

IN MEMORIAM

Aneesur Rahman

1927 - 1987

C.E.C.A.M., Orsay. France
September 1987

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As the European Molecular Dynamics Community owes so much to our dear friend Anees Rahman for guidance, help, suggestions, encouragement that he gave, and, as many of his contacts with this community were made during C.E.C.A.M. meetings and workshops, it seemed most appropriate we should mark our esteem and friendship with a scientific meeting which was held in Orsay on September 11.

This booklet then gives a summary of the papers which were presented at this one day Symposium and gives a view on Anees' very wide scientific activity.

We would have very much liked to have had Jady Rahman with us on this occasion but it turned out she had decided to organize on this very same day a religious Memorial Service in Hinsdale.

However, we were pleased to have received a message from Jady, which was read out and is printed below. I can only affirm that we did in fact remember on this occasion Anees with Joy.

Orsay, September 1987,

Carl Moser

Dear Friends,

I send you a very warm greetings and sincere thanks for your expression of affection for Anees.

Paris is indeed a most suitable place for a scientific gathering to remember Anees, because it was in Paris, particularly in C.E.C.A.M., that Anees had spent some of his most exciting, productive, and enjoyable time of his career. I remember well his marathon computing and nonstop picnicking with some of you at C.E.C.A.M., always with such exuberance. Anees was indeed lucky, not only because he had a life-long hobby for his profession, but also because he had you as his colleagues and friends. On behalf of Anees, I thank you.

Have a good meeting and remember Anees with joy!

Jady Rahman

Minneapolis, September 1987



Preface

When the sad news of Anees Rahman's death spread, the spontaneous reaction of some of his friends was to bring together the European Molecular Dynamics community for an informal one-day meeting in recognition of the strong influence Anees has had in Europe. There could be no better place for this meeting than Orsay, which Anees had visited many times, both in the late sixties with Loup Verlet's group and in the seventies for several CECAM workshops. Despite the short notice, the organizers were convinced that many of Anees' friends and admirers would attend, and the list of more than 40 participants given at the end of this booklet shows that they were right.

The guiding line in the organizations of the meeting was to ask some of Anees' former European collaborators to present several fields, in which he left a lasting imprint. The topics include atomic motion in simple liquids, free energy calculations and structural transitions, water and aqueous solutions, super-ionic conductors, nucleation and amorphous solids, and molecular dynamics simulations of quantum degrees of freedom. Anees was much more interested in the simulation of real systems than in the pursuit of theoretical models in statistical mechanics, an approach that was well-received in Europe. Loup Verlet agreed to open a meeting with analysis of the origins of molecular dynamics, while Herman Berendsen gave a brief account of the long lasting and inspiring relation between Anees and CECAM. The concluding talk dealt with strongly coupled plasma, a field which Anees addressed in one of his last subjects in order to underline the present and future vitality of molecular dynamics as a universal tool.

The announcement of the meeting was voluntarily limited to European participants, but a few overseas visitors, who were attending a CECAM workshop, were present. The organizers would like to express their gratitude to all speakers and participants for making the meeting so successful, and to Carl Moser for his help and support. On such a sad occasion it is a pleasure to see that the European community, to which Anees contributed so much, is alive and full of enthusiasm.

J.P Hansen,

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1. The Origins of Molecular Dynamics

Loup Verlet

Laboratoire de Physique théorique et hautes energies, Orsay

I shall devote my talk to the fundamental 1964 paper of Rahman [1], entitled: *Correlations in the Motion of Atoms in Liquids Argon*. This paper opened a new field of research and originated a lineage of scientists to which we belong. In other words, we are not here only to mourn a beloved colleague but also to commemorate something of a founding father.

Usually, all foundations originate in some kind of heroic, extraordinary accomplishment of the founder: think of Newton's Principia or Boltzmann's H-theorem. In the present case, we have to face a paradox. Looking to Rahman's fundamental paper with our present knowledge, we have the impression that, instead of the required founding feat, we have something completely trivial: there is no new concept and the computation, although done with great care and defining high standards of quality, does not introduce new technical devices. But this impression results from an anachronism: Anees' paper represented a breakthrough, which displayed the boundary separating the infeasible and the obvious. Rahman's feat is a limiting case: the obstacle, which has been overcome by the founder, has no material or technical component and is purely physical (which does not make it less forbidding).

This feat implies a transgression, which can be thought as a desecration: old landmarks are removed and a forbidden domain is opened to the thought. At that moment, repeating on a small scale the transgression of the founder, we leave our ancient certainties and enter personally in the new field, we get "involved" in it. We soon forget those moments of upheaval in our way of thinking because they represent transgressions: they violate the fundamental rule which enabled the tremendous progress in physics by requiring a rigorous separation between the outside reality which is through the scientific impassive eyes of science and the inner, psychic reality which is protected by being ignored.

In order to give some objective for the physical obstacle I am speaking of, I shall parallel the evolution of computers and the development of "exact" solutions of the many-body problem. The first high-speed commercial machine equipped with Fortran, the IBM 704 appeared in 1955. It had a floating-add time of 24 microseconds, when it was of the order of a millisecond for older computers. It was immediately followed, in 1957, by the Monte Carlo computation of Wood and Parker [2] on LJ atoms and the same year by a numerical solution of the HS equation of state both through MC [3] and [4]. There is a 7-years gap between those papers and Rahman's paper. (Rahman's computation was done on a CDC 3600 machine, at 2.25σ , it took 45 sec. per integration step. The same computation, with 256 particles and a cut-off at 2.0σ , took only 40 sec. on the 704).

It may be argued, using the kind of common sense argument often opposed by physicists to psychological considerations, that in the early sixties there were not so many computers and not so many physicists trained to use them, so that the so-called 7-years gap may be trivially explained. This may be so indeed. But it seems to me that if the easiness of MD with continuous potential had been realized, a number of people (including my own group) who were currently performing MC computations would have switched to MD. Alder and Wainwright [5], in their first long article about MD of the HS system (and HS+square well) make the following comment: "Although it is feasible to deal with realistic potentials, it entails a considerable slowing down of the calculation and involves the problem of having to cope with repulsive collisions where the forces the particles experience

change very rapidly". This erroneous opinion expresses the general feeling at the time and reflects the psychical difficulty lying behind the 7-year gap.

Before giving admittedly hypothetical reasons for that gap, let me first speak of the positive evidence which can be obtained by examining Anees Rahman's paper. This paper was written as a consequence of the long standing interest [6] of our friend for neutron scattering theory: the MD computation was carried out in order to test the approximations made at that time for the Van Hove correlation functions. It is clear that Rahman, primarily interested in neutron scattering, was not very familiar with the latest developments in statistical mechanics. Most noteworthy is the fact that he did not compute the total energy and did not check that it was conserved. It is also remarkable that, when commenting the appearance of a negative part in the velocity autocorrelation function, Rahman does not mention that this had already been observed, in the case of hard spheres, by Alder and Wainwright. It may be noticed that this absence of reference is a general characteristic of founders: independent thinkers, they go forwards without caring so much about their links with the past.

The silence of Rahman concerning his eventual sources for MD is the more remarkable when we know his generosity in giving credit to others. The only reference in his paper is to a review paper by Beeler [7], which gives an account of all "exact" computations up to 1964. But it is clearly a last minute reference and it is probable that Anees did not have the opportunity to read carefully that paper. If he had, he would have seen a detailed relations of a paper by Vineyard et al. [8] on radiation damage, where Newton's equation for a thousand atoms interacting through a 2-doby potential are solved. But this MD computation is embedded (and disguised) in a very complicated set-up, because the interest is focused on the various perturbations following the impulse initially given to a particular atom. Vineyard et al. used an integration algorithm different from the ones used by Rahman (both entail an error on the position of order $O(h^3)$, where h is the time integration step; the error with the currently used algorithm is behaving as $O(h^4)$, and he tested the conservation of the total energy.

The apparent priority of Vineyard over Rahman proves paradoxically my point. If the founding feat was mainly technical and boiled down to a problem of numerical analysis, there is no doubt that Vineyard should be regarded as the real founder of MD. But nobody, to my knowledge, ever pretended that. In fact, Anees was the first to "simulate", without any disguise or alibi, real bulk matter by integrating Newton's equation of motion. Rahman's feat, I will try to show, resides in this head-on approach with the psychological difficulties it entails.

Let me first note that strange time lags such as the one I point out here are not unheard of in the history of physics. See for instance Weinberg's account [9] of the late discovery of the 3K sky radiation. The psychical resistance opposed to the discovery can be searched at various levels of consciousness. In our case there is a first, obvious, obstacle, which can be described as an ideological prejudice. Before the advent of "exact" computation, we learned that the many-body problem could not be tackled and that a special branch of science, statistical mechanics, was established in order to find approximative solutions to that problem. It is thus understandable that Rahman, who was less addicted than others to the prejudices of statistical mechanics, was in a good situation to do what he did. I am not entirely satisfied by this explanation because, since 1957, it was known to everybody that the many-body problem could sometimes be solved so that this obstacle was largely removed.

We can reach a deeper level of explanation by realizing that Rahman's computation provides a very adequate figuration of the well-known Laplace fantasy of an omnipotent and omniscient being who knows, at a given time, all the positions and velocities of all the atoms in the universe and is then able, by integrating Newton's equation, to predict the future of the universe and to know all about its past. If you are familiar with the work of Mélanie Klein or Winnicott, you immediately see the psychoanalytic meaning of the Laplace fantasy. I shall try to by-pass the reference to psycho-analysis with which you may be unfamiliar or allergic by appealing to the reactions of many physicists faced with the Laplace fantasy: fascination and rejection, exaltation

and horror. Think of your own reactions or recall the jokes made in your lab. To make it short, I shall refer to the excellent book of Prigogine and Strängers [10], *La nouvelle alliance*, that you probably read. You then noticed the passion with which these authors attack the deterministic ideal which they attribute (somewhat superficially) to Newton and their expressed horror at the evocation of the Laplace fantasy. If you agree that these strong feelings point to the unconscious obstacle that I am considering and that Rahman's feat was to overcome that obstacle by performing an undisguised simulation, then you understand why things were easier for Alder and Wainwright, because they attack what is clearly labeled as a model and stay away from the computer; and for Vineyard who works under cover of a very complicated problem and with the alibi of the necessity of solving a practical reactor problem.

