I am afraid, although the title of this meeting is Nonaqueous Solutions, that I'm going to slip in some work on an aqueous solution. The work I am going to refer to is that of John Enderby and his Group in England, who have worked on neutron diffraction from solutions of various salts in heavy water (4). (The heavy water is there because of its convenience in the neutron diffraction technique.) He has made some extremely interesting measurements on these partial correlation functions. And, as I mentioned before, the situation for a solution is far, far more complex than the situation for the simple pure fluid -- even the triatomic-molecule fluid that I discussed earlier. So one must use a technique in which one can isolate one or two of these partial correlation functions, selecting by this technique those functions which are most significant in setting up a model for the solution.



Fourier Transform shaded part to get g_{NiX}

Isotope	Coherent Neutron Scattering Amplitude
Ni ⁵⁸	1.44×10^{-12} cm
Ni ⁶⁰	0.282×10^{-12}
Cl ³⁵	1.18×10^{-12}
Cl ³⁷	0.26×10^{-12}

Fig. 9.

What Enderby and his co-workers do is the following: they do a neutron diffraction experiment as outlined in Fig. 9, taking a monochromatic neutron beam, scattering it from a sample of their solutions through angle θ into a detector. So they measure intensity as a function of this angle, and that is plotted in conventional way as a function intensity against $\frac{4\pi}{\lambda} \sin(\theta/2)$; and they do this twice. In the example I am going to show, they took a solution of nickel chloride in water, and they took two samples, one containing nickel-60 and one nickel-58, and they obtained two diffraction patterns, the solid line is the case where they had nickel-60 and the broken line is the case where they had nickel-58. And there is a difference between the diffraction patterns obtained with the two nickel isotopes. The reason is shown in the figure where the actual neutron scattering amplitudes for both nickel and chlorine isotopes are listed to illustrate that one can do this trick with the chlorine as well as the nickel. You see that by changing the isotope, what you've done is to change the scattering amplitude of the nickel ion in the solution and, importantly, you've done that without changing the chemistry of the system. The big advantage of this method is that you change the isotope and hence change the way the neutrons see the solution without altering the chemistry of the solution. Secondly, you haven't altered the scattering of any other component, so the change which I have shaded in this diagram is due to correlation functions involving the nickel. In other words, if you take this shaded region and subject it to a Fourier-transformation, you will then get a radial distribution function which you would see if you sat on a nickel ion as your origin. Similarly, if you let the nickel alone and change the chlorine isotopes, 35 and 37, and do the same experiment you will get a radial distribution function for the situation viewed from a chlorine ion as the origin.

The big advantage of this neutron technique as exploited by Enderby is that you can pick out an ion-solvent correlation function, and Fig. 10 shows an example of his work. This depicts the pair correlation function g for sitting on a nickel and looking at X, where X is anything that might turn up in the solution. Now one sees nothing for a while of course, because there is nothing within the size of the nickel ion, then one sees two sharp peaks, and then one comes to something which is almost down to the level that represents nothing being there, and finally one sees the remainder of the solution. The question is, what are these two sharp peaks due to? If you actually look at the distances involved and consider the intensities corresponding to the areas of these peaks, you realize that what you must be looking at is the water in the neighbourhood of the nickel. And if we suppose that there is a charged nickel ion as shown at the bottom of Fig. 10, and that the oxygen is facing the nickel with the deuteriums away from it, that picture would indeed fit in. In other words, there will be a certain number of oxygens at r' and there must be twice the number of deuteriums at r'' , and that would fit in with the exact ratios of the areas of these two peaks. If you make this model assumption here, you can then obviously relate these two distances, namely the position of the peak r' and the position of the peak r'' to the two distances in the lower drawing. Also, if you know these latter distances and the size of the molecule, you can figure out the angle shown as 40° in the drawing. The conclusion from this experiment is that one can say from the areas of the peaks that there are six water molecules in a sphere around the nickel ion, and that the water molecules on the average are inclined to the nickel-oxygen axis by an angle of 40 degrees. So with this kind of partial correlation function experiment one can in fact deduce very positive information about the hydration shell, and from this one can in principle try and construct a model for the solution.

