'Early Days of Classical DFT: purple jeans, some formalism, a summer school and why I should have been wiser'

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Tuebingen Density Functional Days

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When Roland was planning this Workshop he enquired whether I would like to say something about the early days of classical DFT. I said that I had never talked about this topic but given it is 35 years since I submitted my Advances in Physics Article (in August 1978) perhaps it would be amusing to reminisce –provided suitable liquid refreshments were provided. Well they are. So blame Roland. This is a personal recollection and I might be forgetting or misremembering some things.

The Advances in Physics article, that happened to be published on April 1st, 1979, was my first foray into classical DFT. Indeed, from the title of the article 'The Nature of the Liquid-Vapour Interface and Other Topics in the Statistical Mechanics of Non-Uniform, Classical Fluids' you will be forgiven for not recognizing this was about DFT! I do not think I used the term. *I should have been wiser* in the choice of title but I'll return to this. Note also that the article has only three figures: 1. a rectangular box, 2. a *sketch* of the density profile at a liquid-gas interface, and 3. a *sketch* of a liquid-vapour coexistence curve and the spinodal. The article contains a lot of formalism, 5 Appendices and 209 equations. I am not sure it would get published today; certainly I would have to *colour* the rectangular box. By the way I had sent an earlier version to Molecular Physics but the editor turned it down as being too long. I think it was Ian McDonald who encouraged me to send it to Advances in Physics.

How did I come write the article? In my youth I had learnt about electronic structure calculations and from a Bristol colleague Balazs Gyorffy , I vaguely knew about Hohenberg-Kohn-Sham DFT for electrons. In the mid-seventies I worked on the properties of liquid metals and used classical liquid state theories for the pseudo-ions to investigate structure and thermodynamics. I also tried to make theories for the surface tension that took into account the variation of both the ionic and electronic density profiles. With hindsight I can say these theories were not very good! I began to think more about interfaces of classical simple fluids without complications of the conduction electrons. I found approaches by Toxvaerd (1971) based on thermodynamic perturbation theory and started to develop a DFT approach along the lines of what HK did for the inhomogeneous electron liquid. This was in 1976-77. I recall deriving the gradient expansion following HK and feeling proud that I had identified the coefficient of the square gradient term as the second moment of the direct correlation function only to find a nice 1976 paper by Yang, Fleming and Gibbs (Julian Gibbs of Brown University). In the Appendix they derived the same expression as I had but in a less elegant way and with no reference to HK. But that paper was important and guided me into the older literature on the theory non-uniform classical fluids. The papers of De Dominicis, Morita

& Hiroike, Stillinger & Buff, Lebowitz & Percus from the 1960's were full of formalism but did not seem to be based directly on a variational principle-so did not look like DFT. By then I had found Mermin's beautiful 1965 paper which I had not known about in my youth. As you know, he lays out the variational principle for the grand potential of the electron gas. Having read Mermin, it was clear how to write down DFT for classical fluids and how to make connection with much of the earlier formalism on correlation functions etc. I was very pleased. Then in 1977 I found the paper by Ebner, Saam and Stroud (published 1976) on the surface tension of the LJ fluid. (I knew David Stroud who had also worked on liquid metals and was a former student of Neil Ashcroft.). These authors had taken ideas from HK and had developed an approximate functional based on a partial resummation of the gradient expansion.(This approximation has fallen out of fashion but was also the one Ebner & Saam used in their 1977 PRL on the prewetting transition. At the time I did not understand or recognize how significant this PRL was; nor did many others. *I should have been wiser*.) Saam & Ebner had a background in theories of [4]He and knew about DFT in that context. I was disappointed to find that others had already taken over the HK ideas; I was scooped but not too surprised. And I would give Ebner, Saam & Stroud priority in introducing <u>modern </u>DFT methods into the statistical mechanics of inhomogeneous fluids. (Of course, I am not implying that van der Waals and Onsager had not set the scene much earlier. They had.)What *was* surprising is that it had taken many years, from Mermin in 1965 to about 1976, before the electronic-classical cross-fertilization occurred. I thought there were many new things to do. One had to lay out the formal aspects in a careful way and this might help in developing useful approximations.

However, I had not published anything on this. In 1977 I was a SRC Advanced Research Fellow in Bristol which was not a tenured position. I was invited to give a course on Liquid Metals, in September, at a NATO Summer School in Aleria, Corsica.This was an early school , mainly on simple liquids, organised by J.Dupuy & A.J.Dianoux and held in the holiday camp run by the French Union of prison guards located next to a penitentiary. One of the inmates escaped during the period of the school and he hid amongst us. Unfortunately, he made the mistake of attending one of my lectures and decided it was better to go back to the penitentiary. The Lecturers included: J-P. Hansen, I.R. McDonald, D. Buckingham, J. Enderby and P. Hohenberg. The Scientific Committee included: B. Alder & P.G. de Gennes. I was only 31 years old and I should have been a little overawed teaching alongside these distinguished persons. In fact the Participants included persons who are now very famous: A. Angell, D. Ceperely, C.Caccamo, A.Ladd, T. Keyes, W. Freyland, J.E. Hirsch (of the Hirsch index), M.Parrinello, D.Oxtoby, J-J.Weis , M.P. Allen, D.Oxtoby and H. Lekkerkerker. Yes, big Henk himself. It was a memorable scientific and social occasion. We slept in rather uncomfortable huts on the beach and I wore purple jeans.There was a poster session, a relatively new event in those days, and I decided that I would make a nice hand-written poster describing the DFT derivation of square-gradient approximation and show how the same surface tension also follows from the Triezenberg-Zwanzig formula if one approximates $C^{(2)}$. I am not sure anyone understood what I was doing but the session involved much liquid refreshment and de Gennes did take interest. He knew about theories of surface tension for liquid crystals and about inhomogeneous superconductors. (This was well before his interest in wetting.) He encouraged me to write up the material. By the way Pierre Hohenberg had forgotten about the HK paper!