The word simulation used by Rahman points also in the same direction. Like many words denoting imitation, it has a negative connotation: *simulate*, *copy*, *counterfeit*, *feign*: all these words indicate something disputable. But Anees Rahman uses also the word mathematical model. Simulation and model indicate two aspects of theoretical physics which are usually kept apart but that the rahmanian molecular dynamics unite in a more and more closely knit construction.

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2. The Development of Molecular Dynamics at CECAM

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CECAM workshops, which were held since 1972, have played an important role in the development of Molecular Dynamics, and in particular in the application of MD to biological macromolecular systems. Although applications to biological macromolecules such as proteins have developed in several places, notably in the group of Martin Karplus at Harvard, it is probably correct to say that the CECAM activities have been seminal in this field and have stimulated activities both in Europe and in the USA:

In the early stages of this development Anees Rahman's influence has been crucial. Application of dynamic simulation techniques to large molecules was unthinkable in the early seventies and it is doubtful if the (psychological, rather than technical) barrier to apply such techniques to biological macromolecular systems would have been crossed so early without his presence. In the following I shall try to indicate what the role of CECAM and the role of Anees Rahman has been in the beginning phase of this development. I restrict myself to the development of MD in the field of complex molecular systems, thereby neglecting Rahman's important role in other CECAM activities, such as simulations of simple liquids, molten salts, aqueous systems, and solids. Other contributions to this memorial meeting will fill that gap.

Going back to 1971, I remember that I was personally quite impressed by the article of Rahman and Stillinger [1] on the simulation of liquid water. Having worked myself with nuclear magnetic resonance and dielectric techniques on the hydration of biological macromolecules, in a time when deep and experimentally unsolvable controversies existed about the state of water in biological systems, it had for long time been my dream to be able to simply calculate the properties of hydration water on the basis of

Rahman (Argonne)	MD of water: models, drop
Barker, Henderson (IBM)	Monte Carlo, reaction field
Singer, McDonald (Royal Holloway)	Stockmayer model,
Bellemans, Orban (Brussels)	Proton polarization in ice
Berendsen, v.d.Velde (Groningen)	Polarizable water model
Barnes (London)	Cooperativity in H-bonding
Bol (Eindhoven)	MC on simplified water model

Table 1: Workshop on MC and MD of Water in 1972

Interatomic interactions. During the sixties this remained an utopian dream and it was quite thrilling to read Rahman and Stillinger's article: simple, bold simulation came within reach, although at the expense of horrible (and to us unavailable) amounts of computer time.

Full of enthusiasm about this method I happened to burst into a conversation that Carl Moser had with Wim Nieuwpoort in Groningen in 1971 about CECAM activities, which in those times were almost exclusively in the field of quantum chemistry. We discussed the possibilities of a workshop for the following year in Orsay on Monte Carlo and Molecular Dynamics of water. It was immediately clear that in such a workshop Anees Rahman should be the key scientist, whose knowledge –and programs, we hoped- would be available for the other participants. Shortly after this we discussed these ideas with Anees (who stayed in Orsay in the summer of 1971). He was cautious, but agreed. So the workshop was born.

In Table 1 the participants and subjects of this workshop, which lasted for two full months, are listed. The workshop was a worthwhile experience for all concerned. Anees shared his programs with us, patiently explained the details and helped us along with his many practical hints and computational tricks. We learned very much, and very intensely, from him. The discussions, extending often in the train to Paris, were always lively and of considerable depth.

His programs and output listings were quite unintelligible for others: they did not contain a single comment or heading, indeed only numbers appeared on the output listing. He was extremely pragmatic and would not spend one moment on what he considered irrelevant. His original water dynamics program was quite complicated as it solved the Newton-Euler equations: these contain division by the sine of one of the Euler angles, which necessitates a coordinates transformation every once in a while when that angle approaches zero. In addition to this inherent complexity, his programs were not precisely the best examples of good structured programming, but they worked and were error-free.

Many subjects, then recognized as important and difficult, are still among the key problems of today. The majority of the efforts at workshops [2] were concerned with the proper treatment of long-range electrostatic interactions, the relation between dipole fluctuations and dielectric constant, and with polarisability. The problems with the computation of the dielectric constant from fluctuations of the total dipole moment in a sphere, thus preventing the possibility to derive the dielectric constant in a sensitive way from this fluctuation. It was recognized, and pursued by Baker in a Monte Carlo simulation at the workshop, that the introduction of a reaction field could remedy this problem. The formulas to obtain the dielectric constant from the dipole fluctuations in a smaller sphere were also derived. Ian McDonald applied the Ewald summation to compute long-range interactions, but the correct relation between dipole fluctuations, Ewald summation, cut off radius and reaction field were not properly understood until much later [3,4]. The work of Bellemans and Orban on the Kirkwood factor in ice was rather peripheral to this issue, but quite interesting by itself, involving an elegant generator of random proton configurations.

At that workshop it became clear that the BNS (Ben-Naim-Stillinger) interaction potential for water, used in Rahman and Stilleinger's simulation, needed readjustment. We really didn't like the switching function used to prevent a catastrophical interaction between protons and lone pair charges, which were at the unreasonable distance of 1 Å from oxygen.

In a polarizable model we used a distance of 0.8 Å and used another form (due to Wim Bol) to shield the charge at short distance, replacing r in the Coulomb potential by $\sqrt{r^2 + s^2}$ where s is a constant. This works nicely, although it was never used later on. The polarizable potential used a modification of charges and worked reasonably well, although it became clear that a complete reparametrisation would be required.

The notion that *effective pair potentials* are needed in the condensed phase, different from pure pair potentials valid for isolated pairs, became slowly apparent. The BNS model, which was based on a mixture of properties of the solid and the gas phase and thus in its conception far removed from the notion of an effective pair potential, had already been scaled to fit better removed from the true pair potential: it had a dipole moment considerably larger than that of the isolated molecule, and a second virial coefficient about twice that of water vapour. The idea that an effective pair potential was needed to include the average effects of polarization in the condensed phase was then clear [6] and subsequent workable potentials for water, including the SPC model [8] that was later also used by Rahman [7], were parametrised accordingly.

The 1972 workshop showed that simulation of water was possible. Why not more complicated systems? It was my impression that water already contained the principal difficulties of long-range polar interactions and polarisability, while its behavior relies on the proper handling of hydrogen bonding, so crucial for biological macromolecules. If you cannot simulate water, biological macromolecules will be hopeless; if you can, the macromolecules may turn out just to be more

complex, but not more complicated. The interests of Anees were more centered on basic properties of systems of simple composition, however. Nevertheless he remained active in several CECAM activities on the way to large molecular systems.

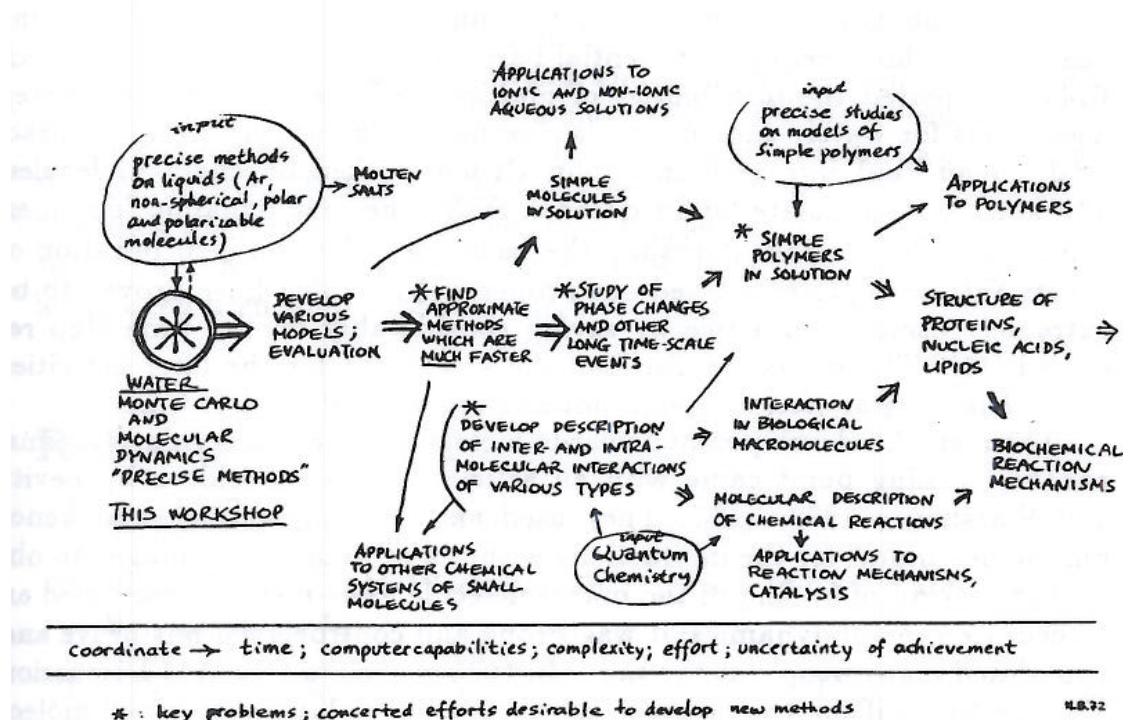


Figure 1: Page 2 of the 1972 Workshop Report [2]

Figure 1 reproduces page 2 of the 1972 workshop report and shows how the developments and bottlenecks were seen at that time. My estimate then was that the right hand side of that figure would be removed by more than ten years. In practice, the first protein simulation was carried out in a 1976 CECAM workshop, and the simulation of biological (macro)molecules is now a thriving field with growing commercial implications.