Now while there are many more static experiments of that kind which one could undertake, I'd like to turn in the remainder of this talk to dynamic studies. We have had at this meeting several papers on Raman and infrared experimental results, but unfortunately we'll have no experimental results on inelastic neutron scattering. So I would like to compare these three techniques and comment on how inelastic neutron scattering can be used for studies of solutions with the same object as those diffraction experiments I was just showing, namely of studying the cage of solvent atoms that might form around a solute. Well, let's look at the three techniques and see how they compare with one another. I have made in Fig. 11 a very, very brief summary. First of all there is the momentum which the radiation will transfer to the system from which it is scattered. Because electromagnetic radiation corresponds to photons of zero mass, the momentum transfer is extremely low in this case whereas, of course, with neutrons being massive particles the momentum transfer can be quite large depending on the energy and the angle that you use. In fact, the momentum transfer is a variable experimental quantity in this case, and this can be very useful in a number of experimental applications. In those that I shall show, however, this particular feature will not be exploited. Then we come to the question of selection rules. One of the disadvantages, as well (I may say) in some cases an advantage, of optical methods is the existence of these selection rules which allow you to see certain transitions and do not allow you to see others. With neutrons there are no selection rules. Neutrons just see everything, which is very good in some cases, but again very bad in others because you see too much, and you don't know how to interpret the data you get. And then finally of course with neutrons we have this big advantage that you can use isotopic substitution to change the scattering from different parts of the system without changing its chemistry. In addition, some properties such as the moment of inertia, may be changed by isotopic substitution leading to effects observable by both optical and neutron techniques.

