Theor Chem Acc (2000) 103:263–264
DOI 10.1007/s002149900020

Theoretical
Chemistry Accounts

Perspective

Perspective on "Correlations in the motion of atoms in liquid argon"

Rahman A (1964) Phys Rev 136: 405

Peter J. Rossky

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712-1167, USA

Received: 19 February 1999 / Accepted: 25 March 1999

Abstract. This article provides a discussion of the title paper by Aneesur Rahman. Here, the use of numerical integration of Newtonian equations of motion to simulate the classical dynamics of a liquid system with arbitrary continuous interatomic potentials was first introduced. Emphasis is placed on the author's motivations, the depth of his investigation, and the legacy that both the methodology and the style of investigation has left us.

Key words: Molecular dynamics simulation – Liquid dynamics

The terminology "molecular dynamics simulation" is no doubt a familiar one to essentially all graduate students in science. It is recognized as a description of a computational procedure for studying molecular motion at an atomic level, based (most frequently) on a defined model for the molecular-level potential energy. The dynamics is simulated via numerical integration of (typically) classical equations of motion. It has now become as common a term as "quantum chemistry", the latter term describing the use of approximate numerical solutions of the Schrödinger equation to describe molecular electronic structure. There is no question that the use of these dynamical methods to study the molecular dynamics of condensed matter systems, ranging from pure liquids to solutions to solids to biological assemblies, has exploded in the last 20 years. The technique has evolved to the point where implementations can be practically routine, allowing wide access outside the theoretical community. In addition, the use of molecular dynamics simulation, when explicitly coupled with supplemental, experimentally derived, structural constraints, has become a critical tool in the refinement of the structural content of X-ray crystallography and multidimensional NMR data on large systems.

The inauspicious first sentence of the abstract of the title paper summarizes the content of the paper succinctly: "A system of 864 particles interacting with a Lennard–Jones potential and obeying classical equations of motion has been studied on a digital computer ... to simulate molecular dynamics in liquid argon ..." Monte Carlo simulation methods [1] had already been implemented in similar contexts, and the classical dynamical simulation of hard-sphere liquids had been implemented in the classic work of Alder and Wainwright [2, 3]; however, the methods used in Monte Carlo approaches did not generalize to Hamiltonian molecular dynamics, and the algorithms for hard-sphere fluids did not generalize to more realistic potentials. This generalization, in the use of a finite-difference numerical integrator, was a key step.

What cannot be seen in the abstract are the several themes of this short (seven-page) paper. These themes set standards both for the quality of simulation and the style of attack on complex systems. The paper discusses the methodology of numerical finite-difference integration of the dynamical equations of motion in detail in an appendix, with proper attention to numerical accuracy. The limitations of the simple pair-additive interatomic potential, of the cutoff range of the interaction, and of the periodic boundary conditions are also all noted. Validation of the underlying potential model is seriously considered via direct comparison with available experimental data for the atomic diffusion constant and for the interatomic-pair distribution function, from X-ray scattering.

Nevertheless, the paper is clearly focused not on the novel methodology, but rather on the physics of the liquid and, more importantly, on the connection of the physics to experimental observables. (In fact, according to one personal account by the author, the significance of the methodological step was not apparent to him at the time of publication.) The methodology was a tool, and the author's goal was to evaluate the physical content of inelastic neutron scattering (which addresses relative interatomic dynamics) and to evaluate the veracity of available analytical models of these dynamics.

In the words of the paper, "If neutron scattering data of unlimited accuracy and completeness was available, then the kind of work presented here would serve the useful but unexciting purpose of confirming the results already obtained with neutrons.'' While perhaps a bit exaggerated, the point of the author was to emphasize that the simulation served in two critical ways that remain essential in all current and future implementations. First, the results of the simulation could be used to interpret experimental observations. In the case at hand for Rahman, the aspect at issue was the physical picture of motion; for example, do the atoms exhibit hopping dynamics, with infrequent relatively large displacements, or small displacement random-walk-like dynamics? Do the statistical dynamical correlations exhibit remnants of solidlike behavior, such as the non-monotonic oscillating decay of velocity fluctuations, or monotonic, simple overdamped frictional decay? Second, recognizing that one cannot reasonably expect to answer all questions directly via simulation, the results could be used to test the validity of simpler and more analytical models, and, further, suggest ways for improvement of the veracity of such models. This emerged as well from the title paper, in the context of Brownian/Langevin dynamics, as well as in the representation of relative-pair motion. It is notable that the paper includes only six literature references, the majority of these being to papers reporting experimental investigations and those describing proposed theoretical models for liquid dynamics.

The capacity of theoretical and computational chemistry continues to expand, and nowhere is the new growth more evident than in combined ``molecular dynamics simulation'' and ``quantum chemistry''. The products, variously referred to as quantum, or mixed quantum–classical, molecular dynamics or as ab initio molecular dynamics, have already been widely used to investigate systems as complex as biological molecules and polymer films as well as electronic processes in solution, without complete dependence on molecular mechanics models. The role of these methods both as primary simulation tools and as methods for development of more reliable model potentials will certainly continue to grow. At the same time, there are substantial opportunities for new methods which can focus on the quantum aspects of nuclear motion, and not just on the quantum electronic structure, and for those which can address quantum state-to-state processes.

The title paper provides a template for such future investigations in a number of fundamental ways. I had the exceptional opportunity to first learn about molecular dynamics methodology by working with Anees for an extended summer workshop nearly 25 years ago. One critical element to his effectiveness that was immediately evident was the importance of connecting a theoretical framework to the physical insight that arose from the numerical output of such ``computer experiments''. Insight into the appropriate framework for an analysis is as important as any other element of molecular dynamics simulation – this feature is evident in the title paper, and it has lost no element of significance in the intervening years or for the future.

References

1. Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E (1953) J Chem Phys 21: 1087
2. Alder BJ, Wainwright TE (1957) J Chem Phys 27: 1208
3. Alder BJ, Wainwright TE (1959) J Chem Phys 31: 459