Range separation: the divide between local structures and field theories

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Abstract

This article discusses some well-known historical developments in the theory of electronic and liquid structure. As topics in physical chemistry, they vascillate without warning between experimental facts and technical theoretical and mathematical details. The topics have been chosen specifically to highlight the debate between local structural and field theoretical models. Note that we have also presented the two topics in an idiosyncratic way to highlight their similarities. Both histories trace their roots to the Herapath/Maxwell/Boltzmann conception of a continuous density (or probability distribution) of discrete molecules, and stretch all the way to the present day, remaining lively research areas that are even in communication on several points. We will find that, like Democritus and Aristotle, not only are there strong opinions on both sides, but progress continues to be made by researchers regardless of whether they adopt discrete or continuum worldviews.

Key words: electronic structure, liquid state structure, density functional theory, Bayes’ theorem, vapor interface, molecular dynamics

Many of the most important scientific theories were forged out of controversy – like particles vs. waves, for which Democritus claimed (with his teacher, Leucippus of 5th century BC) that all things, including the soul, were made of particles, while Aristotle held to the Greek notion that there were continuous distributions of four or five elements. It is telling to note that that Aristotle’s objection was strongly biased by his notion that the continuum theory was elegant and beautiful, and does not require any regions of vacuum. In addition, his conception of kinetic equations were first order – like Brownian motion or Navier-Stokes, but not second order like Newton’s. Newton sided with Democritus. In 1738, Daniel Bernoulli first explained thermodynamic pressure using a model of independent atomic collisions. That theory was not scheduled to be widely adopted until the caloric theory was overthrown by
James Joule in the 1850s. Wilhelm Ostwald was famously stubborn for refusing to accept
the atomic nature of matter until the early 1900s, after Einstein’s theory of Brownian motion
was confirmed by Jean Perrin’s experiment.

The working out of gas dynamics by Maxwell and Boltzmann in the 1860s depended
critically on switching between a physical picture of a 2-atom collision and a continuum pic-
ture of a probability distribution over particle velocities and locations (Fig. 4). Five decades
later, Gibbs would argue with Ehrenfest over treating dynamics in a probabilistic (continu-
ous phase space density) vs. an exact, atomic mechanical way, and the controversy was only
resolved by the advent of the age of computation, since we forgot about it. Three decades
further, the physicist Jaynes championed the maximum entropy viewpoint while mathe-
maticians like Sinai, Ruelle and Varadhan moved to do away with the whole subjectivity
business (or at least restrict it to uniform distributions).

Table 1: Contrasting long and short-range ideas showing stages of debate over atoms and
electrons (top two sections), along with concepts from hybrid theories (lower section).

| SR/Discrete     | LR/Continuous          |
|-----------------|------------------------|
| (Democritus)    | atoms                  |
| (Ehrenfest)     | microstate             |
| (Einstein)      | particle               |
| (Boltzmann)     | distribution function   |
| (Wein)          | $n(\nu)$               |
| (Mott)          | insulator              |
| (Hartree-Fock)  | Slater determinant     |
| (Born-Oppenheimer) | nuclei |

|                                  | $\nu^d d\nu$                      |
|                                  | $n(r), V^\text{ext}(r)$           |
|                                  | Jellium                           |
|                                  | conductor                         |
|                                  | Electron density                  |
|                                  | correlation hole                  |
|                                  | polarization response             |