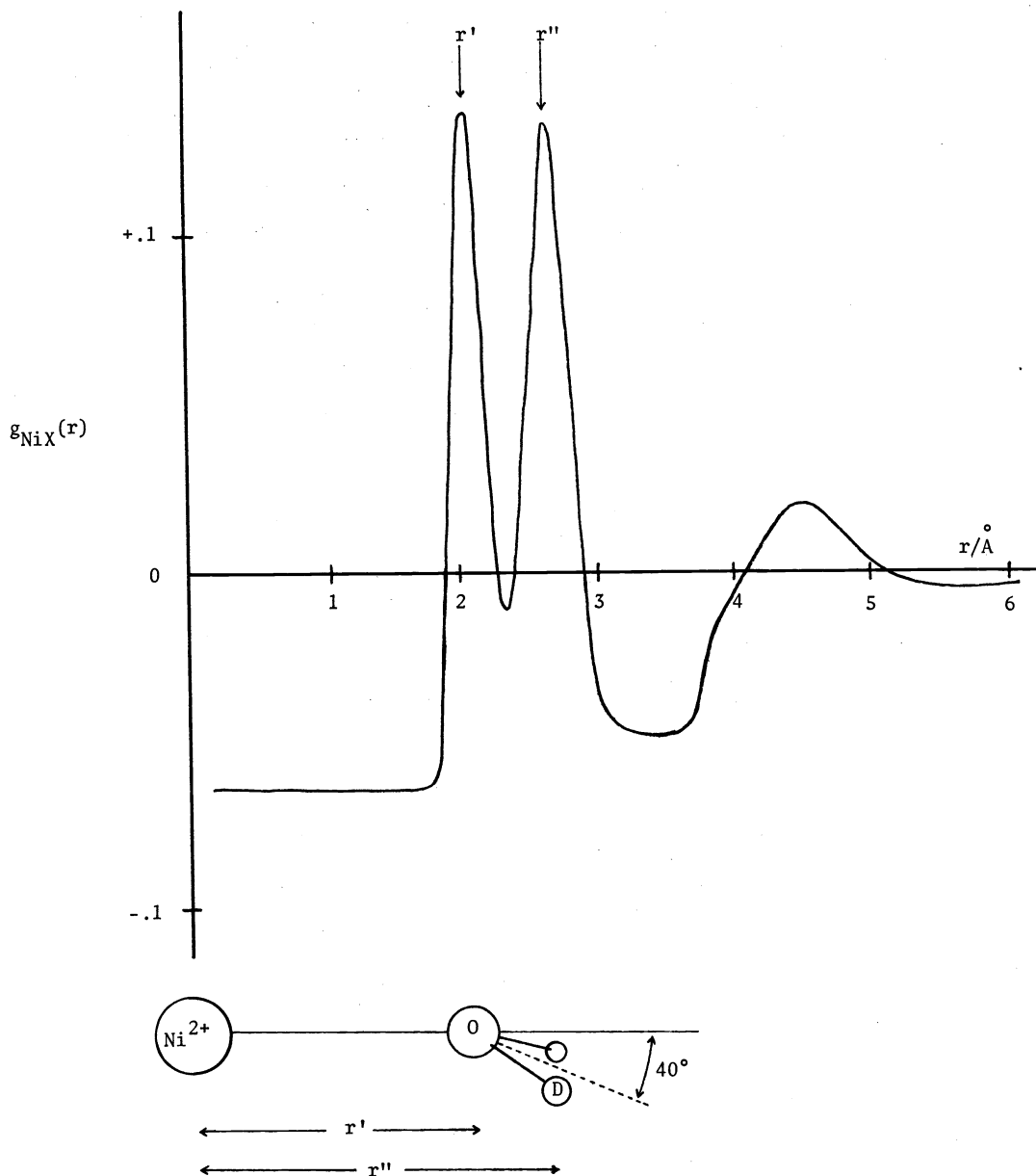


Fig. 10. Nickel isotope difference ($g(r)$) in 4.41 molal solution of NiCl_2 in heavy water.

Well, how are these neutron experiments done? One takes a pulsed monokinetic beam of neutrons, fires it at a solution, and looks at the scattered neutrons with a detector as shown. Now if a pulse of neutrons, all of which have the same velocity, were scattered without any change in velocity then they would obviously arrive at the detector all at the same time. Thus if the intensity is plotted as a function of the time of arrival at the detector a sharp peak would be obtained. In practice, however, a distribution of the kind shown in this diagram is found, and this corresponds to the fact that the neutrons are Doppler-shifted by the motion of the nuclei in the sample. As the nuclei move around in the sample, whether by translation or rotation or any other motion, the neutrons observe that motion and receive a Doppler shift. Sometimes that Doppler shift will correspond to an acceleration, so the neutrons travel more rapidly over their path and arrive early, and sometimes the shift will correspond to a deceleration so they travel more slowly and arrive late at the detector. And so one gets a broad distribution of times of arrival, that corresponds to the motions that are going on in the solution, and all motions that are going on are in fact observed.

<u>Method</u>	<u>Momentum Transfer</u>	<u>Selection Rules</u>	<u>Isotopic Substitution</u>
I.R. Absorption Raman Scattering	Low	Yes	No
Inelastic Neutron Scattering	Wide Range	No	Yes

Neutron Time-of-Flight Technique

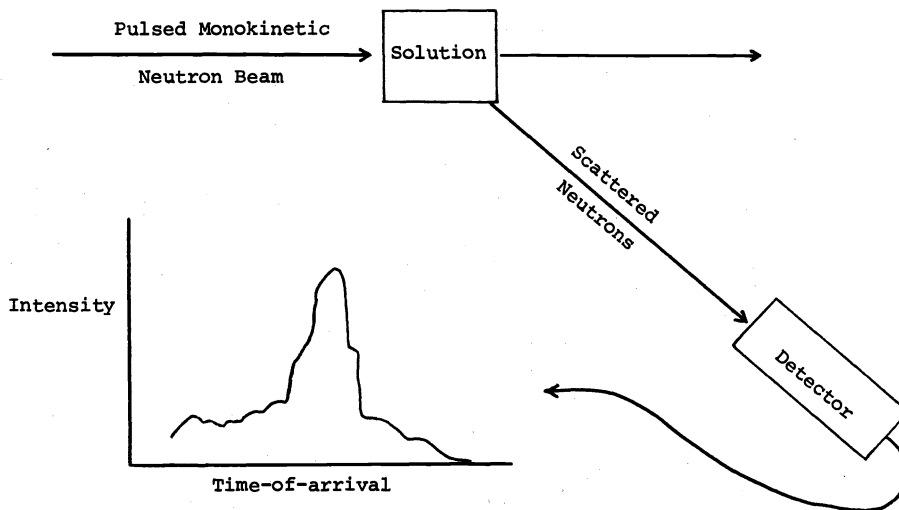


Fig. 11. Comparison of optical and neutron techniques.