In 1973 we held the first CECAM Discussion Meeting to see in what direction the development should go. It was held in a small castle in Warffum in the far north of the Netherlands, quite removed from civilization. Two workshops – to be held in 1974 – resulted from that Discussion Meeting: one on *ionic liquids*, organized by Konrad Singer, and one on *long time scale events*, organized by me, to tackle the basic problem that could be envisaged for large molecules: how to treat events that take place on a time scale longer than brute-force dynamics can handle. Rahman took part in both workshops.

In the workshop on *long time scale events* several approaches to circumvent “slowness” were adventured. The basic problem is not the “slowness” itself, but the occurrence of a *range* of time scales for the motional modes in a system: in the case of a large range long times must be simulated with short time steps. Some ideas were more original than practical. Anees Rahman worked with Gianni Jacucci on the clever idea to change masses of particles at will, so as to produce more homogeneous temporal behavior and hence to sample the configuration space more efficiently. In classical statistical mechanics the special equilibrium distributions do not depend on the masses of the particles; this static equilibrium properties related to translational motion (diffusion, viscosity) retain their meaning to a considerable extent. Charles Bennett from IBM

carried this idea much further and simulated a ten-atom polymer model with masses modified to a *mass tensor* such that all normal modes are of equal frequency and really large steps can be taken. The problem was that –due to the anharmonicity in the system- the mass tensor had to be recalculated too often and since this involved a time consuming normal analysis the method never became very practical. I tried to develop a kind of *damped dynamics* to cut off high frequency components of the atomic motion, but I kept running head-on into large repulsive potential barriers. John Finney from Birkbeck College explored the possibilities of multirange forces and multi-timestep algorithms for water: such methods give modest gains but are quite practical. Jean-Paul Ryckaert and John Orban worked on chain molecules, and started to simulate liquid decane: really the first dynamic “polymer” simulation [9]. In this workshop the basic ideas for the incorporation of *constraints* arose, later worked out properly [10], which have proved to be extremely useful in practice by saving considerably on the time step required [11]. The workshop also had the seeds in it for the later activities of in *stochastic dynamics*, although nothing crystallized at that time.

Then, in the development towards biological macromolecular systems, another turning point came with the article on protein folding by Levitt and Warshel in 1974 [12]. They used an incredibly crude –and hence unreliable- model for the interactions within a protein, but managed to obtain some kind of folding of the macromolecules. The method resembled an inaccurate type of dynamics; it was wrong and controversial but brave and stimulated many people at the time. In 1975 we held a CECAM Discussion Meeting to see if the two approaches: accurate simulations on small molecular systems, and crude simulations on biological macromolecules, could be brought together.

They could, and they were, in a huge two-month workshop on *Models for Protein Dynamics* with 22 participants. In practice the accurate simulators and the crude biophysicist formed two groups with highly deviating interests and preferences. But there was a lot of interaction and some could bridge the gap. Anees Rahman worked with Jan Hermans from Chapel Hill on the dynamics of water in a crystal of the protein BPTI (*basic pancreatic trypsin inhibitor*), treating water with the new method of constraint dynamics, and with Peter Rossky and Martin Karplus from Harvard on the complete dynamics of a dipeptide in ST2-water. The first activity in stochastic dynamics took place in that workshop by John Ermak, who already had developed the basic algorithms for solving the stochastic equations of motion. Also in this workshop the first protein simulation was carried out on BPTI in vacuum by Andy McCammon from Harvard, where the program had already been developed, based on potential functions for proteins worked out in Karplus’group. Van Gunsteren and I modified the protein simulation program to incorporate constraints.

This is not the place to enlarge on what happens later in this field; let it suffice to show the many CECAM activities in Table 2. The role of Anees Rahman in this development extended until 1976, after which he was active in many other fields of physics, and took part in many other CECAM activities not listed here. In my opinion his role in the development of dynamic simulations of complex (macro)molecular systems has been crucial, though indirect. He has taught and stimulated those who had the courage to attack the large molecules which he himself would not like to touch. He contributed a lot of common sense and good physics, and –best of all- a lot of deep friendship that remains.

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1)	Year	2)	Place	Subject	Organisers
*	1972	w	Orsay	MC and MD of water	Ber
*	1973	m	Warffum	Molecular Dynamics	Ber
*	1974	w	Orsay	Ionic Liquids	Singer
*	1974	w	Orsay	Methods in MD (Long time-scale events)	Ber
	1975	m	Bilthoven	Proteins	Ber
*	1976	w	Orsay	Models for proteins dynamics	Ber
	1977	m	Brussels	Stochastic dynamics	Bellemans
	1977	m	Bilthoven	Enzymatic reactions	Ber
	1978	w	Orsay	Stochastic dynamics and polymer dynamics	Bellemans, Ciccotti, Ber
	1978	m	Leiden	Quantum mechanics of enzyme reactions	Mulder
	1978	m	Nancy	Prediction of protein structure	Maigret
	1979	w	Orsay	Enzyme reactions	V. Duijnen, Hol
	1979	w	Orsay	Prediction of protein structure	Maigret
	1979	m	Bilthoven	Hydrodynamic interactions in stochastic dynamics	Ber
	1980	m	Amersfoort	Multidimensional stochastic dynamics	Ber
	1981	m	C��rissy-la-Salle	Protein Dynamics, experiment and theory	Karplus
	1981	m	Bilthoven	Simulation of small molecules binding to proteins	Ber
	1982	w	Orsay	Phosphate binding proteins	Hol
	1982	m	Ommen	Multi-timescale dynamics	Ber
	1982	m	Velthoven	DNA	Buck
	1983	w	Orsay	Dynamics of DNA	Olsson, Ber
	1984	w	Orsay	Non-equilibrium molecular dynamics	Bellemans, Frenkel
	1984	m	Amersfoort	Vaccine and drug design	Hol
	1985	m	Orsay	Electronic problems	Andersen

Table 2: CECAM activities in (Macro-)Molecular Dynamics

1) * Presence of Anees Rahman

2) w=Workshop, m=preparatory meeting

3.

Diffusion in Non-Ionic and in Ionic Liquids

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In this article an attempt is made to high-light some of Rahman's major contributions to the understanding of self-diffusion in different types of liquid. Reference will be made to the following papers:

Paper 1

- A. Rahman, *Correlations in the motion of atoms in liquid argon* Phys. Rev. **136 A**, 405 (1964)

Paper 2

- A. Rahman, *Liquid structure and self-diffusion*, J. Chem. Phys. **45**, 2585 (1966)

Paper 3

- A. Rahman and F.H. Stillinger, *Molecular dynamics Study of liquid water*, J. Chem. Phys. **55**, 3336 (1971)

Paper 4

- C.E.C.A.M. Report on the Molecular Dynamics Workshop on Electrolytes and Molten Salts, ed. K-Singer, p. 263 (1974)

Paper 5

- G. Jacucci, I.R. McDonald and A. Rahman, *Effects of polarization on the structure and dynamics of molten salts*, Phy. Rev. **A13**, 1581 (1976)

Paper 6

- A. Rahamn, R.H. Fowler and A.H. Narten, *Structure and motion in liquid BeF₂ LiBeF₃*, J. Chem. Phys. **57**, 3010 (1972).

Paper 1 is the first molecular dynamics (MD) study on a realistic pair potential; the computed diffusion constant is in fair agreement with experiment. The velocity autocorrelation function (VAF) does not conform to the Langevin equation which proves that Brownian motion is not a valid model for self-diffusion. It is also shown that the spread of the van Hove $G_5(r_1 t)$ is not Gaussian. *Paper 2* contains a brilliant analysis of the mechanism of diffusion in a simple liquid (argon at the triple point, simulated by a exp-6 potential). In the first part the liquid structure is analysed on terms of Voronoi polyhedral (VP) generated by the bisection by normal planes of the vectors linking a particle to its neighbours. The structure is characterised by the statistics of the VP, i.e. the number of faces, vertices, etc. The 1st, 2nd, ..., VP, P_1, P_2, \dots , can be regarded as defining the 1st, 2nd, ..., coordination shells.

Rahman then turns to the fluctuations of the centroid of the 1st polyhedron, P_1 . If the z -axis is parallel, and the x - and y - axes at right angles to the displacements of the centroid, the mean displacement along z increases with t up to 0.8σ (at about 0.5 ps) and slowly decreases; the mean x - and y -displacements remain small ($<0.1\sigma$) "and fluctuate about zero.

The displacement of particles (rather than centroids) is described in terms of a direction-dependent radial distribution function. The direction of the displacement in $t_1=0.5$ ps (corresponding to the time of the mean maximum displacement of the centroid) is again singled out. With respect to this direction there is in the first coordination shell an excess of near neighbours at repelling distance ($r < \sigma$) "behind", and an excess of near neighbours at attracting distances ($r > 1.1\sigma$) "in front" of a particle. The particles are therefore – on average- accelerated in the direction of the position which they will reach after 0.5 ps. Of crucial importance is the fact that for this time interval the directions of displacement of the centroid of P_1 and of the particle (roughly) coincide.

Finally, Rahman resolves the velocities at $t=0$ into Cartesian components, with the z -axis in the direction of the displacement after 0.5 ps. The normalised VAF of this component is found to be very different from those along the other two axes. The former decays slowly after passing through a shallow minimum, and is termed $S(t)$ (indicative of a "slipping motion"); the x and y components on the other hand decay twice as fast after passing through a deep minimum and are termed $R(t)$ (a "rattling" kind of motion). If $S(t)$ is further resolved into $S^+(t)$ and $S^-(t)$ according to the sign of the z -component at $t=0$, $S^-(t)$ turns out to be similar

to $R(t)$, so that the contrast between $S^+(t)$ on the one hand and, and $R(t) + S^-(t)$ on the other, is even stronger. The difference is well illustrated by the Fourier transforms which consist of quite distinct humps with maxima at 3 and $7 TH_z$.

Self-diffusion is therefore described as a “slipping motion” in the direction favoured by the elongation of the enclosing cage, and a “rattling motion” which contributes little, at right angles to this direction. The correlation between the anisotropic density fluctuation and the direction of the displacement is the essential result.

