

Aneesur Rahman

A Pioneer in Computational Physics

Kalidas Sen and Srikanth Sastry

Aneesur Rahman made seminal contributions to computational physics, the forerunner of the widespread application today of computation in the study of physical, chemical and biological phenomena. This year marks the 50th anniversary of his paper in 1964, which heralded the use of the *molecular dynamics* method, an essential tool for research in materials and biological sciences today, which he is most known for. A biography of Rahman, along with a summary of his scientific contributions is described below.

1. Biography

Aneesur Rahman (Anees to friends) was born in Hyderabad, Deccan, India, on 24 August 1927. His father, Professor Habibur Rahman, a legendary citizen and prominent 'Nawayath'¹ of Hyderabad will always be remembered for generously donating his properties towards the creation of the Urdu Arts College and the Urdu Hall, Himayat Nagar, Hyderabad. Aisha, Anees's mother, was from a prominent family in Hyderabad. One of her brothers, M Fazlur Rahman, was the Pro-Vice Chancellor of Aligarh Muslim University during 1965–72. Aneesur Rahman had his early education in Hyderabad, where he obtained a BSc(Mathematics) degree in 1946. He received his Tripos in Mathematics (1948) and Physics (1949) at Cambridge University. Rahman participated in the symposium on Crystal Physics organised in Hyderabad by the Indian Academy of Sciences, Bangalore, on 30 December 1950. Participants at this symposium included C V Raman, G N Ramachandran, S Ramaseshan, V Chandrasekharan and



Kalidas Sen (PhD, IIT-Kanpur) joined the University of Hyderabad in 1977 where he continues to serve as Professor of chemistry. His research contributions in electronic structure theory include 9 monographs and 196 research papers.

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¹ A Muslim community in South India of Arab descent; web:<http://islamicvoice.com/July2005/ReadersRight/>.

Keywords

Aneesur Rahman, computer simulations, molecular dynamics.



² <http://www.ias.ac.in/php/acadsymp.php3?alpha=H>

³ Five in *Physica*: Vol.19, No.112, pp.145–165; pp.377–384, 1953; Vol.20, No.16, pp.497–500, 1954; Vol.23, No.15, pp.26–30, pp.31–36, 1957; and one in *Current Science*, Vol.24, pp.370–371, 1955.

Rahman was interested in exploring the structure of water molecule during his early scientific career.

V M Padmanabhan among others². After the award of DSc in 1953 under the supervision of C Mannenback, Institute of Physics, Louvain University, Belgium, Rahman returned to Hyderabad to teach Physics at Osmania University (1953–57).

During the time Rahman was in Osmania University, he published six papers³ on molecular structure of diatomic molecules which include topics such as polarizability of the hydrogen molecule ion (*Figure 1*), configuration interaction calculations on hydrogen molecule (*Figure 2*), computation of intensities of vibrational bands of light diatomic molecules, and excitation energies of lithium molecule. Rahman was interested in exploring the structure of water molecule during his early scientific career (an interest that later found full expression in the work on simulating water; see below) and used a FACIT mechanical calculator for his research at Osmania. In 1956, Rahman was awarded a National Postdoctoral Fellowship from Delhi which enabled him to carry out full-time research at the Physics Department of Osmania University. The fellowship was awarded for 3 years.

During the period (1953-57) he worked in Osmania University, Rahman remained in constant contact with Professor Mannenback's laboratory. In 1951 as a young research scholar, Aneesur Rahman met Yueh-Erh Li, a Chinese student pursuing an MD degree in Louvain University. After Li successfully completed her M D, Rahman went back to Belgium to marry her on November 3, 1956. Subsequently, Rahman returned to Osmania University. Aneesa, their daughter was born on 17 December 1957 in Hyderabad. After the completion of the three-year fellowship at the end of 1957, the Rahmans left for Bombay. Rahman worked at the Tata Institute of Fundamental Research for a little over a year (1958–59) during which time he also gave regular lectures at the DAE training school. Thereafter, the Rahmans returned to Belgium and stayed there for about a year. Aneesur



Rahman, A.
1953

Physica XIX
145-165

POLARIZABILITY OF THE HYDROGEN MOLECULAR-ION

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Synopsis

The electric polarizability of the hydrogen molecule-ion has been calculated using as a basis the rigorous solution of the Schrödinger equation for H_2^+ . The energy of polarization has been calculated by means of exhaustive variation functions involving 9 terms for the parallel polarizability and 6 terms for the perpendicular case; it is shown that to an accuracy of four places after decimal the convergence with the above chosen variation functions is complete. An analytical method is developed to show how some insight can be obtained into the form of the variation function for the calculation of the polarizability and hence making the choice of terms for inclusion in the variation function not entirely empirical. The first two derivatives of the polarizability with respect to the internuclear distance are calculated. On the basis of data available up to date it is shown that if the parallel polarizability is calculated by means of Schrödinger second order perturbation theory then the convergence is extremely rapid.