Now as an example of this method I will give some results that were obtained roughly ten years ago by Eder & Chen on a solution of hydrogen in argon (5). Here I would like to emphasize a point, namely that in studying solutions it would be an advantage to study very simple things. One is forced to some extent by the selection rules in IR and Raman work to choose complicated things, whereas with neutrons you can choose simple things because you can observe effects in simple things. Theoretically it is an advantage, of course, to pick a simple molecule like hydrogen and a simple solvent like argon; I mean, that makes a system which is much more amenable to a theoretical understanding. It would also be nice to pick spherical molecules and study a spherical solvent and a spherical solute, but that creates difficulties, of course for IR and Raman work but no difficulty for neutrons, as I will show in an example in a moment.

The example given in Fig. 12 is hydrogen dissolved in argon at the temperature and pressure shown, and these are results taken with 5.3 angstrom neutrons at an angle of 45 degrees. The intensity has been converted to a differential cross section, and the inverse of the neutron velocity (that is, the time of arrival of the neutrons at the detector) is plotted as abscissa. The little peak at the shortest time (that is the fastest neutron) corresponds to conversion of ortho to para hydrogen, $j=1$ to 0 conversion. Of course this is a line which is forbidden in the optical work, but is accessible in neutrons because with the interaction of the neutrons with the protons you can flip the spin of the proton and hence change the spin state of the molecule. So you get this ortho to para conversion line, but that is not really of great interest. What is of greater interest are the remaining two features in the spectrum. The peak marked A corresponds to the translational motion of the molecules, a diffusive motion; and the peak marked B corresponds to the motion of the hydrogen molecule in the cage of surrounding argon atoms. You can try to invent a theoretical model to describe the confining influence of that argon cage, and the frequency with which you might imagine the hydrogen molecule would vibrate in the potential well created by those argon atoms. Sears has worked on such a model, called the itinerant oscillator model, which produces the broken line which has all the qualitative features of the experiment but does not have the quantitative features (6). So this kind of experiment tells you something, but really not enough again about the nature of the cage of solvent atoms that form around a solvent molecule.