One must beware of misinterpreting this picture through oversimplification (which is not justified by the text). Diffusion should not be thought of as unhindered slipping of particles (though 0.8σ) into spaces (holes) created by the elongation of the enclosing cage. The histogram of free flights in the dense hard sphere fluid shows that the largest intervals between collisions is small compared with the particle spacing (and hence with 0.8σ) [1]. Inspection of the trajectories in the LJ liquid shows that they are quite contorted on the scale of σ ; more importantly: the histogram of distances traversed before the sign of the velocity along the initial direction changes, shows that values of the order of 0.8σ are improbable [2]. Rahman only proved that the directions of the displacement of the centroid and of the particle (in 0.5 ps) coincide. The magnitude of the former appears to be larger than that of the latter.

In the famous *Paper 3* it is shown that while the VAF of liquid argon decays after passing through one minimum, the VAF of ST2-water passes through two maxima and three minima before decaying. The oscillatory behaviour is ascribed to the structural rigidity produced by hydrogen bonding: “the hydrogen bonds between neighbouring molecules are continually subject to varying degrees of strain. Accordingly each molecule is tugged around in a random fashion by its imperfectly aligned neighbours... The amplitude of these highly anharmonic motions is sufficiently high at the ambient temperature that the settling down into a relatively unstrained arrangement is overwhelmingly unlikely”. The MD data shows that the absence of jumps into well-defined crystalline sites also applies to the rotational motion – although the opposite had been suggested by some experiments.

In *Paper 4* Rahman examines whether an ion pair in ST2 water will separate through solvation on a time scale which is accessible by a modest computing budget. Confronted with seemingly very complicated problem, he tackles it with characteristic ingenuity and directness. By reversing the sign of two of the four fractional charges in the ST2 model he obtains a quasi-ion pair of $q = \pm 0.94e$ and thereby also models the ion-water potential. The ST2 code can be used with minimal changes. The ions begin to separate after about 0.5 ps and reach in separate runs distance plateaus of 1.3, 1.9 and 2.5σ after about 2-3 ps.

The coordination number of water around each ion is then six. During the separation the mean potential of around each ion is then six. During the separation the mean potential of both ions decreases. After equilibration fluctuations of the water-ion potential completely eclipses the ion-ion potential of mean force. The fractional charges rather than the dipoles determine the orientation of the neighbouring water towards the ion. At the plateau distances of 1.9 and 1.3σ the solvating water molecules are arranged roughly in two octahedra which share a vertex or a face (Fig. 1). It is unfortunate that this stimulating work has not led to a publication.

Although completed later, *Paper 5* also originated in the 1974 workshop on ionic systems. It is the first MD implementation of the shell model originally devised to model polarizability in lattice dynamical calculations. The model consists of a mass-less shell carrying an appropriate fractional charge which is linked to the ion core by spring force. The MD simulation presents considerable problems. Although these were not entirely solved, definite results were obtained for the comparison between the rigid ion and the shell model. In solid NaCl the agreement with the experimental I.O frequently is improved as expected; in liquid KI the diffusion constant if both ions, but particularly of K^+ , increases, the viscosity is reduced but the electrical conductivity is unchanged.

Paper 6 is the first of several simulations of molten salts. The high viscosity of BeF_2 melts is shown to be caused by a network of BeF_4^- tetrahedral with shared F^- vertices. For the same reason the mobility of Be- and F-ions is also small in $LiBeF_3$, while that of Li^+ is much larger. In liquid LiF both ions have normal (high) mobility.

This paper is one of the first proving that a tetrahedral coordination need not be associated with covalency but can arise in a purely ionic model with a correctly chosen radius ratio.

Rahman's interest in ionic systems continued until the end of his life and included such topics as: free energy of molten salt mixtures, complexing in melts of polyvalent ions, pair potentials of polyvalent ions in water, solvation of an electron in water and in liquid KCl. These papers mostly appeared in *J. Chem. Phys.* and are outside the scope of this article.

Aneesur Rahaman's work revealed a wealth of possibilities and insights for which scientist have reason to be deeply grateful. Those who have known him feel privileged to have experienced the impact of this intellectually and morally inspiring –and lovable–man.

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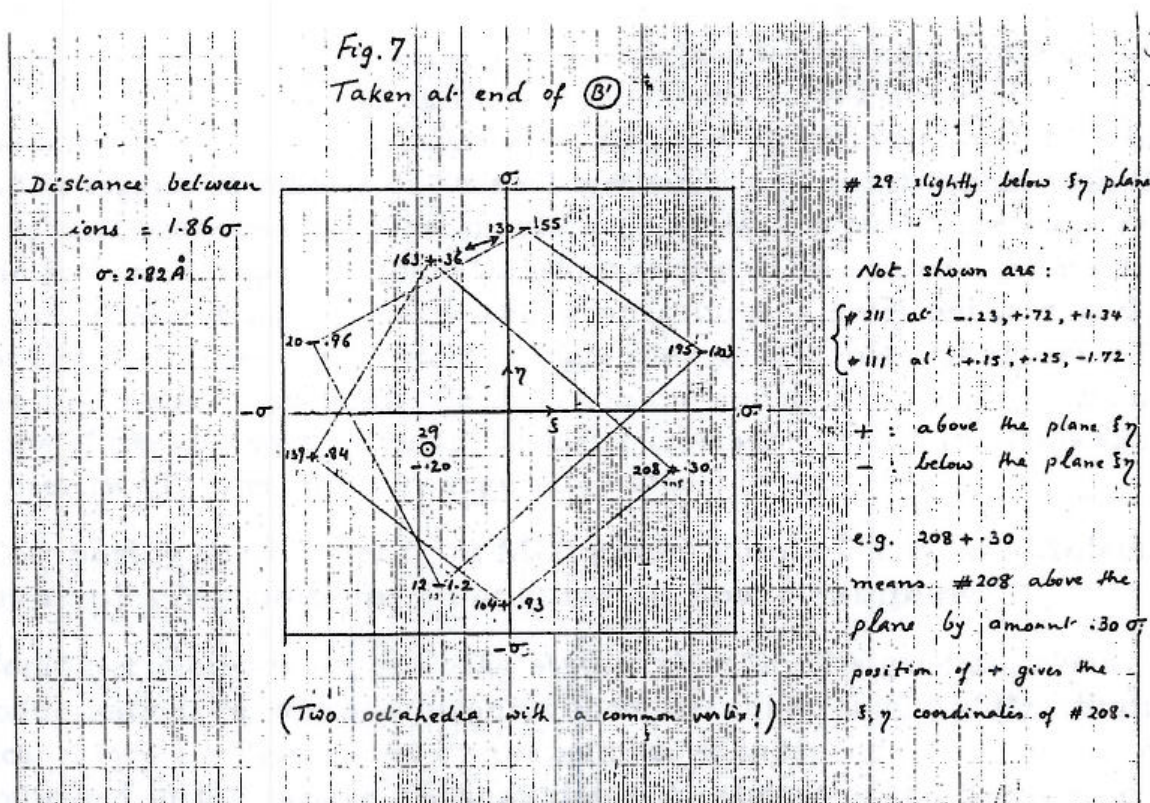
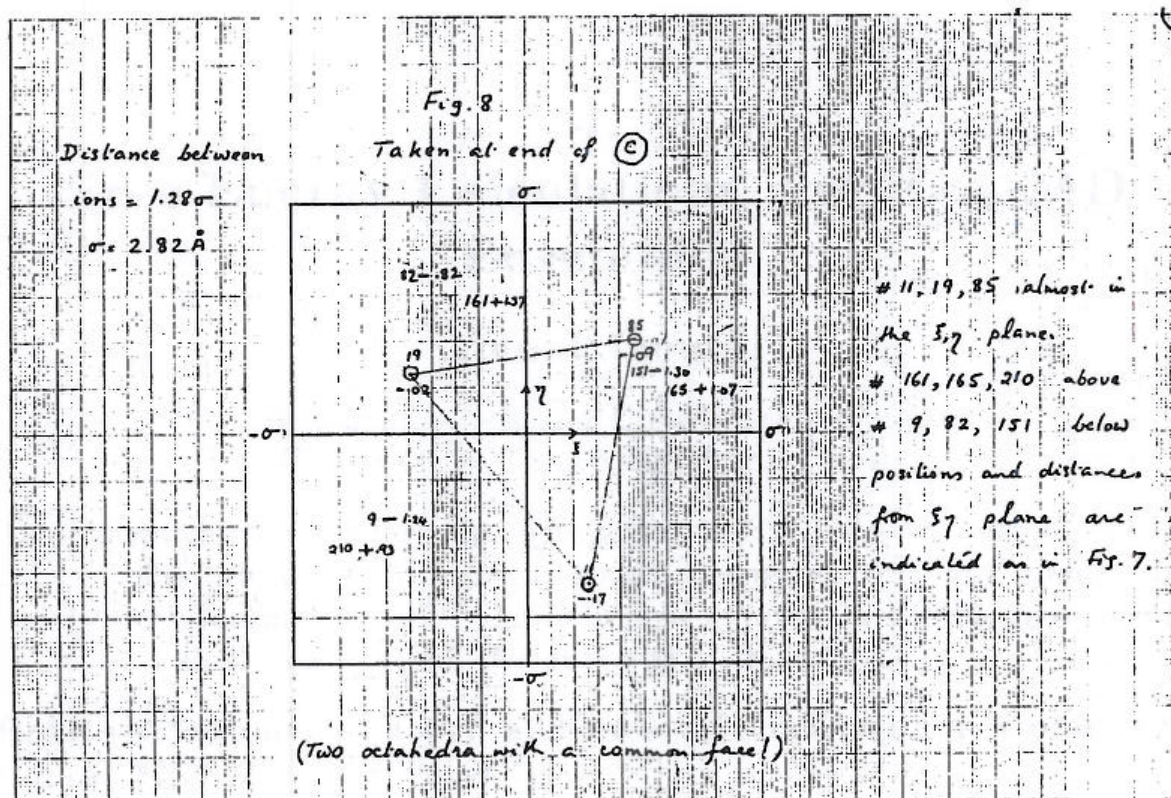


Figure 1: Two of Rahman's original drawings of typical metastable configurations of water molecules around an ion pair. The plane of drawing is perpendicular to the vector connecting the two ions and midway between them; water positions are projections onto that plane.

