

3.3 Aneesur Rahman and Molecular Dynamics for Real Systems

With his 1964 paper, Aneesur Rahman laid a cornerstone in the history of computer simulation and became one of the founding fathers of molecular dynamics. Indeed, his paper was an inspiration to many, since, as Loup Verlet wrote, it «opened a new field of research, and originated a lineage of scientists to which we belong».¹¹ In short, this meant an unprecedented acceleration in the study of molecular dynamics. This new field concerned the computer simulation of real systems. The next generation of scientists would thus use computer simulations, not only for the dynamics of abstract hard spheres, but also for real systems of both atoms and molecules.

Aneesur Rahman (Anees to his friends), the new star of molecular dynamics, was born in 1927 in Hyderabad, a city in today's Federal State of Telangana, in the heart of India. He belonged to a cultured and influential Islamic family. His mother, Aisha, had quite powerful relations in the city. His father, Professor Habibur Rahman, was an outstanding figure in the Nawayath, a Muslim community typical of southern India. Professor Habibur was at the same time prominent and generous, and was considered as such in his environment, since he donated his own property for the establishment of the Urdu Arts College, as well as for the Urdu Hall, so as to encourage the cultural development of young people within his community.¹²

The influence and reputation of the Rahman family in Hyderabad were reinforced when, between 1965 and 1972, Anees' brother, Fazlur, became vice-Chancellor of Aligarh Muslim University, a public university which was defined as an institute of national importance.

In this environment and belonging to this family, Anees received a good education, which allowed him to obtain a diploma in mathematics at the high school in his home city in 1946. He then moved to England, where he took the "tripos" in mathematics and physics at the University of Cambridge in 1948 and 1949.

Once he had got his degree, he left the United Kingdom (he felt ill at ease in the old-fashioned imperialist atmosphere that still reigned there) and moved to continental Europe, to the University of Leuven in Belgium, where he worked with Charles Mannenback, a chemical physicist. In 1951, he met Yueh-Erh Li, a Chinese woman attending the medical school there, and fell in love with her. In 1953, Anees Rahman obtained a PhD in Physics at the age of 26. He went back to India to teach physics at Osmania University in Hyderabad, and continued his research at the Tata Insti-

¹¹L. Verlet, *The Origins of Molecular Dynamics*, in J.P. Hansen, G. Ciccotti, H.J.C. Berendsen (eds.), *In Memoriam. Aneesur Rahman. 1927–1987*, CECAM, Orsay 1987.

¹²K. Sen, S. Sastry, *Aneesur Rahman. A Pioneer in Computational Physics*, Resonance, August 2014, pp. 671–683.

tute for Fundamental Research (TIFR) in Bombay, a government research centre established in 1945, under the authority of the Department of Atomic Energy. During the following four years, Rahman published several papers on the structure of diatomic molecules. Meanwhile, in 1956, he obtained a three-year National Postdoctoral Fellowship, which allowed him to work as a full-time researcher at the Physics Department of Osmania University.

In this period, he developed an interest in the structure of a rather important and also chemically peculiar triatomic molecule: water. For his research, Anees only had access to a mechanical calculating machine, FACIT. Working conditions in India were very different from those of his colleagues in the US and Europe. Rahman realized this, and always stayed in touch with Charles Mannenback's laboratory, determined to pursue cutting-edge science.

On November 3, 1956, when he was almost 30 years of age, Anees went back briefly to Belgium to marry his Chinese fiancé, Yueh-Erh Li, who had in the meantime obtained her degree in medicine. He then immediately went back to India. Just one year later, on December 17, the young couple had a baby girl, Aneesa.

In 1958, Anees moved with his family to Bombay, to work at the Tata Institute for Fundamental Research. This institute was considered at the time to be the best in India. TIFR was involved in fundamental research: physics, chemistry, biology, mathematics, and computer science. Rahman stayed two years in Bombay. Then he went back to Belgium, since he had been hired by IBM, which had recently inaugurated its research centre in Brussels. By now, computers—the most advanced computers—had become the tools of his trade. Anees also taught at Digital Arts & Entertainment (DAE), a computer science school in Howest University College, in Western Flanders. Meanwhile his wife, Dr. Yueh-Erh Li, was able to work in Leuven, at the laboratory of Christian de Duve, a first-class researcher, who obtained the Nobel Prize for Medicine in 1974.