Maxwell described light propagation by filling the continuum with ‘idler wheels,’ and the
resulting partial differential equations inspired much of 20th century mathematics. Planck
saw his own condition on quantized transfer of light energy as a regrettable, but necessary
refinement of Maxwell’s theory. Planck believed so strongly in that theory that he at first
rejected Einstein’s 1905 concept of the photon. It was also five decades later, around 1955,
when quantum electrodynamics was gaining acceptance from precise calculations of the gy-
romagnetic ratio, radiation-field drag (spontaneous emission) and the Lamb shift. Quantum
field theory and its second quantization understands particles as wavelike disturbances that
pop in and out of existence in a field, which we treat as a continuum. The technical foun-
dation of that theory are derived by integrating over all motions of Maxwell’s idler wheels. As a consequence, infinities characterize the theory, so that the mathematical status of open-ended path integrals is still not settled except in the Gaussian case and where time-sliced limits are well-behaved. This article discusses some well-known historical developments in the theory of electronic and liquid structure. As topics in physical chemistry, they vascillate without warning between experimental facts and technical theoretical and mathematical details. The topics, outlined in Table 1, have been chosen specifically to highlight the debate between local structural and field theoretical models. Note that we have also presented the two topics in an idiosyncratic way to highlight their similarities. Differences between electronic and liquid structure theories are easy to find. By the nature of this type of article, we could not hope to be comprehensive. There has not been space to include many significant historical works, while it is likely several offshoots and recent developments have been unknowingly overlooked. Both histories trace their roots to the Herapath/Maxwell/Boltzmann conception of a continuous density (or probability distribution) of discrete molecules, and both remain active research areas that are even in communication on several points. We will find that, like Democritus and Aristotle, not only are there are strong opinions on both sides, but progress continues to be made by researchers regardless of whether they adopt discrete or continuum worldviews.

Electronic Structure Theories

Between the lines of the history above, we find Bose’s famous 1924 Z. Physik paper describing the statistics of bosons, which Einstein noted ‘also yields the quantum theory of the ideal gas,’ and the Thomas-Fermi theory of 1927-28 of the electron gas at a fixed external potential. Their basic conception was to model the 6-dimensional space of particle locations, \( r \) and momenta, \( p \) with the volume element,

\[
g(p')\,dp' = dp' \int \delta(|p| - p') \, d^3r \, dp^3 = 4\pi V h^{-3} p'^2 \, dp'
\]  

(1)

Using \( p' = h\nu/c \) for photons of frequency \( \nu \) provides \( g(\nu) \), the number of available states for photons near frequency \( \nu \). Applying Bose counting statistics to \( n(\nu) \) photons occupying \( 2g(\nu) \) possible states for each frequency gives Bose’s derivation of Planck’s law. In the Thomas-Fermi model, \( p' \) is electron momentum. Applying Fermi statistics to the occupancy number \( N = 2 \int_0^{\hbar k_F} g(kh) \, d(kh) \) now gives a Fermi distribution for an ideal gas of electrons under a constant external potential. In both cases the number of states is doubled – counting 2 polarizations for photons or 2 spin states for electrons. The result of the first procedure is a free energy expression for the vacuum. The result of the second is a free energy for electrons under a constant local voltage, \( \phi \).

This idea of a gas with uniform properties uses a long-range field to guess at local structure. Quantitatively, if the voltage at point \( r \) is \( \phi(r) \), then the theory predicts electrons will fill states up to maximum momentum of \( k_F = \sqrt{2m_e \phi(r)/\hbar} \), (where the kinetic energy is
$E_F = \hbar^2 k_F^2/2m_e$) so the local density is,

$$n(r) = \frac{k_F^3}{3\pi^2}.$$  \hspace{1cm} (2)

The resulting model is then usually found to predict long-range properties of metals relatively well. Fig. 1a and b show plots of free energy vs number of electrons in an independent electron solution of the Schrödinger equation for a well of positive potential. Panel b shows a simple adaptation of that model where electrons bind in pairs. The states of the electrons in these exact solutions still represent momentum levels, and are thus qualitatively very close to those of the Thomas-Fermi theory.

