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## SPECIAL ISSUE IN HONOUR OF JEAN-PIERRE HANSEN

### History and perspective of the Car–Parrinello approach applied to classical systems<sup>1</sup>

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In the seminal approach of Car and Parrinello, published in 1985 [1], molecular dynamics simulations of classical ions were combined with quantum mechanical density functional theory for the electrons interacting with the ions via a pseudo-potential at zero temperature. One of the key ideas of Car and Parrinello was to update and move in a single time-step both the coordinates of the ions and that of the electronic density field ensuring the adiabaticity constraint.

Density functional theory though originally invented for quantum mechanical electrons can also be formulated for classical systems at finite temperature. It was one of the ingenious ideas of Jean-Pierre Hansen to exploit this analogy and to describe nonlinear screening in colloidal suspensions using the Car–Parrinello approach applied to classical systems. The idea is documented in a letter by Jean-Pierre – dated 24 February 1989 – which he sent to me explaining possible research projects for my postdoc which I could perform in Lyon in the years 1990–1991 under his supervision. A quote from this personal letter is as follows: ‘As regards possible research projects, we could consider the following general topic: Statistical mechanics of inhomogeneous fluids and plasmas and of freezing. More specifically some of the problems which you could investigate are the following: . . . e) A further ambitious project would be to formulate a density functional theory of equilibrium (static) properties in partially degenerate systems. More specifically can one reformulate density functional theory to treat dense plasmas which contain both classical ions and degenerate electrons? The starting point here is the classic paper by D. Mermin (Phys. Rev. 137 A1441 (1965)) generalized to such two-component systems, and the recent “adiabatic” Molecular Dynamics algorithm of Car and Parrinello (Phys. Rev. Lett. 1985).’

In the explicit context of charged colloidal suspensions, Jean-Pierre explained this idea on the blackboard in his office later on in July 1990 during the first Liquid Matter Conference discussing it with Berni Alder, David Oxtoby, Giovanni Ciccotti and me (I hope I did not forget anybody

else). So, the basic idea was born and it was a very lucky coincidence that Paul Madden then arrived in Lyon holding the Louis Néel chair. Paul came with a very well-documented simulation code for quantum mechanical Car–Parrinello [2] which we could use as a template to reformulate the theory for classical counterions. The result [3,4] was a microscopic approach of screening for charged colloidal particles (‘macroions’) which included effective many-body interactions induced by the classical counterions at large charge asymmetries. In contrast, direct simulations of the primitive model were not possible in these days. The real bottleneck was the idea of the pseudo-potential which had to be developed for and adjusted to classical systems. The underlying approximation scheme was later on confirmed by full primitive-model simulations [5].

As a simulation scheme, the approach can be applied for different set-ups and situations subsequently. It was extended to include explicit salt-ions (i.e. counter- and coions) [6] and to rod-like macroion shapes [7]. Then, it was used to describe situations different from charged colloids namely colloids in a liquid crystalline solvent [8] and to a solvent which performs a fluid–fluid phase transition [9] anticipating a bit the very fruitful research area of fluctuation-induced Casimir forces between colloids [10,11].

Finally, the technique was applied to tackle the dynamics of colloids. Hydrodynamic interactions were described by coupling the solvent flow field to the colloidal coordinates [12] and even chemotactic dynamics in active colloids can be described by coupling the colloidal dynamics to a chemo-attractant field [13,14].

This classical version of the Car–Parrinello approach is, however, by far more than just a simulation scheme for classical systems. Its exact formulation with the exact density functional also provided the starting point for future theoretical developments. This includes the phase separation in charged colloidal suspensions calculated by Rene van Roij and Jean-Pierre Hansen [15] and a systematic theory to describe effective triplet interactions [16] and

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<sup>1</sup>This is a historical perspective to honour Jean-Pierre Hansen.

inhomogeneous situations like macroions in confinement and in a gravitational field [17–19] as well as solvation for complex solutes [20–21].

As a future perspective, there is still a high and not yet exploited potential of the Car–Parrinello approach applied to classical systems. This applies in particular to the dynamics of strongly asymmetric colloidal mixtures. The still unexplored idea is to make Car–Parrinello fake dynamics physical by using dynamical density functional theory for the Brownian system of small depletant particles [22–24] in the field of the large colloidal particles. This can be directly generalised to rod-like depletants [25,26]. These and many other problems remain to be solved for the future.

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No potential conflict of interest was reported by the author.

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