Once again, however, the Rahmans did not stay there long. Indeed, in the month of March 1960, Aneesur left Europe and moved to the United States, accepting an invitation from the Solid State Division of the Argonne National Laboratory. Rahman welcomed this new job, and his second change of continent, also because his wife Yueh-Erh Li obtained a position at the Biomedical Division of a large research centre, a branch of the Metallurgical Laboratory where Enrico Fermi had worked, established in Illinois, 40 kilometres from Chicago, in 1946.



Anees Rahman (1927–1987) in a picture taken in 1967
(Springer)

Rahman stayed at the Argonne National Laboratory for 25 years. At first, he was involved in spectroscopy, and tried to elaborate a new theory. Later on, he became a pioneer of computer simulations of physical systems, and one of the founding fathers of molecular dynamics.

We thus arrive in 1964, the year he published his paper in the *Physical Review*. This is how it starts: «A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4 K and a density of 1.374 g cm^{-3} ».

The Lennard-Jones potential is calculated empirically, and is largely used to describe molecular interactions. The fundamental idea is that, when two atoms (or two molecules) get very close to each other, the electronic clouds (strictly speaking, the electronic densities) surrounding the two nuclei superimpose, thus generating remarkable repulsive forces which have a very short range, but grow quickly as the two atoms get closer. To these, London's dispersive (attractive) forces are added: these

are instantaneous dipole–induced dipole interactions between non-polar molecules. They act at relatively short distances, distinctly longer, however, than the repulsive forces.

There is no theoretical equation describing the repulsive forces. That is why one must use empirical potentials. The potential derived by the English physicist John Lennard-Jones is the one most widely used.

This is the novelty: Anees Rahman did not simulate the molecular dynamics of an extreme model, such as the hard-sphere system, on a computer, but focused rather on a realistic model of a physical system, made up of real (argon) atoms. Thus the Indian scientist inaugurated a crucial new research field which opened up molecular dynamics and computer simulation to the study of molecular systems.

The difference with Alder and Wainwright’s model is clear. The only interaction between the hard spheres taken as a model by the two researchers at Livermore was the collision when they hit each other. On the other hand, Rahman’s real atoms “felt” each other, both through the repulsive forces generated by the superposition of their respective electronic densities and through London’s attractive forces.

Rahman solved the classical equations of motion of the argon atoms, confined in a given volume with a density and temperature typical of the liquid state, thus succeeding in calculating a series of structural and dynamical properties of the system, which he then compared with the values obtained experimentally, by observing a similar system of liquid argon. Simulation and experiment agreed.

The scientific community immediately acknowledged this result. In 1965, just one year after the publication of Rahman’s paper, Robert Zwanzig, a well-known expert in statistical mechanics, wrote: «Rahman’s calculations provide the most detailed “experimental” information currently available about dynamic processes in liquids».¹³

Zwanzig thereby affirmed that computer simulation provided “experimental” evidence, and as Kalidas Sen and Srikanth Sastry remarked, announced the twofold key role that computer simulations of molecular dynamics would play in the following decades, both in terms of almost experimental evidence, capable of providing detailed information about the behaviour of a system of atoms or molecules, and in terms of theoretical prediction. This was a genuine phase transition. Indeed, molecular dynamics is theory, but it is so powerful that it gets very near to experiment.

A peculiar route led Anees Rahman to study for the first time the molecular dynamics of a real system. Since he was in Argonne, in fact, Rahman had become interested in the theory of neutron scattering in condensed matter, in particular, matter in the liquid state. What Rahman wanted to discover was how neutrons were deflected when they hit liquid matter. His studies were very thorough. Very soon Rahman elaborated a theory of neutron scattering in liquids, thus placing himself at the cutting-edge in this field of study.

Up to this time, Rahman had not been particularly interested in statistical mechanics and knew very little about molecular dynamics. In his 1964 paper, he did not even

¹³Quoted in K. Sen, S. Sastry, *Aneesur Rahman. A Pioneer in Computational Physics*, Resonance, August 2014, pp. 671–683.

mention the papers by Alder and Wainwright. It seems likely that he had not even read them.

However, since he was not satisfied with his own theoretical approach to neutron scattering, he started searching for new models which would allow him to check its validity. This research steered him towards computer simulation of the dynamics of liquids, using procedures of numerical integration of the classical equations of motion of individual atoms. In other words, he independently reinvented molecular dynamics, applying it to a realistic model of a system of atoms. And he achieved that notwithstanding all the novelties involved.