By reference to previous calculations it is shown that the polarizability calculated on the basis of inaccurate unperturbed wave functions can deviate considerably in both directions from the true value. From this point of view a short discussion is given of the case of the hydrogen molecule arriving at the conclusion that even the best wave functions available for this molecule are not sufficiently accurate for the purpose.

A Morse type potential has been fitted for the energy of the molecule-ion and it is shown that the anharmonicity of this potential plays an important role in the calculation of the transition moments even for the lowest vibrational states of the nuclei.

1. *Introduction.* The problem of the electric polarizability of a quantum mechanical system is a typical problem in the perturbation theory of quantum mechanics and has attracted attention ever since the beginning of quantum theory. The polarizability of atomic

*) Now at Institut de Physique de l'Université, Louvain, Belgique, while on leave from Osmania University.

Figure 1. Cover page of Rahman's paper in *Physica*, 1953; received on 27 Oct 1952.

Rahman worked in Brussels at the newly started IBM Belgium and Y Rahman-Li (Jady Rahman to friends) worked in the laboratory of Christian de Duve (Nobel



Current Science pp 370-371 (1955)

CONFIGURATION INTERACTION IN $^1\Sigma_g^+$ STATE OF H_2 MOLECULE

THERE is a close analogy between the way in which appropriate H-atom-like wave functions can be used for building up wave functions for atomic He and the way in which H_2^+ -ion-like wave functions can be used for building up wave functions for molecular H_2 ; this analogy has been noted by Mulliken¹ who has suggested several lines of work regarding the computation of configuration interaction in H_2 molecule. A detailed calculation by Taylor and Parr² has exhibited the accuracy that can be

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the value -2.3180 a.u. can be pushed further towards the best value of James and Coolidge.

Similar calculations at smaller internuclear distances are in progress and details will be published separately.

1. Mulliken, R. S., *Proc. Nat. Acad. Sci., U. S. A.*, 1952, **38**, 160.
2. Taylor, G. R. and Parr, R. G., *Ibid.*, 1952, **38**, 154.
3. James, H. M. and Coolidge, A. S., *J. Chem. Phys.*, 1933, **1**, 825.

The Editor

[Current Science

attained by a proper choice of H-like functions for treating configuration interaction in the case of atomic He.

No calculations of configuration interaction for molecular H_2 have been made so far, following the analogy noted above. A programme has been undertaken by the author to study configuration interaction in H_2 molecule, at various internuclear distances, using single electron wave functions which arise in the solution of the H_2^+ problem. The following is a preliminary notice of the computation made for the energy at the equilibrium nuclear distance, namely, 1.4 atomic units (a.u.). The energy which the author has calculated at 1.4 a.u. is lower than any other value reported so far. It is even lower than the value -2.3154 a.u. which James and Coolidge³ have thought to be the best possible without the explicit introduction of the interelectronic distance in the wave function.

In terms of the usual confocal elliptical coordinates, the three configurations used were:

$$\begin{aligned} (1s\sigma) (1s\sigma)' &: \psi_1 = e^{-\delta} (\xi_1 + \xi_2) \\ & [1+p (\xi_1 + \xi_2) + r\xi_1\xi_2] (1+c\eta_1^2) (1+c\eta_2^2) \\ (2p\sigma)^2 &: \psi_2 = e^{-\lambda} (\xi_1 + \xi_2) [\eta_1\eta_2] \\ (2p\pi)^2 &: \psi_3 = e^{-\mu} (\xi_1 + \xi_2) \\ & [(\xi_1^2 - 1) (\xi_2^2 - 1) (1 - \eta_1^2) (1 - \eta_2^2)]^{\frac{1}{2}} \\ & \cos(\phi_1 - \phi_2). \end{aligned}$$

In the $(1s\sigma) (1s\sigma)'$ configuration it was found more convenient to open out the shell by taking p and r as shown, rather than by taking two exponentials δ and δ' ; for the sake of avoiding unduly elaborate computations, λ and μ were taken equal to $\delta = 0.75$, which is the James and Coolidge exponential at 1.4 a.u.