4.

Free Energy Calculations and New MD Ensembles

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Aside from shorter interactions arising during CECAM workshops, my scientific collaboration with Aneesur Rahman has regarded two areas: free energy calculations, and the simulation of superionic conductors. In the following I shall briefly recall the outcome of this work.

Relative Stability of f.c.c and b.c.c Structures for Model system at High Temperatures [1]

Free energy, entropy, and volume differences between face-centered and body-centered cubic structures have been evaluated for model rare gas and alkali metal crystals by using the method of overlapping distributions. Stable phases are predicted in agreement with the behavior of real materials in the regions of validity of classical mechanics and in agreement with the results of previous dynamical simulation studies of crystal nucleation from the melt and the polymorphic transformations. The existence of a stable B.C.C phase at high pressure and temperature f.c.c. phase is expected for model Rb and Cs systems. We also show the possibility of making calculations of free-energy barriers to displacive crystalline transformations along a prescribed trajectory in configuration space.

Comparing the efficiency of Metropolis Monte Carlo and Molecular- Dynamics Methods for Configuration Space Sampling [2]

Computer methods for sampling statistical ensembles generate chains of configurations in which subsequent members differ only slightly. Statistical errors are determined by the number of independent configurations contained in the sample. A quantitative treatment of the persistence of correlation shows how the first two moments of the autocorrelation function of a variable f along the chain are connected with the expected variance of its mean. The variance of the potential energy in the canonical ensemble is shown to be larger than that in the microcanonical one by a factor which is the ratio of the system heat capacity to that of an ideal gas. A comparison has been made of the efficiency of Metropolis Monte Carlo (MC) and modification of molecular dynamics for canonical ensemble sampling (MDC). The analysis is focused on three aspects: the mean square displacement of a representative point in configuration space, the persistence of correlation in the potential energy \mathcal{V} , and also in a function of interest in free-energy-difference calculations. In MDM simulations of crystalline solids, it was found that \mathcal{V} behaves as an "oscillatory" variable and that the variance of its mean is reduced by antithetic variations of its value.

Diffusion of F^- ions in CaF_2 [3]

It is shown in a model of the dynamics of CaF_2 that the decay with time of the Fourier transform, $\langle \exp [i\mathbf{k} \cdot \mathbf{u}(t)] \rangle$, of $\mathbf{u}(t)$, F^- displacement, for various wave vectors \mathbf{k} can only arise from diffusive motion occurring between the simple cubic anion sites of the fluorite structure. Most of the jumps (80%) occur between near neighbour sites (i.e. they are in the 100 direction).

The motion of F^- ions can be understood in the terms of a spontaneous creation of anti-Frenkel pairs which diffuse and eventually get annihilated. At the temperature of this calculation (1590 K) the average number of such pairs at any instant is found to be 7.9 in an assembly of 216 anions. A detailed breakdown of the nature of various types of atomic jumps arising out of the dynamics of these pairs is also presented.

Ionic Motion and Neutron Inelastic Scattering in α -AgI [4]

Contrary to the current interpretation of inelastic neutron-scattering data on α -AgI, molecular dynamics calculations show that inelastic neutron scattering arises from Ag^+ ions that diffuse by jumps between tetrahedral sites, the consequences being in complete accord with the Chudley-Elliott model only if the full geometrical complexity of these sites is included. Phonon modes due to the I- motions are predicted for certain wave vectors (with Guido L. Chiarotti).

Further work

Free energy-difference calculations have recently been extended to quantum mechanics [5, 6].

A new high-frequency short-wavelength collective mode specific to binary liquid mixtures with large mass difference, called fast sound, has been recently observed in a computer simulation of Li_4Pb [7], entailing motion of the lighter atoms only, and discussed with the framework of the MoriZwanzig formalism. The existence of a higher frequency sound in a system characterized by two species having a large mass difference, namely water, had been previously observed by Rahman and Stillinger [8] and is still waiting for a proper explanation. It may be closely connected with fast sound in binary mixtures.

The use of artificial intelligence, logic programming, and computeraided symbolic manipulation in computational physics, has been explored in studies [9, 10] included in a recent issue of J. Phys. Chem. Dedicated to Anees Rahman.

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5. The Simulation of Water and Aqueous Solutions by Aneesur Rahman

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The pioneering simulation of liquid Argon by Aneesur Rahman in 1964 had created a strong interest in this new method amongst condensed matter physicist. The amazing spread and general acceptance of the molecular Dynamics technique in chemistry and biology started however, when the paper of Anees Rahman and Frank Stillinger, titled *Molecular Dynamics study of Liquid Water*, was published in 1971 [1].

The abundance of this substance, its ubiquity in biological, chemical, geological and technical processes, its anomalous behaviour as pure liquid and its unique properties as a solvent had lead to an immense literature and jungle of observations and speculations. The various models of the microscopic structure of water, which could be grouped roughly into categories like “continuum models”, “mixture models”, “interstitial models”, etc., were tailored to explain particular properties in a more or less qualitative way and were mostly incompatible with each other.

In contrast to that, the MD simulation was able to reproduce quantitatively a wide spectrum of properties of liquid water, ranging from structure and thermodynamics to microdynamics. An achievement which could not have been expected in foreseeable future from any analytic theory for this rather complicated liquid. The structural details, which were extracted from the simulation run, clearly confirmed the continuum model picture. Accordingly, water can be described as a quasi-infinite network of continuously varying hydrogen bonds, which is subject to a constant and fast restructuring.

The success and the conceptual simplicity of the simulation, immediately suggested an extension to other aqueous systems. For this purpose, in the following years several workshops were organized at CECAM in Orsay, which largely profited from the presence of Anees Rahman. Many of the ideas that were discussed and treated during these meetings for the first time, influenced the further development of the ME method for the first time, influenced the further development of the MD method to a great extent.

The appending list of those of Anees Rahmans publications, which are devoted to aqueous systems (not including the CECAM reports), show that most of this part of his work emerged from the intense collaboration with Frank Stillinger. From this list, one can extract three major lines of interest: the development of new interaction potentials, the investigation of various properties of pure water and the study of water as a solvent in aqueous solutions.

For the majority of these investigations, the rigid effective pair potential ST2 [5], with its tetrahedral arrangement of interaction centres, was used. Later, it was shown that also flexible three-centre potentials were able to reproduce the properties of water [9, 10, 15]. The quality of the ST2 potential was tested by studying temperature and pressure dependences and it was possible to reproduce for example the characteristic density maximum of water [5,8]. A major role in the explanation of the unusual properties of this liquid plays the structure of its hydrogen-bond network. Therefore, not only pair distributions, but also higher order arrangements were studies.

The distributions of hydrogen-bond polygons suggest that water can not be considered just as a disrupted version of an ice or hydrate crystal structure; the location of a bond percolation threshold indicates the existence of a globally connected, space-filling network [4, 12].

One of Anees Rahmans motivations to study “real” liquids by MD simulations was the prospect to overcome the difficulties encountered, when evaluating and interpreting neutron scattering data. So in one of his papers with F.H. Stillinger [6] it is shown that the spectrum of the proton velocity autocorrelation is a good replica of neutron inelastic scattering at not too low – experimentally attainable- scattering vectors. Also, other details of usual data analysis procedures, as well as the problem of comparison with classical simulations, are discussed critically.

When analysing the density fluctuations in water, evidence for a previously unsuspected property was presented: the presence of high frequency sound waves with a velocity almost twice that of ordinary sound [7]. Only very recently, inelastic neutron scattering data, which support this finding, have been published. As it had been emphasized by A. Rahman and F.H. Stillinger, it is this ability to predict unexpected properties (starting from an accurate representation of known experimental facts), which demonstrates the power of the MD simulation technique. Other examples of this predictive power can be found in the literature, for example an unexpected shape of the filed gradient time correlation function, which determinates the nuclear magnetic relaxation of ionic nuclei. This will force a reinterpretation of many experimental data.

The MD simulation of aqueous solutions started with the treatment of an ion pair in ST2 water at the CECAM workshop on Ionic Liquids of 1974. Later, a pair of uncharged Lennard-Jones solutes was used to study the hydrophobic hydration and hydrophobic interaction effect [11]. As in the case of pure water, experimental observations could be reproduced and several model ideas could be confirmed, whereas others had to be rejected, like the literal application of the so-called “iceberg” picture. The simulation of an aqueous solution of a dipeptide in water [13] was the starting point for a fascinating development, which is continuing to more and more complicated biomolecular systems.

One more milestone in the development of the simulation technique and an opening of a new filed of applications was the simulation of the hydrate electron via the Feynman path method [16]. According to this study, the hydration shell structure of the electron is far less pronounced than expected from quantum mechanical calculations. This method opens the possibility to study electron transfer reactions in aqueous solutions; one of the model processes being the electron exchange between ferrous and ferric ions. In the last paper of A. Rahman that appeared in the filed under consideration [17], the hydration of just these ions is treated, possibly planned as a preparatory work for the study of the electron transfer. One of the results of this paper was the demonstration of the importance of manybody forces, which have to be explicitly added to the *ab initio* ion-water pair potentials, but which can also be taken into account, when using carefully constructed effective pair potentials.

The work of Anees Rahman has clarified and widened our knowledge about the most important liquid on our planet to a degree that could not have been expected before. Even more important, he has given us a powerful tool to continue his work. The impetus that has emerged from his first simulation of water has already caused an ever-increasing number of activities. For the future, besides the further study of basic phenomena of water structure and dynamics, the improvement of experimental data evaluation will be an important filed. Most fascinating will be the study of chemical reactions of of bio-molecular action in aqueous environments.