The free electron gas evolved into the famous ‘jellium’ model of electron motion rather quickly, as can be seen by the earliest references in a modern discussion of that model. The term jellium was coined by Conyers Herring in 1952 to describe the model of a metal used by Ewald and others consisting of a uniform background density of positive charge. The electrons are therefore free to move about in gas-like motion. At high density, the electrons actually do act like a free gas, so it was possible to use the Thomas-Fermi theory to qualitatively describe the electronic contribution to specific heat, $C_v = \pi^2 k_B^2 T/2E_F$, as well as the spin susceptibility and width of the conduction band (after re-scaling the electron mass). These are long-range properties arising from the collective motion of many electrons. The predictions become poor for semi-metals and transition metals. It also rather poorly described the cohesive energy of the metal itself. Those cases fail because of the importance of short-range interactions that a free electron theory just doesn’t have.

It turns out that the electron gas in ‘real’ jellium behaves rather differently at low and high density. At low density, the electron positions are dominated by pairwise repulsion, and organize themselves into a lattice with low conductivity. At higher densities, collective motions of electrons screen out the pairwise repulsion at long range. This gives rise to

Figure 1: Long-range (left) and short-range (right) theories of electronic structure. (a) and (b) show free energy vs. electron number for a potential well. (c) shows ‘Epstein’ profile of dielectric response at a metal/vacuum interface numbered surface/bulk conductivity ratio, (d) shows surfaces of constant voltage at a water/vacuum interface, (e) and (f) show the correlation function of jellium from accurate calculations.
a nearly ‘free,’ continuous distribution of electrons with higher conductivity more like we would picture for a metal. Fig. 2a from a well-known particle-based simulation of Ceperly and Alder\textsuperscript{26} shows the Wigner lattice as well as both spin-polarized and unpolarized high-density states.

Taking the opposing side, early applications of self-consistent field (Hartree-Fock or HF) theory to molecules and oxides noticed that the long-range, collective ‘correlated’ behavior of the electrons was usually irrelevant to the short-range structure of electronic orbitals. Getting the short-range orbital structures right allowed HF theory to do well describing the shapes of molecules and the cohesive energy of metal oxides\textsuperscript{27} as well as magnetic properties.\textsuperscript{28} More recent work has shown explicitly that a model that altogether omits the long-range tail of the $1/r$ potential still allows accurate calculations of the lattice energy of salt crystals.\textsuperscript{29}

The insulator/conductor transition remained somewhat difficult though because it involved a cross-over between both short- and long-range effects. Because of this mixture of size scales required, relying exclusively on a theory appropriate for either short- or long-range produces results that increasingly depend on cancellation of errors. This sort of error cancellation is illustrated by the phenomenology of ‘overdelocalization.’

Well known to density functional theorists, ‘overdelocalization’ is the tendency of continuum models for electron densities (having their roots in the long-range TF theory) to spread electrons out too far away from the nucleus of atoms. The result is that electron clouds appear ‘softer’ in these theories, and polarization of the charge cloud by the charge density of a far molecules contributes too much energy. On the other hand, induced-dipole induced-dipole dispersion forces are not modeled by simple density functionals, and so their stabilizing effect is not present. It has been found that the over-delocalization can be fixed by making a physical distinction between short and long-range forces. However, the resulting binding energies are not strong enough. After the correction, they need a separate addition of a dispersion energy to bring them back into agreement with more accurate calculations.\textsuperscript{30} Thus, a bit of sloppiness on modeling short-range structure can compensate for the missing, collective long-range effects.

**Hybrid Theories in Electronic Structure**

When looking at properties like the cross-over between conducting and insulating behavior of electrons, its not surprising that successful theories strike a balance between short-range, discrete structure and long-range continuum effects. Even in the venerable Born-Oppenheimer approximation from 1927, we see that atomic nuclei are treated as atoms (immovable point charges), while electrons are described using the wave theory. The separation in time-scales of their motion makes this work. By the time the atoms in a molecule have even slightly moved, the electrons have zipped back and forth between them many times over.