The results of the calculations with ψ_1, ψ_2 and ψ_3 given above are as follows:

(i) Using ψ_1 only and taking $\delta = 0.75$, the energy was found to be minimum when $p = 0.01134$, $r = -0.03693$ and $c = 0.255$, the minimum value being -2.2727 a.u.

(ii) Using ψ_1, ψ_2 and ψ_3 , taking $\delta = \lambda = \mu = 0.75$, $p = 0.01134$, $r = -0.03693$ and $c = 0.255$, the minimum value of the energy is -2.3180 a.u.

The value computed by James and Coolidge with their 13 term wave function is -2.34705 a.u. Thus the correlation energy is more than halved in including the 'angular' configurations $(2p\sigma)^2$ and $(2p\pi)^2$ and a very close agreement with the actual energy has been obtained by taking one electron molecular orbital functions of the type $(1s\sigma)$, $(2p\sigma)$ and $(2p\pi)$. Of course a certain amount of advantage has been lost in taking $\delta = \lambda = \mu$ which means that

Figure 2. Excerpts from Current Science, 1955.

Laureate in Physiology or Medicine, 1974) in Louvain. To quote Jady Rahman, "Because Anees was invited to join a new Solid State Division at the Argonne National Laboratory and I also had an offer to work at the Biomedical Division at Argonne National Lab, we left Europe for the US, in March 1960 to join Argonne National Lab." Rahman worked at Argonne for the next 25 years, after which he moved to the University of Minnesota in 1985 as a Professor of Physics and Fellow at the Supercomputer Institute. A photograph of Aneesur Rahman taken in 1967 obtained courtesy Jady Rahman is presented in Figure 3. Jady Rahman served at the Biology Division, Argonne, during 1960–85. In 1996, she



completed her term as Head, Department of Pharmaceutics, College of Pharmacy, University of Minnesota from where she retired in 2000. She now lives in San Diego. Their daughter, Aneesa Baker, presently works at Hewlett-Packard as a senior quality engineer in the greater San Diego area. The Rahmans finally decided to become US citizens during the year 1978–79. Unfortunately, after a prolonged treatment at the Mayo Clinic, Department of Radiation Oncology, Rochester, Minnesota for a medical condition due to non-Hodgkin's lymphoma, the world lost Aneesur Rahman on 6 June 1987, at a rather young age of 59.

2. Scientific Contributions

Aneesur Rahman was a pioneer in the use of computation to study physical systems. His celebrated paper in 1964 (see *Figure 4*), describing his computational study of liquid argon, is generally considered to mark the beginnings of the molecular dynamics method, one of the two pillars⁴ upon which rest the vast body of computational studies of a wide range of physical, chemical and biological systems and processes. Remarkably, Rahman's own work straddled a large swathe of this domain of potential applications of the technique he pioneered. His work explored the application of the computational technique of molecular dynamics to areas in

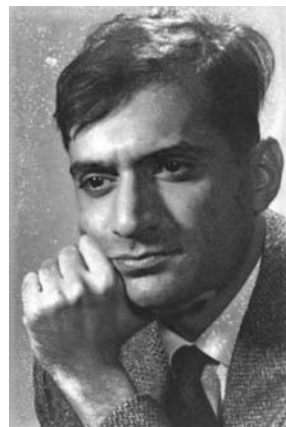
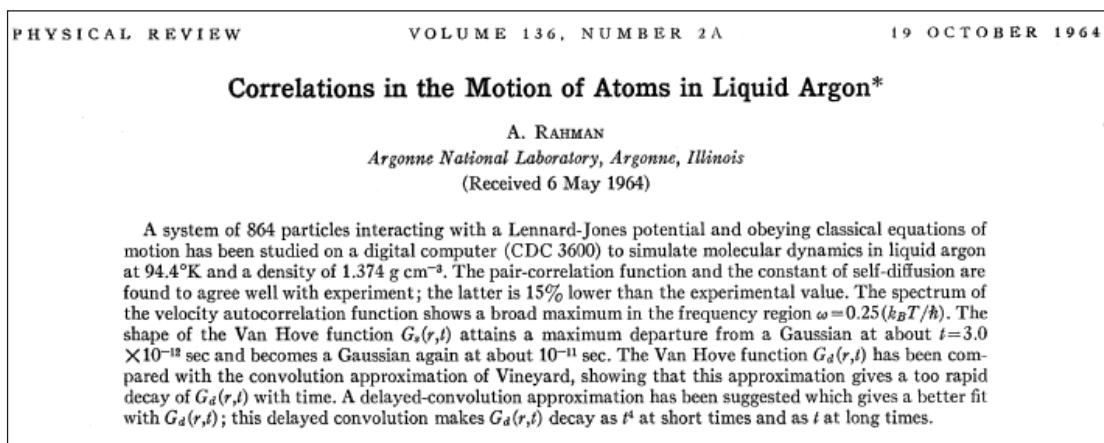


