A method to break all barriers

Nature Materials asked Michele Parrinello about his research and the way in which his work with Roberto Car 25 years ago has influenced the materials science and quantum chemistry communities.

What made you decide to study physics?
It was almost a natural choice. In my school years I attended a *liceo classico*, which focuses on humanistic studies, with plenty of Greek and Latin. Still, even though there was not much mathematics or science, it felt as if I had an inclination for these subjects. It was no effort for me to learn them, so I decided to attend a scientific faculty at university. Initially I was undecided between physics and engineering. Eventually I chose physics because at the time I thought it was more abstract and speculative. I do not necessarily have that impression any more, but back then it helped me to make a decision. It worked out well, because I was able to study mathematics combined with the empirical aspects of physics, which is what I liked — and still do — most. I started studying in my hometown, Messina. At the time there were a few young, bright academics who had come back from the United States. But they all left when I was in my second year, so I then decided to move to Bologna to finish my degree.

So, theoretical physics was also a natural choice given your love for mathematics?
Not quite, I was more inspired by empiricism. It was really one particular episode that drove my decision, and I still remember it very well. My quantum mechanics professor had given me an exercise in which I had to calculate the shift of the energy levels of a 1*s* electron in a hydrogen atom taking into account the finite size of the nucleus. I was incredibly fascinated by the possibility of calculating with just pen and paper something that can eventually be checked with experiments. It was at that precise moment that I decided on theory.

What happened after your degree?
When I was about to finish, Mario Tosi moved from Argonne National Laboratory to Messina with a chair in solid-state physics, and I joined him as a young researcher. This corresponded also with a switch in my interests from relativistic field theory to condensed-matter many-body systems. I was in Messina for about six years before moving to Trieste, where I stayed for another thirteen. However, a fundamental part of my career was a sabbatical in the United States while I was in Trieste. I spent two years in Argonne, working with Aneesur Rahman, who is one of the founding fathers of molecular dynamics. Up to that moment I had been working with pen and paper. Working with him converted me completely to computational methods and molecular dynamics in particular.

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How was your and Car's *ab initio* molecular dynamics method conceived?
It was really a combination of factors. Shortly after I came back from Argonne, Roberto Car also arrived in Trieste and we started exchanging ideas. One of the big challenges in condensed-matter physics at the time was describing the complex phase diagrams of various materials. Silicon was the main one; it was metallic in one phase and semiconducting in another and it was difficult to understand exactly what was going on. Marvin Cohen and his colleagues had shown that with density functional theory (DFT) one could predict reasonably well some of the main features of the phase diagram of silicon. But there was a need to go further and study more complex situations. Roberto was an expert in electronic structure calculations and I knew about molecular dynamics, so we thought about the idea of combining the two. No-one at the time believed that it would work, but we weren't particularly discouraged by that, and maybe there was an element of naivety. I didn't know enough about DFT and Roberto didn't know enough about molecular dynamics to be worried about it. So we set to work in the very cold winter of 1984 — we worked day and night, and we succeeded.

Did you realize immediately the success that your work would have?
Not really. My colleague and friend Erio Tosatti was immediately aware of the importance of the result. But to be honest we did not think about it. We were excited when we had the first calculations going, atoms and electrons moving — Roberto and I were almost like children in a toy shop! There were all these problems that previously were thought to be impossible to solve and now we had a way to try. All we were thinking about was which system we could apply the method to next. It was just a great moment, and we were not thinking about the future. Then of course we started being invited to give many lectures and the citations of the paper skyrocketed, so I guess we realized it in retrospect.

This probably happens often.
Sure, and in the case of some works they do not even receive the recognition they deserve. In my view for example, the real breakthrough in molecular dynamics simulation, from which many works derived, including ours in part, was a paper by Hans Christian Andersen, who is now at Stanford. Basically he introduced the first version of constant-pressure molecular dynamics. He wrote a Lagrangian and allowed the volume to vary. This was really a paradigm shift, because up to that moment the molecular dynamics community was only working with Newton's equations in their original form, and his brilliant idea was to add new variables and modify Newton's equations, in a controlled way. He gave the community the courage to use Netwon's equations as a starting point on which to build, rather than consider them as something untouchable. In many ways he himself did not realize that he had really broken a barrier, for which in my view he should be regarded as one of the fathers of modern molecular dynamics.