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plus: CECAM reports

6. The MD Simulation of Superionic Conductors

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Rahman's beautiful paper on "Particle motions in superionic conductors" [1] opened a new area in the theory of solids. It showed for the first time what is really happening in these fascinating and important materials, and led to a whole series of simulation studies both by Rahman himself and by other people. In this short review I am going to talk mainly about what Rahman did, though I shall add some comments about other work.

First, I must recall what superionic conductors are. It is a familiar fact that all ionic crystals have a small electrical conductivity due to the diffusion of the ions. This diffusion is caused by motion of thermally-generated point defects. E conductivity is often proportional to $\exp(-\Delta E/k_B T)$, where ΔE is related to the formation energy of the defects (it also contains a contribution from their migration energy). Normally, $\Delta E/k_B$ is much greater than the melting temperature, so that the concentration of defects is very small. Because of this, there is usually a very large increase of conductivity when the material melts. But there are some ionic materials, which attain a liquid-like conductivity before they melt. These are called superionic conductors. Two famous examples are CaF_2 (and many other materials having the fluorite structure) and AgI . In superionic conductors, the ions of one species have a liquid-like mobility in the solid state. In CaF_2 the anions (F^-) are mobile ions, while in AgI it is the cations (Ag^+).

The paper of Rahman I mentioned described a molecular dynamics simulation of CaF_2 . The calculations were straightforward, but extremely illuminating. The interactions were described by the traditional ionic model, the short-range contributions being taken from calculations by Kim and Gordon [2]. The simulation started from the perfect-crystal configuration, and the ionic trajectories were generated in the usual way. Rahman's results for the time-dependent mean square displacements (m.s.d.) of the cations and anions are shown in Figure 1. These results show that the cations are confined to their lattice sites, but that the anions are diffusing through the lattice. The slope of the m.s.d gives the anion diffusion coefficient, whose value $2.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (comparable to that of liquid argon) is in reasonable agreement with experiment.

The success of this simulation meant that it was possible to find out about the details of the diffusion mechanism. This was already discussed in Rahman's original paper, but was studied in more detail by Jacucci and Rahman [3]. The characteristics of the single-particle motion can most usefully be described by the "self" intermediate scattering function $F_\alpha^a(q, t)$ defined by:

$$F_\alpha^a(q, t) = \frac{1}{N_\alpha} \langle \sum_{j=1}^{N_\alpha} \exp[iq \cdot (r_{aj}(t) - r_{aj}(0))] \rangle \quad (1)$$

where the sum goes over N_α ions of species α , with q the wave vector and $r_{aj}(t)$ the position of the j th ion of species α at time t . In a liquid, this function would depend only on the *magnitude* of q , but in crystal it will depend also on the direction. Jacucci and Rahman showed that diffusion of the F^- ions occurs by discrete jumps between lattice sites, and by analysing $F_\alpha^a(q, t)$ they were able to determine the jump lengths and directions. It turned out that most of the jumps (79%) were between nearest-neighbour regular-lattice sites in the $\langle 100 \rangle$ directions, the remainder being almost

entirely between second-neighbour sites in the $\langle 110 \rangle$ directions. Further simulation work has shown that this mechanism is general characteristic of diffusion in superionic fluorites. Several years after Jacucci and Rahman's work, their results were experimentally confirmed by incoherent quasielastic neutron scattering [4] on $SrCl_2$, which yielded almost exactly their values for the fractions of jumps in the two directions. In the same paper, Jacucci and Rahman showed that the single-particle diffusion could be analysed in terms vacancy and interstitial defects, a conclusion that was arrived at independently at about the same time as Dixon and Gillan [5]. This defect analysis has turned out to be crucial for the understanding of collective motion in superionic fluorites, a topic that I shall return to a little later.

The success of Rahman's simulation on CaF_2 was impressive, but (with hindsight) perhaps not too surprising. After all, CaF_2 is a fully ionic material whose ionic interactions are fairly well understood. His subsequent work on superionic AgI is in this sense even more interesting. By the usual criteria, the bonding in AgI is on the borderline between ionic and covalent. The interactions here are certainly not well understood, and it was far from clear before the work of Rahman and his co-workers that any simple model would satisfactorily describe the superionic conduction. It must be recalled also that AgI has a rather complicated phase diagram. Below 420 K at normal pressure it has mixed wurzite/zincblende structure (the β -phase), which is not superionic. Above this temperature it goes to a b.c.c. structure (the α -phase), which is fully superionic. The melting point is at 830 K. Under pressure, (≥ 0.5 GPa), the stable structure is f.c.c., and recent experiments have shown that this surprising if a simple interaction model could reproduce all this complex behaviour. Nevertheless, this is what happens. The interaction potentials developed by Rahman and Vashishta [6] have this form:

$$V_{ij}(r) = -i - \frac{j}{r} + \frac{A_{ij}(o_i + o_j)n}{r_n} - \frac{C_{ij}}{r^6} - \frac{1}{2}(\alpha_{i-}^{-1})/r^4 \quad (2)$$

where the first three terms represent the usual Coulomb, core-overlap and van der Waals contributions. The last term is an attempt to include the interaction between the ionic charges z_i and of the various other parameters were empirically fixed by what can only be called inspired handwaving. This simple model formed the basis for an outstanding successful series of simulations.

In the original work of Rahman and Vashishta, the material was put into the b.c.c structure and the time-dependent mean square displacements were calculated, just as for CaF_2 . The system spontaneously reproduced the observed superionic conductions, with a Ag^+ diffusion coefficient which for three different temperatures agreed with experiments to within about 20%. In addition, the probability distribution of the Ag^+ ions in the unit cell agreed very satisfactorily with diffraction measurements. Even more remarkably, a slight modification to the model turned out to give a good account of the phase transformation for the β to the α -phase. Here I have to disagree to mention the constant stress technique developed by Rahman and Parrinello [7]. Normal m.d. is performed with a periodically repeated cell having constant volume and shape. These constraints would prevent the occurrence of structural phase change even though these might result in a lowering of the free energy. Rahman and Parrinello, building on ideas of Andersen showed that it was possible to perform m.d. with the size shape of the repeating cell treated as dynamical variables. Their work [8] on AgI provided a very striking demonstration of the power of this method. They found that if their simulated material was started at low temperature in β -phase, then when the temperature was raised above about 480K the system spontaneously transformed to the α -phase. This they demonstrated by quenching the system suddenly to a low temperature and examining the coordination numbers of the ions. The temperature of the transition turned out to be in quite close agreement (within about 60K) with the experimental value.

It has been shown very recently that this particular story can be developed much further. Tallon [9] has used the same interionic potentials with the constant-stress technique to map out the

full phase diagram as a function of temperature and pressure. Not only is the high-pressure rock-salt phase correctly reproduced, but even the experimentally observed superionic conduction in this phase at high temperature occurs spontaneously. There is also evidence of some kind of weak transition within the α -phase, which has been hinted at experimentally. All this shows that the empirical ionic potentials of Rahman and his co-workers have an amazing wide range of validity.

I want to conclude by returning to the fluorite story. There has been considerable interest recently in coherent inelastic neutron scattering on superionic fluorites [10]. The experiments measure essentially the dynamical structure factors $S_{\alpha\beta}(qw)$, which represent the spectra of collective density fluctuations. It should be recalled that in normal solids the $S_{\alpha\beta}(qw)$ consist mainly of phonon peaks, the frequencies of these peaks being the phonon frequencies at each wave vector q . In superionic state, the fluorites (and other superionic conductors) show a new feature: an intense “quasielastic” peak, centred at zero frequency. The origin of this peak has been controversial for several years. Molecular dynamics, since it provides complete information about the dynamics of ions, allows one to give an unambiguous interpretation of this effect. An extensive series of simulations of superionic CaF_2 has recently been performed with the aim of doing this [11]. The $S_{\alpha\beta}(q, w)$ of the simulated system exhibits the experimentally observed quasielastic peak, whose intensity and frequency width as a function of wavevector and temperature are in quite close accord with experiment. The key to the interpretation of this peak is defect analysis of the kind developed by Jacucci and Rahman. What has been demonstrated is that the density fluctuations responsible for the peak arise directly from the motion of vacancy and interstitial defects and their surrounding lattice distortion.

This recent work on collective motion in superionic conductors is only one example out of many that would have chosen to illustrate the consequences of Rahman’s original paper. His influence in this, as in so many other fields, will be an enduring one.

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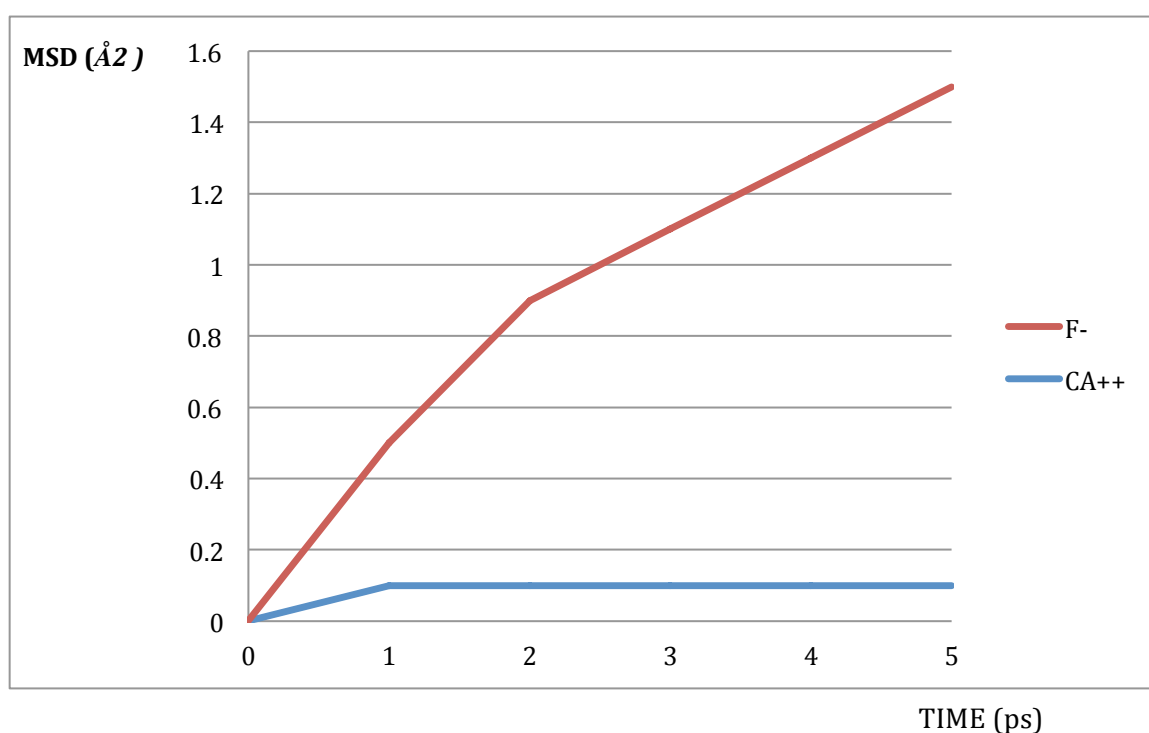


Figure 1: The mean square displacement of cations and anions (lower and upper curves) in Rahman's simulation of CaF_2 at 1590 K [1]

7.