Figure 3. Aneesur Rahman in 1967.

Courtesy: Dr. Jady Rahman.

⁴ The other is the Monte Carlo method.

Figure 4. Title and abstract of Rahman's paper in *Physical Review*, 1964 on the molecular dynamics simulation of liquid argon.



Rahman's work explored the application of the computational technique of molecular dynamics to "areas in particle physics, condensed matter physics, chemistry, and the simulation of biomolecular solutions."

particle physics, condensed matter physics, chemistry, and the simulation of biomolecular solutions, to name a few broad areas. The awarding of the Nobel Prize in 2013 to Martin Karplus, Michael Levitt and Arieh Warshel "for the development of multiscale models for complex chemical systems", is recognition for one of the major lines of development in the application of computation in present-day science. Whether Rahman himself would have been a contender for the Nobel Prize had he lived longer is a matter of speculation, but his towering contributions are acknowledged through the annual award by the American Physical Society in the form of the 'Aneesur Rahman Prize in Computational Physics', to be given to a scientist from any country for outstanding achievement in computational physics. The Prize is funded jointly by IBM and the Argonne National Laboratory.

So, what is molecular dynamics and why is it such a powerful tool in the hands of scientists today? To answer this question, and to place Rahman's contributions in proper context, we must step back briefly to the beginnings of attempts to understand the properties of matter from knowledge about the atoms and molecules that they are made of. In the nineteenth century, while atomic theory was not yet well accepted, Ludwig Boltzmann and James Clerk Maxwell addressed the conceptually simple, but practically impossible, proposition of studying the movement of a large number⁵ of individual atoms, in interaction with each other, in order to determine a small number of *thermodynamic* properties, such as the density of water at room temperature and pressure. In principle, such *macroscopic* properties can be obtained by averaging over the measurement time interval of *microscopic* quantities that depend on the time-dependent positions and momenta (or *trajectory*) of all the atoms. Though Newtonian mechanics offers a method, in principle, for calculating such trajectories,

⁵ A mole, or 18 grams of water contains 6.022×10^{23} (Avogadro's number) of H_2O molecules.



doing so in practice was beyond hope. The conceptual revolution, brought about by Boltzmann, Maxwell, and J Willard Gibbs, in creating *statistical mechanics*, was to replace the computation of averages over trajectories by the computation of *distribution functions* for key properties (the energy, for example), and to evaluate macroscopic properties of substances as *statistical averages* over such distributions. The formalism of statistical mechanics, developed since, provides a basis for understanding the properties of matter in bulk, and together with quantum mechanics, forms the foundation for understanding much of the world around us. The calculation of appropriate averages for most substances is still a formidable task, but useful, accurate, approximations can be achieved in a wide variety of cases.