You seem to have become very close to chemistry. Would you say that you are more a chemist than a physicist now?
Well, maybe there is also a chemist in me, in the sense that I am in a chemistry department, I have many collaborators and friends who are quantum chemists, and I attend numerous meetings in their field and so on. However, I also think that if you were formed as a physicist you are going to remain one, in terms of attitude I mean. The topics that I study nowadays are maybe closer to what chemists do, but I do believe that the way I approach them is still that of a physicist.

And you have worked substantially on biomolecules. What is it that attracts you to these systems?
There are several factors. There is certainly an incredible reward given by the potential applications that your work may have one day; there is something about the way in which nature works, the subtleties of these systems, that is fascinating in itself. Then of course there is the technical challenge, because these are very complex systems. There is always the problem that the computer time available is much too restricted to follow the slow changes in protein configurations.

What would you say is the greatest challenge for computational materials science today?
Again, there are really many issues that have to be solved. One of them is the necessity of going beyond DFT as the basis for *ab initio* calculations. A way has to be found to include higher levels of correlation. Something has to be introduced in the codes for this purpose, maybe a quantum chemical method or quantum Monte Carlo; I don't know which one will succeed, but I really think that something has to happen. Then of course there is the need to cope with larger and more complex systems, although in my view this is more a technical issue, and with larger machines and all the new methods, progress will be made. In molecular dynamics, it is typical to use the Born–Oppenheimer approximation, but there are many reactions for which this is not suitable. There really is plenty of work to be done. Some of these things will be absorbed by computer power, but others will need new concepts and ideas. From my personal perspective, however, sampling is really the most important aspect to be improved and this is mainly the reason why the focus of my present research is on this aspect.

So, after 25 years, what would you say has been the greatest achievement of the Car–Parrinello method?
That is really impossible to say. There have been so many remarkable applications and it is impossible to select just a few. But what I am very proud of is the way in which our work influenced the theoretical community more generally. Before, there used to be isolated communities, separated by virtual walls. There were people doing electronic structure calculations on one side of the wall, and those doing molecular dynamics on the other side. Quantum chemists did not really talk to physicists, and even the way in which they performed electronic structure calculations was different. Our work had the great merit of breaking the barriers and making these communities talk to each other. People from different fields now reach out to each other much more than in the past. In my view this is probably the biggest success of our effort.

INTERVIEW BY FABIO PULIZZI

From *ab initio* onwards

Roberto Car tells *Nature Materials* how the Car–Parrinello molecular dynamics method originated and how his research career has evolved since then.

You studied engineering. What drove you to this choice?
I was broadly interested in science, but the distinction with engineering wasn't that clear to me before I went to university. I also had a sort of prejudice that studying physics would have meant necessarily an academic career, and I wasn't sure that would have been right for me. So I chose engineering with the idea that it would open more doors. However, very soon after starting to attend courses I realized that I was much more interested in science, and physics in particular. I was fascinated by the way in which mathematics allows you to describe the physical world

At that point I had to decide whether to stay at the Politecnico di Milano and study engineering or move to physics at university. Luckily, I had good enough grades to be admitted to a programme of nuclear engineering that left me almost all the freedom I needed to attend physics courses while officially studying engineering. So I stayed at the Politecnico.

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When did you start working in Trieste?
I moved there permanently in 1984, coming back from the United States, where I had been a postdoctoral researcher at the T. J. Watson centre of IBM, but my contacts with Trieste had already started before, during the time that I worked in Lausanne. There was a close relationship between the community in Lausanne, guided by Alfonso Baldereschi, and that in Trieste. I had also spent a few months working in Trieste, where I interacted mainly with Erio Tosatti and Michele Parrinello.

What was the environment like there?
It was rather unique. The Intentional Centre for Theoretical Physics (ICTP) was already established, and Erio Tosatti was assembling a very good group of people to create the Scuola Internazionale Superiore di Studi Avanzati (SISSA). But everything was in the same place — the ICTP, SISSA and also the Department of Theoretical Physics of the University of Trieste. On the one hand it was quite uncomfortable, as there were simply too many people in a tiny space. On the other hand, the overlap — physical, as well as scientific — was such that it was just natural to interact with others. Also, the ICTP was a very international place; there were always