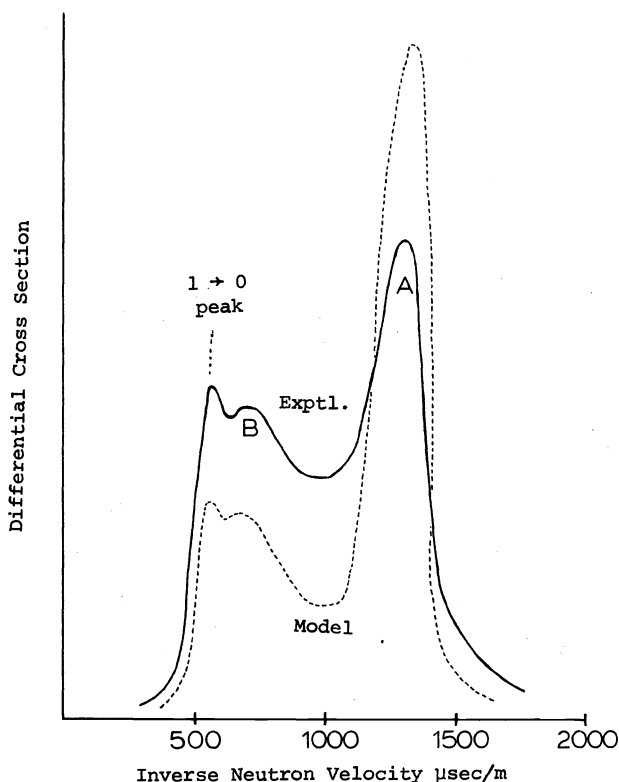


Fig. 12. 3.3 mol % ortho - H₂ in argon

$T = 100$ k

$P = 26.5$ Ats

5.3 Å Neutron beam

$\theta = 45^\circ$

It would be nice if we could look at how that cage begins to form; how do these molecules pack stepwise as you increase their number around the hydrogen molecule? With a system like this we can do that because we have the whole of the phase diagram readily accessible. So we take the case, which I think is very neglected, of the solution of one gas in another. We can take hydrogen gas mixed with argon gas and in that case even in a dilute solution we'll have just a few argon atoms which are in the neighbourhood of the hydrogen molecules, and we can study the interaction on that scale. McPherson has made a measurement of that kind, and in Fig. 13 is shown one simple example of his results to demonstrate in principle how it works (7). In this case he has 20% of hydrogen in argon at room temperature and a pressure of 6000 p.s.i., and of course in this case, rather than compare with a model, experimental results can be compared. This is rather analogous to the way Enderby was thinking in his work. You take two experimental results and compare them, to make or draw your conclusions. In the first case, one can use pure hydrogen gas as the reference system, and here of course the hydrogens are being scattered from other hydrogen molecules of light mass. When the argon is introduced the curve narrows. It narrows because the hydrogen is now being scattered from a much heavier mass: the neighbouring particles to the hydrogen molecules, being argon, are of heavy mass. In the collisions you lose energy and therefore the width of this spectrum, which corresponds to the rate at which the neutrons lose energy, is less. Again with the aid of a model of this cage you can try and describe this difference between hydrogens being scattered from hydrogens compared with hydrogens being scattered from argons. So the point I wish to make very simply is that, by exploiting the full range of the phase diagram, you can try and understand the model you are putting forth -- namely of a cage surrounding the hydrogen. You can try and understand that model in greater detail.

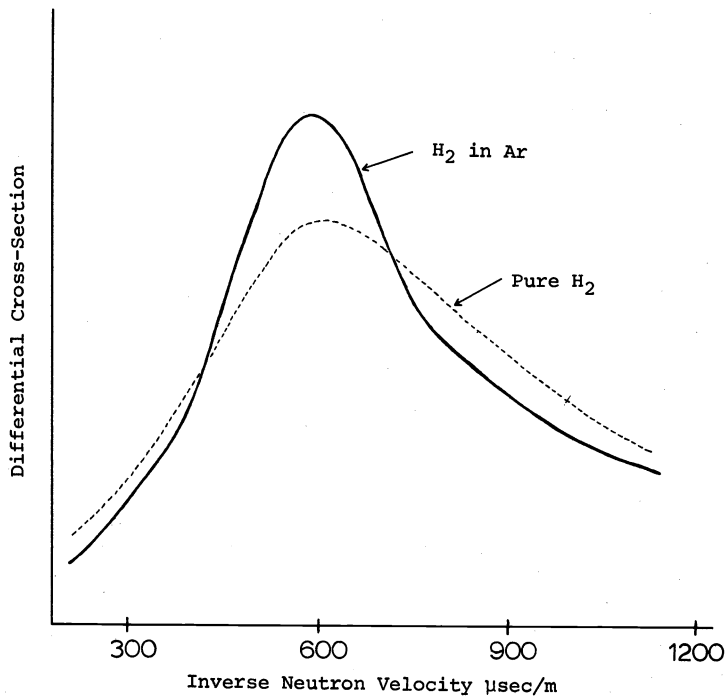


Fig. 13. Inverse neutron velocity $\mu\text{sec/m}$
 20 mol % normal H₂ in argon
 T = 297 k
 p = 6000 p.s.i.
 2.4 Å Neutron beam
 $\theta = 22^\circ$