But, what if we could, indeed, calculate the trajectories of large numbers of interacting atoms with ease? The history of science may have been different if this was true in mid-19th century. By the mid-20th century, even though well-developed formulations of quantum mechanics and statistical mechanics were already in place, a large and growing scientific activity probing diverse materials and phenomena stood to benefit from the availability of tools that would allow such explicit calculations. The new tool that had come on the scene in the intervening period was the *computer*. Computers, developed around the period of the second world war, were beginning to be available in the nineteen-fifties for exploration of the spectrum of problems for which they could be useful. Computers could be used to numerically compute the trajectories of interacting atomic (and other) systems, which could not otherwise be calculated. The computation of trajectories in this way requires the repeated evaluation of forces, velocities and positions for at least many thousands of cycles, for at least hundreds of atoms, which is precisely the kind of task that is not humanly possible, but is tailor-made for comput-

What if we could, indeed, calculate the trajectories of large numbers of interacting atoms with ease?



ers. This simple idea forms the basis of the molecular dynamics method. An introduction to molecular dynamics simulations may be found in D Frenkel and B Smith, *Understanding Molecular Simulation*, Academic Press, 2002.

Molecular dynamics generates trajectories of interacting particles by numerically solving Newton's second law, $F = ma$, provided the forces between particles, however complicated, are specified.

Molecular dynamics generates trajectories of interacting particles by numerically solving Newton's second law, $F = ma$, provided the forces between particles, however complicated, are specified, along with initial conditions that incorporate macroscopic properties such as temperature, density, etc. Then, matter in different states, such as solid and liquid states can be studied, and transitions between these states, as well as properties of any other system, e.g., proteins in solution, that may be similarly specified. A key assumption is that Newton's laws are adequate in describing the behavior of the particles (atoms, molecules) in question. Such an assumption is not valid for electrons, and thus, describing electronic structure requires a different set of techniques, but for most atoms and molecules, Newtonian or *classical* mechanics is adequate in principle. The earliest attempt at molecular dynamics, by Alder and Wainwright, considered a system of hard spheres, which bounced elastically off of each other. The problem of solving the equations of motion amounts to tracking the collisions between these particles and applying the collision rules to update the velocities of particles. Alder and Wainwright applied this method to study the transition between liquid and solid phases, and compared their results with Monte Carlo simulations. The presence of a freezing transition, in a system of particles which only interacted when in contact, was a surprise, and was significant in forming theories of phase transitions. Nevertheless, the development of a framework with which any system of atoms and molecules, with any specified type of interactions, could be simulated, and analyzed with the tools of statistical mechanics, had to await the work of Rahman⁶.

⁶The works of Vineyard and co-workers (1960), and Fermi, Pasta and Ulam (1955), however, anticipate some aspects of Rahman's work.



In his classic paper in 1964, Rahman considered a system composed of 864 Argon atoms, which were modeled to interact *via* the Lennard–Jones potential, proposed to be suitable for noble gases:

$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right].$$

The equations of motion arising from this interaction potential were solved numerically on a digital computer, for conditions that corresponded to a liquid. Rahman calculated a range of structural and dynamical properties, some of which were compared with experimental data. Apart from being the first molecular dynamics simulation for a realistic model of an atomic system, this paper was significant in a number of ways. The first is the choice of a liquid state point. At the time of Rahman's work (and since), the liquid state of matter had proved to be the most intractable theoretically, and experimental techniques (to some of which Rahman himself made significant contributions) with which to characterize 'condensed matter' (liquids and solids, for example) were just emerging, alongside important theoretical developments. Robert Zwanzig, a leading figure in the development of time-dependent statistical mechanics, noted in an influential review written in 1965: "Rahman's calculations provide what is probably the most detailed "experimental" information currently available about dynamical processes in liquids", presaging a key role played by computer simulations in subsequent decades, of being 'experiments' wherein detailed information about the system under study could be 'measured', and compared with theoretical calculations. Computer simulations have thus doubled as numerical experiments, as well as theoretical 'computations', carving over time a niche that encompasses traditional roles played both by theory and experiment.

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– Robert Zwanzig,
1965

In the context of molecular dynamics, the tone was certainly set by Rahman's style, which sought to make solid contact with the latest experimental and theoretical approaches to the studied systems and phenomena.



In a series of about a dozen papers, Stillinger and Rahman studied various aspects of the thermodynamics, structure and dynamics of water, that set the stage for an extensive study of water in many situations over the coming decades.

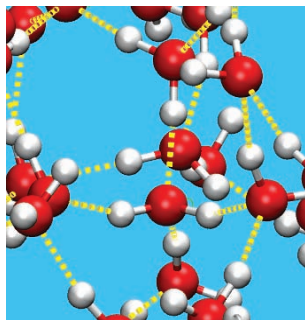
tainly set by Rahman's style, which sought to make solid contact with the latest experimental and theoretical approaches to the studied systems and phenomena. This work is a landmark, and in 1984 a commemorative meeting (Rahman Festschrift) was held in Argonne National Laboratories to celebrate 20 years of its publication, with 129 participants, many of whom were leading experts in computational research (*Figure 6*). Celebrations are planned this year to commemorate 50 years of its publication.