Of course, he considered argon, among the least reactive of atoms, as similar as possible to hard spheres, whose interactions were well described, though nevertheless approximately, by the empirical Lennard-Jones potential. Unlike hard spheres, these are atoms endowed with electronic clouds which, as they get nearer, generate both repulsive and attractive forces, the ones that must be taken into account. And this is precisely what Rahman did.

His work was not only the first simulation of the molecular dynamics of a realistic model, no small matter in itself. It was also a study of the liquid state, a state which, at the beginning of the 60s, could still not be handled from a theoretical point of view, and had hardly been investigated from an experimental point of view. In sum, the physics of “condensed matter” was taking its first steps. The only exception at the time was harmonic crystals, for which a theory already existed.

Rahman’s work was no small contribution to that development. In short, his work provided a preliminary but clear demonstration of what computer simulation could do: it could realize “computer experiments” in which detailed information about the system under study could be calculated and compared both with experimental results and with the predictions of analytical theories, where applicable. Rahman calculated the theory with such precision that he allowed a direct and detailed comparison with experimental data.

This was a real success. However, seven years had elapsed between the first paper published by Alder and Wainwright about the molecular dynamics of hard spheres and Rahman’s paper on the molecular dynamics of real argon atoms. Why had it taken such a long time to go from the study of an ideal hard-sphere model to a system of real atoms? This is what Loup Verlet refers to as the «7-year gap»: the gap between two phases of a process which, a posteriori, seems almost to be taken for granted, natural, and immediate.

Science hardly ever follows linear or obvious paths. Its historical trajectories almost always have many causes. One explanation for the «7-year gap» was indicated by Alder and Wainwright in their 1957 paper: «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». Therefore, it was not only a question of computing power. There was a physical problem that had to be faced, namely, the repulsive forces due to the electrons, which change quickly, depending on the distance between atoms. There was a mental barrier here: the idea that “many-body” problems don’t have exact solutions.

Anees Rahman was the first scientist to face up to this physical problem and break through the mental barrier. Indeed his paper, published in 1964, was the starting point that «led to developments related to construction of potential models for other real systems and the use of molecular dynamics to explore more complicated systems, in particular molecular fluids».¹⁴

That computer simulation had become an invaluable tool for the physics of molecular clusters was shown in the paper *Structure of water. A Monte Carlo calculation* published by John A. Barker and Robert O. Watts, two Canadian researchers (who were actually born in Australia), working in the Department of Mathematics and Applied Physics at the University of Waterloo, Ontario (Canada). In this paper, they studied the best-known fluid and derived, using an adequate model of the potential, the energy, the specific heat, and the radial distribution function of water at a temperature of 25 °C. Their results agreed well with experimental data.¹⁵

This particular work used the Monte Carlo method rather than molecular dynamics. However, it was clear by then that computer simulation was raising more and more interest. The conditions were right for the informal establishment of a new scientific community, cutting across classical disciplines, since it involved both mathematicians and physicists, chemists, and biologists. Berni Alder gave this new community a further reference point by establishing a new scientific journal in 1966, the *Journal of Computational Physics*, which would cover all aspects of computation relating to physical problems, presenting all the most significant new techniques of numerical solution to problems in every area of physics. This journal was particularly attentive to methods crossing the borders between the various traditional fields of scientific knowledge, and was in itself interdisciplinary.

The *Journal of Computational Physics* complemented the book series *Methods of Computational Physics* which had been established four years earlier. Thus, by the mid-60s, a group of scientists started meeting at conferences and publishing papers in the same specialized journals and books in the same series. This was a clear sign that a new scientific community had been created, namely, the molecular simulation community.

3.4 Alder's Discovery and Rahman's Water

Meanwhile, there were more and more computer simulation studies of the molecular dynamics of fluids using the Lennard-Jones potential. Among the protagonists of this research was the Frenchman Loup Verlet, a disciple of Victor Weisskopf. In 1967, he published a paper with the title *Computer Experiments on Classical Fluids*, in which he introduced both the algorithm currently bearing his name, for the numerical

¹⁴R. Kapral, G. Ciccotti, *Molecular dynamics: an account of its evolution*, in C. Dykstra et al., *Theory and Applications of Computational Chemistry*, Elsevier, 2005, pp. 425–441.

¹⁵J.A. Barker, R.O. Watts, *Structure of water; A Monte Carlo calculation*, *Chemical Physics Letters* **3**, 144, 1969.