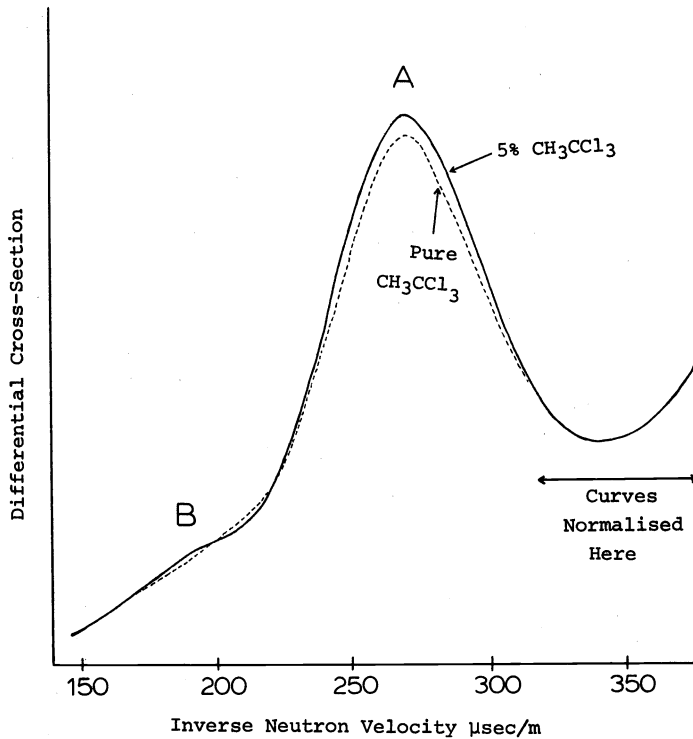


Fig. 14. 5% Methyl-chloroform in carbon tetrachloride
 T = 297 K
 P = 1 atm
 2.4 Å Neutron beam
 θ averaged from 20° to 80°

The last example I would like to consider, and one I think we ought not to leave out of a talk of this kind, is the case where we have an internal mode of motion of one of the molecules, either the solvent or the solute. Obviously the simplest case we would like to take is the case with the highest symmetry, and the example I have chosen is that of methyl chloroform dissolved in carbon tetrachloride. Methyl chloroform is essentially the same as carbon tetrachloride but with one of the chlorines removed and replaced by a CH_3 group. The size of the CH_3 group is almost the same as that of a chlorine, but now there is an internal mode of rotation in the molecule. If I were thinking of this in terms of pair potentials I'd then have a lot more variables to take account of. Not only would I have all the variables I discussed in my rigid molecule case, but I'd have additional variables to take account of the internal degrees of freedom of the molecule. That would hopelessly complicate the problem. What I would like to be able to say, of course, is that the internal mode is independent of the environment of the molecule, so I can treat it as an independent oscillator. In that case I could construct a model of the interaction of the solvent and solute on the basis of independent oscillators. But to do that, I have to study that internal mode of rotation by some technique and see how it changes with the environment.

Fig. 14 shows some work carried out by Litchinsky on solutions of methyl chloroform in carbon tetrachloride (8). This particular case is that for a 5% solution at room temperature and one atmosphere pressure. The figure shows a section of the neutron inelastic scattering pattern, a section of the pattern corresponding to situations in which the neutrons have been highly accelerated. The situation in which the neutrons were scattered elastically would correspond to a point on the inverse velocity scale which is way off the diagram at $610 \mu\text{sec/m}$. The peak which he observes corresponds to the torsional oscillation of the methyl group; this is the first-order peak at A and there is a weak second-order peak or bump at B. Two cases are plotted, that of the 5% solution, and the second case is that of the pure methyl chloroform. So we imagine in the 5% solution that the molecules are relatively isolated from other molecules of the same kind, and we are seeing the shape corresponding to the independent oscillator. Then when we transfer to the pure methyl chloroform there may be couplings between neighbouring molecules and therefore the peak shape should be distorted. The amount of distortion is extremely small, showing that the picture of the independent oscillator is roughly correct. Thus, within the goodness of that approximation we can use a picture of methyl chloroform in carbon tetrachloride which is analogous to the picture we could use for hydrogen in argon.

So I have tried in this simple way to show how one might do experiments to construct models, and hopefully then with the models to develop a theory to explain the properties of the system. I mentioned in the beginning that my title had a message in it. The message is really that we are working in an impossible field because we cannot measure the basic information and put the field on a proper footing, and therefore we have to leave out a great deal, and I have tried to emphasize that by leaving out the equations. In the absence of the equations I have tried to sketch some of the considerations one might include in building a crude but perhaps representative model of the systems we would like to study.

REFERENCES

1. W. B. Streett and J. L. E. Hill, *J. Chem. Phys.*, **54**, 5088 (1971).
2. L. J. Lowden and D. Chandler, *J. Chem. Phys.*, **59**, 6587 (1973).
3. W. B. Streett and D. J. Tildesley, *Faraday Society*, Discussion No. 66 (1978).
4. A. K. Soper, G. W. Neilson, J. E. Enderby and R. A. Howe, *J. Phys. C.*, **10**, 1793 (1977).
5. O. J. Eder, S. H. Chen and P. A. Egelstaff, *Proc. Phys. Soc.*, **89**, 833 (1966).
6. V. F. Sears, *Proc. Phys. Soc.*, **86**, 953 (1965).
7. R. McPherson (unpublished).
8. D. Litchinsky (unpublished).