Subsequently, Rahman's work involved the development and application of the molecular dynamics methods to a wide variety of physical systems, which are too numerous to be listed. Instead, two representative highlights are described here. But as noted by Michele Parrinello, a close colleague of Rahman, any such choice would be peaks on top of a very high plateau.

The first is the work by Rahman and Stillinger on simulating water using the 'ST2' interaction potential. As recalled by Frank Stillinger, Rahman and Stillinger met in a Gordon conference on the 'Chemistry and Physics of Liquids' in 1969, with Rahman presenting his pioneering work mentioned above, and Stillinger his work on a model of water he had developed with a colleague, A Ben-Naim. Discussions between the two led to a collaboration that resulted in the development and extensive simulation study of improved potentials for water. In a series of about a dozen papers, Stillinger and Rahman studied various aspects of the thermodynamics, structure and dynamics of water, that set the stage for an extensive study of water in many situations over the coming decades. In particular, computer simulations of water played a crucial role in the subsequent attempts to simulate biomolecular systems, since all biologically active matter exists in a medium of water.

Another notable work, done in collaboration with Michele

Figure 5. Water snapshots. Courtesy: Amalendu Chandra, IITK.





RAHMAN FESTSCHRIFT
November 12-13, 1984
Argonne National Laboratory

Figure 6. Group photograph at the 1984 'Rahman Festschrift' celebrating 20 years of Rahman's 1964 paper, with many leading computational scientists in attendance.



Parrinello and Rahman overcame this difficulty by devising a method which also allowed for the shape and size of the simulation volume to change, clearing the way for the study of structural transitions in solids and much else.

⁷ A cube of $10 \times 10 \times 10$ atoms will contain 488 atoms on the surface.

A large number of outstanding scientists recall fondly his unassuming style, passionate engagement with his work, a deep appreciation of theory and experimental results available.

Parrinello, was to develop a method, now known as the ‘Parrinello-Rahman’ method, for performing molecular dynamics simulations of solids that may undergo phase transitions between crystalline forms with different symmetry. In computer simulations, one works with a small number of atoms as a matter of practical necessity, but employs tricks to prevent such small numbers from causing significant distortions. A major distortion that can arise is due to a large number of atoms being on the surface⁷ which does not represent the experimental system well. The trick employed to get around this is called *periodic boundary conditions*, which considers a larger system made up of copies of the set of atoms being simulated, periodically repeated in certain directions. In simulating crystals, these directions have to be compatible with the symmetry directions of the particular crystal simulated. These directions, however, change when the system undergoes a phase transition to another crystal structure, thus rendering the previous choice of boundary conditions unsuitable. Parrinello and Rahman overcame this difficulty by devising a method which also allowed for the shape and size of the simulation volume to change, clearing the way for the study of structural transitions in solids and much else.

As mentioned earlier, Rahman’s body of work included diverse areas of physics: lattice gauge theory in particle physics, studies of solids and liquids including dynamics, structure, phase transitions, nucleation, freezing and glass formation, quantum mechanical simulations using the path integral approach, etc. These studies were carried out in collaboration with a large number of outstanding scientists, who recall fondly his unassuming style, passionate engagement with his work, a deep appreciation of theory and experimental results available, and of computers, and the sensitivity and personal care he showed towards his colleagues. He acted as a mentor to many younger colleagues in the US and Europe, and



shared his computer codes with many. Thus, in addition to his scientific contributions, Rahman's legacy also rests on such interactions in nurturing computational research among a large group of talented individuals at a pivotal period in the history of computational science.

Acknowledgements

KDS remains most grateful to Dr. Jady Rahman for several email communications. SS thanks Profs. Frank Stillinger, Michele Parrinello and Sidney Nagel for sharing their experiences working with Aneesur Rahman, and Prof. Daan Frenkel for pointing to the short biography published in *Physics Today*. We thank Prof. Michael Klein and Prof. S Balasubramanian for making available the 'Rahman Festschrift' photograph.

Suggested Reading

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