On the contribution of Anees Rahman to the Studies in Nucleation and Glassy State Physics

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As a scientist involved mainly in liquid state studies, at least in the beginning, and particularly in the dynamics of simple liquids, Anees Rahman was naturally led to address the various problems posed by glassy (i.e. quenched from liquid) state matter. As is underlined by the list of publication, he did. To the best of my knowledge, the first aspect of this contribution to this field, was the pioneering development of new methods, or their renewal, which proved later to become important tools for the glassy state physicist. This is the case for the introduction of molecular dynamics simulations with the continuous L.J. potential (1964), the use of Voronoi polyhedral in structural characterization [1] or the “quench echoes” method applied to the dynamics of glasses [9]. The second aspect was the work he devoted to the solution of physical, and in a proportion increasing with time also of material science, problems.

It is this second aspect on which I would like to lay the accent here, in developing a bit more his contribution in crystallization studies.

The liquid-solid transition being first order is prone to hysteretic phenomena linked to the metastable character of the undercooled liquid below, but not too far from, the equilibrium liquid-solid line. In this range of shallow quenches, the classical nucleation and growth model, as developed mainly by Turnbull in the solidification case, is known to work fairly well. But for deep quenches the picture is less clear, as for increasing undercooling, in a naïve picture, the size of the critical nucleus should decrease to such an extent that the liquid could become mechanically unstable with respect to the crystal, in a quasi-spinodal fashion. What is the really the mechanism of crystallization in deep-quenched liquids?

This was the subject of the work of Rahman performed, with M.J. Mandel and J.P. McTague, on a L.J. system. In the first step [4] they showed, for the first time the possibility to produce a L.J. glass by quenching (at 10^{13} K/sec) a well equilibrated liquid. At a reduced temperature of $T^* = 0.25$ they observed simultaneously a glasslike pair distribution function and a vanishing diffusion coefficient. However at lower quench rates (approx. $2 \cdot 10^{11}$ K/sec), the quenched liquid crystallized spontaneously around T or P , nor the structural one, $S(k_i)$, showed any marked time evolution, contrary to the second step where temperature rose and pressure dropped markedly.

These results were more systematically developed by them, and later by Rahman and Hsu [7,8] using also a rubidium-like potential

The overall results of these simulations can be summarized as follows:

- In all cases the crystallization proceeds by the formation, in the above sense, of a well defined nucleus, the size of which would be around 70 particles.
- The structure of the formed crystal can be either f.c.c. or b.c.c for a given potential (the stable phase of L.J. and Rb-like potentials are respectively compact and b.c.c.)

- Whichever the quench temperature, the studied systems crystallized for a high quench rate, but not systematically for a lower one.
- The results are not free from spurious effects due to the finite size of the calculation box, since the crystallization temperature for a given, slow, quench rate decreases with increasing box size.

The intriguing role of the quench rate be now confirmed by the work of Mountain and Basu, and also later of Nose and Yonesawa. The first authors studied systematically the role of the quench rate and the final temperature of the quench: they could show that a simple liquid, when too rapidly quenched, maintains during the cooling a high temperature structure, which is therefore out of equilibrium, and also displays a high mobility. Both characteristics allow for a very easy crystallization whichever the temperature (except zero): the system experiences simultaneously a large thermodynamic force, due to its strongly non-equilibrium structure, and a high mobility. On the contrary a low quench rate allows the development all along the cooling process of the equilibrium structure of the supercooled liquid, known to be icosahedral for a L.J. potential and probably also for most simple pair potentials with spherical symmetry. The liquid is therefore stabilized with respect to the crystal, both by a lower mobility and by a lower free enthalpy difference. The crystallization becomes now difficult both at high temperature, due to the large critical size in a shallow quench, and at a low one, since the mobility becomes small and simultaneously the critical size remains finite thanks to the structural relaxation.

The presence of both b.c.c. and f.c.c embryos, also confirmed by the same authors, is not surprising in the sense that if the free enthalpy of both phases is small for a given potential, the frequency of formation of both kinds of embryos can be of the same order of magnitude. Some criticism have been raised against these simulations by Andresen, mainly on the basis *i)* of the size effect underlined above, and *ii)* of the vanishingly small critical sizes calculated in the framework of the classical nucleation theory, if one uses macroscopic values of the thermodynamic parameters. Indeed, the critical sizes estimated by Rahman are probably not very safe since the “growth” step in his calculations is probably the most prone to finite size artifacts. But the key step, the formation of a nucleus, is certainly much less perturbed, and the qualitative aspect of the crystallization mechanism in deeply quenched liquids is most probably well pictured. The criticism *ii)*, based on the use of classical nucleation theory and of the macroscopic values for the parameters in it, does not take due account of the reorganization of the liquid during quench. Its validity is therefore undoubtedly questionable. Its validity is therefore undoubtedly questionable.

In this respect a good way to pursue Rahman’s work on nucleation and on the glassy state would be to grapple the various aspects of both the study of the statics and the dynamics of the competitive developments of crystalline and non-crystalline orders in supercooled liquids. This competition is probably the key to both the very existence of the glassy state and the relevance of the nucleation picture at large undercooling.

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8.

Path Integral Simulations of F-centres and Bipolarons in Molten Salts

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In this very short note, I will briefly review the contribution of Aneesur Rahman to the field of simulation of quantum systems and I will try to put his work into an historical perspective.

The interest of A. Rahman in the subject was first stimulated by discussions with experimentalists who introduced him to the complex and fascinating phenomenology of metal-molten salt solutions. Discussion with different theorists and especially with D. Chandler then focused his attention on the possibility that numerical path integral simulation might provide a suitable tool for this problem. Results were first communicated at various conferences and subsequently after about two years appeared in the literature. The main results of that research were to establish on a rigorous theoretical basis that in the limit of extreme dilution the extra electron released by the excess added metal is localised on a state that is the liquid state counterpart of the F-centre in solids. Namely the electron is self-trapped in a cavity which is mostly surrounded by positive ions replacing a Cl^- anion in the charge-ordered structure of the fluids. From a more technical point of view this paper demonstrates for the first time on a realistic case that systems where quantum degrees of freedom are important can be simulated using the path integral approach.

Several technical problems had to be solved for the first time. These included the determination of the appropriate form of the Ewald summation to be used within the isomorphism. An analysis of the estimators for the kinetic energy was also given. For this particular problem it turned out that the virial estimator was recast in a form in which corrections coming from the pressure term need not be taken into account. An estimator for the diamagnetic susceptibility was also provided. The study of the single solvated electron was then extended to the two electron case. Here the well known difficulties associated with the fermion many-body problem had to be faced. These were not solved, but rather circumvented by electron-spin consideration. In fact, the spin part of the wave function is antisymmetric in the singlet case and can be separated if one ignores the rather small spin orbit interaction. The spin contribution to the partition of a Bose-like partition function for the configurational part. Thus if one then confines oneself to consideration of the singlet case, one can carry out the calculation by a relatively simple extension of the single electron case. This was done and the calculation led to the discovery of a very interesting physical phenomenon, namely two electrons in a molten salt bind together in a liquid cavity and form a bipolaron state in which the inter-electronic repulsion is overcome by the electron-ion energy that is gained by the electron sitting in the same cavity. These findings were amply confirmed by experiment, in addition to computer simulations and theoretical work. I have added this last remark in order to demonstrate once more that although A. Rahman was able to discuss and interact with people from varied backgrounds. This is witnessed among other papers by an important contribution that he has made to the field of lattice gauge simulation, which I recall here since it is related to the field of the simulation of quantum systems. In this paper he demonstrated that a microcanonical sampling of the partition functions associated with lattice gauge theories can be extremely effective. This approach sometimes conveniently modified is currently adopted by practitioners in the field.

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9. Molecular Dynamics Studies of Strongly Coupled Plasmas

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Introductions

I haven't met A. Rahman during his life, but as many students beginning in Molecular Dynamics, I used to refer very often to his very famous paper Argon, writing in 1964 [1]. This paper had been for me a guide during the years. I think, I needed some years to understand in depth all implications of this historical work and to learn the background.

One of the salient features of MD simulations is that it's not necessary to be an expert before running an experiment. That is why I've been able to do such simulations very quickly. As a matter of fact, the method is very simple, the validity of the simulation is easy to check and we have to deal with a small number of particles. Bit after the run, what to do with a big set of particle coordinates? First of all, draw the trajectories of each particle. For me it's the easiest way to understand the microscopic behaviour and that is why I spent a lot of time drawing trajectories and watching them; fascinated. I think that trajectory plots is the first significant output of MD simulations, and most of the others diagnostics are only a transcription of a direct observation of microscopic behaviour.