I started to write the Advances in Physics article putting the main thrust on the theory of the liquid-vapour interface. There was much interest on this topic –as there still is today. In particular there was an ongoing debate as to whether the capillary wave treatment of Buff, Lovett and Stillinger (1965) that predicted the interface was always rough, i.e. the interfacial width diverged in the limits of infinite interfacial area and vanishing external field, was correct. This prediction is contrary to the classic van der Waals picture of a finite width away from the critical point. There were several fine papers, especially those of Wertheim (1976) and Weeks (1977). Wertheim left open the issue whereas John Weeks gave arguments as to why the divergence was correct. Ben Widom was unsure. In the Advances in Physics article I came down on the side of the van der Waals picture, perhaps over-influenced by DFT ideas and knowing that minimizing a more sophisticated functional would still lead to a finite interfacial width. Now we know this argument is incorrect. With hindsight the free interface was not the problem to tackle first with DFT methods. *I should have been wiser*. I sent a draft of the article to John Weeks who said nice things about the first sections but John certainly did not like the piece about the non-diverging width of the interface and the conclusions that I drew. I sort of ignored his comments.

Then I added Section 9 on spinodal decomposition. I had read papers by Farid Abraham on this topic and thought that a DFT formulation might generalize the seminal work of John Cahn (1961). With hindsight this Section sits uneasily. The discussion of the free-energy associated with fluctuations is okay. I then used the continuity equation and defined the current in terms of the one-body direct correlation function to arrive at the basic equation of what we now call dynamical DFT. Of course, I had *no idea* what I was doing-it was the flush of youth. And as you all know, we had to wait for Umberto Marini Bettolo Marconi and Pedro Tarazona (1999) to provide, much later, a decent derivation of DDFT that was followed by Andy Archer and me (2004) in a return to spinodal decomposition. The current state of play in this area lies in the splendid work of Joe Brader and Matthias Schmidt that we heard about at this Workshop.

Back to the story. Margarida Telo da Gama, whom many of you know as an eminent professor in Lisbon and a senior figure in European Science, was an undergraduate in Bristol. She decided, in 1977, to carry out her final year Bachelors' project under my supervision. Perhaps it was my long hair or the purple jeans that persuaded her to work on liquids. (Margarida always tells me she wanted to work with another, more handsome supervisor.) In the project Margarida used the square gradient approximation to investigate surface tension and interfacial density profile for LJ fluids, i.e. a simpler functional than that of Ebner et.al. In fact Ebner sent us his Percus Yevick direct correlation functions. We sent off a paper to Molecular Physics in November 1978. Margarida also did some calculations on the extension of the Cahn theory of spinodal decomposition that I had written down and we published a paper on this in 1979. In her PhD thesis at Bristol Margarida worked on binary liquid mixtures and molten salts. Most of the work was aimed at surface tension and used square gradient approaches. When

Pedro Tarazona arrived for a postdoc in Bristol in 1981 we started to work on adsorption and wetting transitions using a Local Density Approximation (LDA) for the hard sphere functional and a standard mean-field treatment of attraction. This approach was motivated by brilliant work on wetting by Don Sullivan. It was Pedro, now an eminent professor in Madrid, who had the great insight to try to construct a non-local weighted density approach for the hard-sphere functional. Pedro found work by Nordholm 1980 and then proceeded to develop better treatments. He used for these for freezing and he and I applied these to drying. It took him some time to convince me that it was possible to make reliable theories beyond LDA. *I should have been wiser*. Developing new DFT approximations then became popular. I wrote a review about classical DFT, submitted in November 1990, where I mentioned briefly the work of Yasha Rosenfeld 1989 on FMT - not really doing justice to it. *I should have been wiser*.
The group assembled here certainly knows many of the more recent developments.

Back to the 1970's. They were interesting times. There was no fax, no email, no web of science, no on-line archive and fewer conferences/workshops. Letters from our American cousins took 7 days to reach Europe. Can you imagine such a world? How did we manage to do science?

Perhaps I am wrong but there seemed to be more time to sit and read, digest and even *think* before writing. This does not mean that the end product was necessarily good or better than in later, electronically driven, times. However, it did mean the *style* of publication and presentation was different. You can all see this.

As to the purple jeans? They wore out.

R.Evans
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