One of the first attempts at accounting for electron-electron interaction was to use perturbation theory to add pairwise electron interactions back into the uniform gas model. The first order perturbation is the exchange energy, since it comes from pairs of electrons with the same spin exchanging momentum.\textsuperscript{23} The resulting change to the electron density can be explained at the level of correlation, $g(r)$, measuring the relative likelihood of finding an electron at the point, $r$, given that one sits at the origin. For the noninteracting gas,
\( g(r) = 1 \), while in the first perturbation, \( g(r) = 1 - \frac{9}{2}(\sin(k_F r) - k_F r \cos(k_F r))^2/(k_F r)^6 \) between electrons with parallel spin.

Full calculations of \( g(r) \) and its Fourier transform, \( S(k) \) using an accurate particle simulation technique are presented in Fig.1e,f. The function \( S(k) \) is called the structure factor by crystallographers. If the system consisted only of electrons, the structure factor would be proportional to the intensity scattered out at angle \( \theta = 2 \arcsin(\lambda k/4\pi) \) when the system is placed into a weak beam of electrons or photons of wavelength \( \lambda \) pointed in the \( \theta = 0 \) direction. The curves are labeled by \( r_s = (3/4\pi n)^{1/3} \) Bohr.

There is a duality between short and long range perspectives inherent in \( g(r) \) and \( S(k) \) as well. Long-range behavior appears at large \( r \) when \( g(r) \) approaches 1. At small \( r \), the geometry of inter-particle interactions determines the shape of \( g(r) \). Because particle dynamics is carried out in real-space, \( g(r) \) tends to be used by its practitioners to characterize short and long-range structure. Analytical solutions of many models, and especially those aiding experimental measurements, are simpler in Fourier space. There, \( S(0) \) is the integral of \( g(r) \). It provides information on the total fluctuations in the number of particles, and is a long-range quantity from which the compressibility, partial molar volumes, and other properties can be computed. Short-range structures that repeat with length \( d \) show up as peaks in \( S(k) \) at correspondingly large \( k = 2\pi/d \).

Back to the metallic/insulator problem, between 1950 and 1953 Bohm and Pines pioneered the idea of explicitly splitting the energy function (Hamiltonian) governing electron motion into local and long-range degrees of freedom. Using the intuition that long-range collective motions of electrons should look like the continuous plane-wave solutions to Maxwell’s theory, they added and subtracted those terms and called them ‘plasmons.’ (Fig. 4d) Just like photons, the plasmons are continuous waves when treated classically, but are quantized particles when understood quantum mechanically.

What remained after the subtraction was a Hamiltonian whose interactions were only short-ranged, but could not be treated with a continuum description. Instead, the short-range part describes interactions between effective discrete particles which Bohm and Pines dubbed ‘quasiparticles.’ The quasiparticles were like packs of electrons surrounded by empty space, ‘holes.’ The quasiparticles thus have larger mass and softer, screened, pair interactions (explaining why the mass has to be fixed when applying the free electron theory to metals). These new ‘renormalized’ electron quasiparticles could even have effective pairwise attraction. This latter effect was a central component to the BCS model of superconductivity, where the quasiparticles are known as ‘Cooper pairs.’ Because of its dual representation, the Bohm-Pines model gave good answers for both cohesive energies and conductivities – and described the cross-over between insulating and metallic regimes as electron density is increased.

For all its descriptive power, the Bohm-Pines approach was often lamented for its requirement for a specific set of approximations. Most damningly, it required inventing a continuum of plasmons to describe the long-range interactions of a finite set of electrons. This adds infinite degrees of freedom to a system with an initially finite number. It also required the plasmons to stop and the particles to commence at some cutoff wavelength. These troubles lead us into the problem of renormalization group theory, which is beyond the scope of the present article.

In fact, in 1954, just after the publication of the last article in the Bohm and Pines series
Four separate phases were observed (at zero temperature). Note that the density axis is reversed by the transformation $1/n = 4\pi r^3_s/3$. Reprinted figure with permission from Ref. 26. Copyright 1980 by the American Physical Society.