I have found in the 1964-paper very intuitive and useful definitions of diagnostic such as self-diffusion, pair distribution function, Lindemann ratio, velocity autocorrelation function and so on. For each diagnostic I had to build a new program to check my knowledge on well defined situations. So, between my exercise books and my computer I've learned a large part of the things needed in statistical physics. I would say that, for me, this self-teaching aspect of Molecular Dynamics is a very important feature. And I think that it would be possible to adapt some MD simulation codes in order to use them with microcomputers in high school. In the next part I am going to show how it's possible to discover subtle mechanisms with snapshots and trajectories, and to build "a posteriori" the relevant diagnostics. After two examples I would comment briefly one of Rahman's last papers which is an illustration of this method, that could be called: *the molecular dynamics investigation method*.

Two Examples

1. The melting transition of the Two-Dimensional One-Component Plasma

It is well known that at low temperature the One-Component Plasma crystallizes as predicted by E.P. Wigner. In two dimensions the electrons arrange themselves in a triangular lattice, which is perfect at zero temperature. As we raise the temperature, the electrons oscillate more and more and at a certain temperature T_c , the crystal melts.

Just below the melting transition, with a very unphysical labelling experiment, we have displayed exchange mechanisms such as cyclic permutations of 6 or more particles, or gliding rows. These cooperative phenomena have been observed previously by Alder *et al.* [3] in hard disk systems; this suggests an effective core diameter description of the melting of the OCP. In

other words, the crystal melts when the particles have enough room to move between their neighbours. This steric description can be traced back to the strong correlation between electrons at melting.

2. The delocalisation transition of the Two-Dimensional Coulomb Gas

If instead of a uniform positive background, we consider positive point particles, we obtain the Two-Dimensional Coulomb Gas. Provided we add to the electron-ion potential a short range cut off or regularization, the system is stable at low temperature, and exhibits a dielectric-plasma transition. In our model [4], by fixing the ions on the sites of a triangular lattice, we have mapped this Kosterlitz-Thouless transition onto a classical delocalisation transition. This delocalization transition can be put into evidence by plotting the trajectories just at the delocalization threshold. In this situation the behaviour of the electrons differs strongly from the previous example. Most of the electrons are tightly bound, at each ionic site, but some electrons are seen jumping from site to site, independent of the vacancy of the ionic site (this behaviour is very reminiscent of jump diffusion in superionic conductors). A detailed investigation of the trajectories shows that sometimes an electron can come very close to an electron-ion pair. The computed electron-electron pair distribution function $g_{ee}(r)$ tends to a non-zero limit at vanishing distance, which is very unusual.

So, with the help of two snapshots (the labeling experiment and the trajectories at the delocalisation threshold), we are able to characterize two opposite behaviour, the melting transition and the delocalisation transition. In the molten OCP the electrons are still strongly correlated, which can be measured by the computation of the static structure factor, whereas in the delocalised Coulomb Gas the electrons are weakly coupled. In a certain sense the delocalised system is more disordered than the molten one.

One of A. Rahman's last Papers

Such MD experiments on Two-Dimensional systems may seem slightly academic, but we show that contact can be made with realistic situations.

In a recent paper [5] A. Rahman reported a MD simulation of the structure of the ions in a heavy-ion storage ring. Such devices are close to being realised in West Germany. The salient features of such beams are that the frame moving with the beam (at 10^{10} cm/s , the ions are very cold, about 1K, for a density range between 10^5 and 10^8 ions/cm. Since the ions are highly charged, the resulting plasma is strongly correlated. One of the assumptions made by A. Rahman consists in idealizing the restoring force by a parabolic potential in the $y - z$ plane perpendicular to beam axis x . Adding the particle-particle term, the total potential becomes:

$$V = \sum_i \sum_{j>i} 1/r_{ij} + \sum_i \frac{1}{2K} (y_i^2 + z_i^2) \quad (3)$$

which can be interpreted as the Three-Dimensional Coulomb interaction ($1/r_{ij}$) with a two-dimensional restoring force; the same one as in the Two-Dimensional One-Component Plasma.

Very unexpected results of the MD simulation are displayed by two snapshots. In the first one, we can observe a radial stratification perpendicular to the beam axis; on the second one, which is the distribution of the particles in the outer shells, we recognise the triangular pattern of the Two-Dimensional One-Component Plasma in the solid phase discussed earlier. The subsequent diagnostics are quantitative measurements of these direct observations through the computation of adapted pair distribution functions. In this case MD simulation is utilised to investigate a new model whose properties are not well known.

Conclusion

Why is molecular Dynamics a very popular method? For me, the main reasons are:

- The method is very simple and gives accurate results (but sometimes diagnostics can be very complex).
- Snapshots and trajectories are very exciting outputs, close to the microscopic reality.
- Very often, the good diagnostic are suggested by a snapshot.
- The method can be used to teach physics.

All of these reasons are laid down in the papers of A. Rahman.

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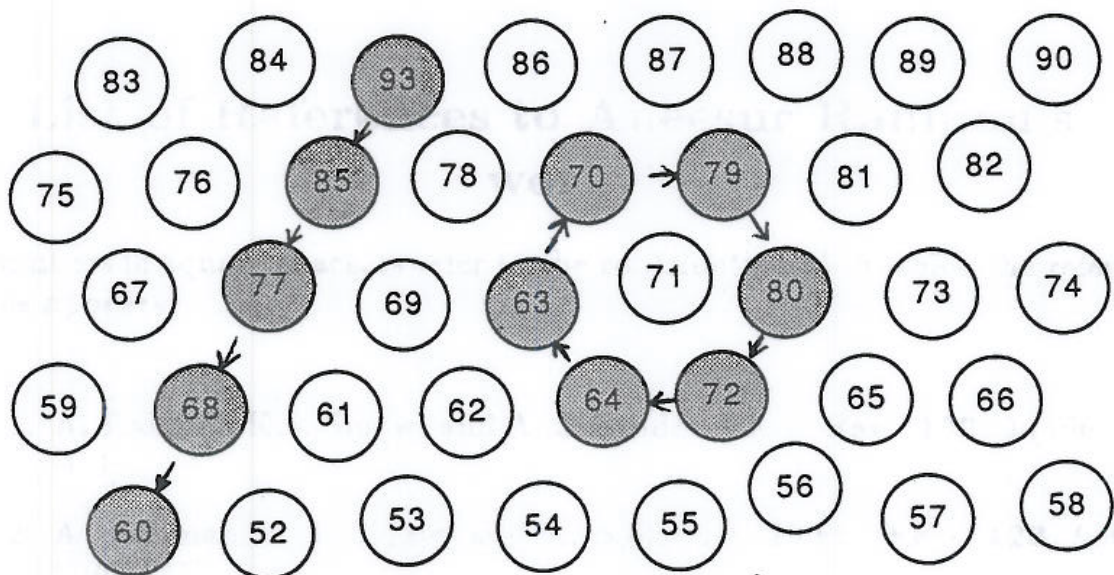


Figure 1: Cooperative phenomena below the melting point in the 2D one-Component Plasma

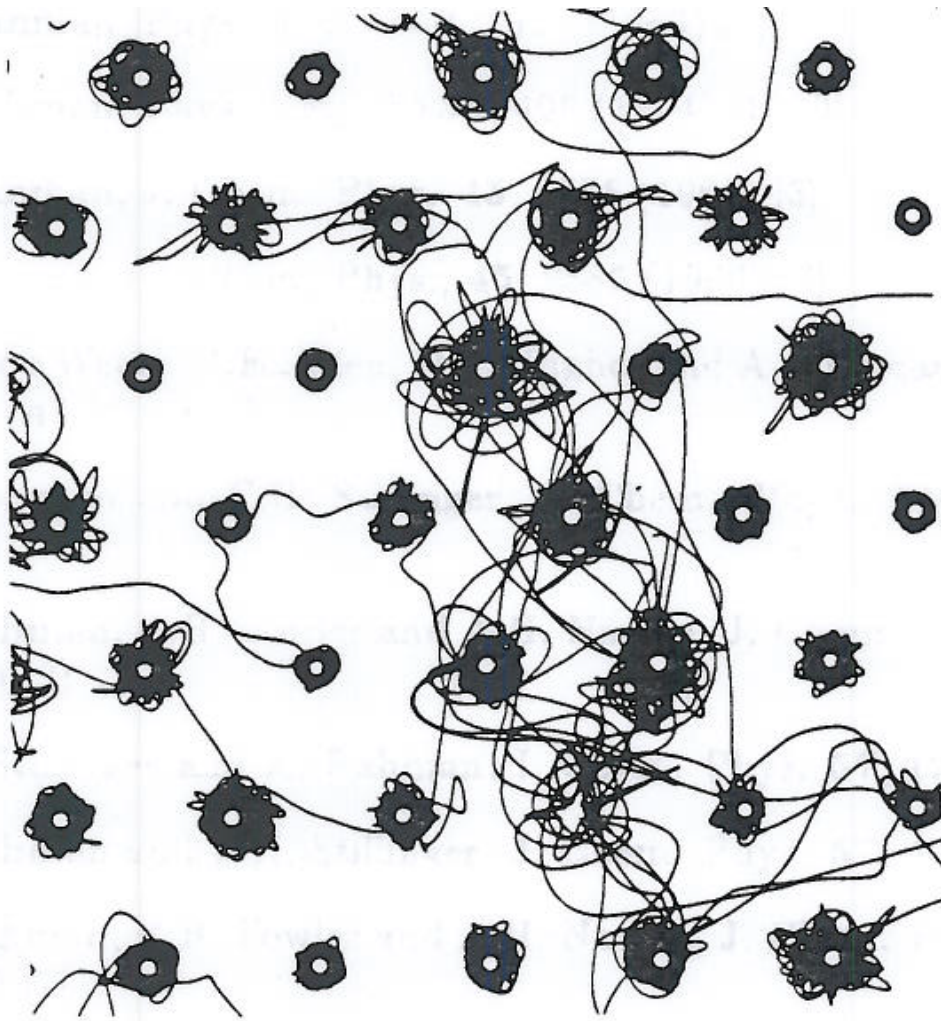


Figure 2: Trajectories of the electrons at the delocalization threshold in the 2D Coulomb Gas

10.

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Colophon

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