(b) Phase diagram of a $\mathbb{Z}_2$ electrolyte like NaCl where $n$ is the cation concentration. Lines show the position of the spinodal using methods appropriate for each theory, and the minimum indicates a critical point for fluctuation in ionic concentration. Note the temperature axis is reversed by $\beta = z^2/dk_BT$ and $\eta = \pi nd^3/6$, $d$ is the ion diameter. Reprinted from Ref. 33, with the permission of AIP publishing.

Figure 2: Both show an insulating phase at low density (labeled Wigner crystal in (a)) and a conducting phase at high density. The corresponding transition in an electron gas has not been well studied, but critical temperatures feature in the phase diagram of superconducting cuprates (where $n$ is percent of solid impurities).

above, Lindhard provided a model for collective electronic response of a metal that involved only the metal’s correlation function (by means of its dielectric coefficient, $\epsilon$). Following a decade later in 1964-65 was Hohenberg, Kohn and Sham’s density functional theory. Both developments rephrased the description of electronic structure in terms of a continuous field of electron density. Perturbation theory says that a homogeneous density $n_0$ responds to an applied field, $\phi$ as,

$$\delta n(r) = n_0 \int \chi(r, r') \phi(r'),$$

where $\chi(r, r')$ is the Fourier transform of the structure factor above. Their defining characteristic is the focus on continuous response of that density to a continuous external field, $\rho(r) = \rho[\phi(r')](r)$.

The theory may be understood as a fully long-ranged point of view that includes short-range effects indirectly through $S(k)$. It shows how to use integration to calculate all thermodynamic quantities from structure factor. The only problem is that it does not broach the issue of how to predict the structure factor. One well-known method is to assume the probability of $n(r)$ is a Gaussian on function space. In that case, the inverse of the correlation function is a self-energy term plus the inter-particle energy function. This is known as the random phase approximation (RPA), named because of its historical discovery by
Bohm and Pines following from neglecting couplings between a set of linearly independent (Fourier) modes, $n_1(r), n_2(r)$, etc. This ends up excluding all non-Gaussian fluctuations.

The ‘dielectric’ ideas encapsulated in the perturbation theory of Eq. 3 can be combined with the free electron model of Eq. 2 ($T[n]$ proportional to $n^{5/3}$), or a wavefunction calculation of the kinetic energy, $T[n]$, to synthesize modern density functional theory (DFT).\textsuperscript{17,36}

$$A[\phi] = \inf_{n(r)} T[n] + E_{\text{XC}}[n] + \int n(r) \left( \phi(r) + \frac{1}{2} \int \frac{n(r')}{4\pi\epsilon_0 |r - r'|} \right) \, dr^3. \quad (4)$$

Now the correlation function of the electron, $\chi$, is obtained from the curvature of $A[\phi]$. The unknown structure factor has been turned into an unknown functional, $E_{\text{XC}}[n]$.

Again moving forward 40 years, the relative unimportance of long-range Coulomb interactions for local structuring noticed by Lang and Perdew\textsuperscript{29,37} lead to the suggestion that the density functional method itself should also distinguish between short and long range structural effects. Implementation of this idea was perhaps first carried out by Tolouse and colleagues in 2004.\textsuperscript{38} There, the local density approximation deriving its roots in the TF theory is applied to describe short-range interactions, while the HF theory is used to ensure proper electron-pair repulsion (exchange) energies at long-range. The association of HF with long-range and density functional (DF) with short-range apparently runs counter to our association between continuum, density-based, models for long-range interactions \textit{vs.} discrete, particle-based models for short-range interactions. A major complication with our association is that it is known that the HF method describes the long-range (asymptotic) electronic interactions well, whereas the DF method does not. DF methods were historically used to describe the ‘entire’ energy function, and have thus been tailored to describe quasi-particles (the so-called exchange hole), rather than asymptotics. This association was put to the test shortly after by Vydrov and co.\textsuperscript{39} using an earlier DF called LSDA that is not strongly tailored in this way. They separately averaged the short- and long-range components of HF and DF and checked their ability to predict the cohesive, formation energies of small molecules. Doing so, they discovered that models with no HF at long range had similar descriptive power to those that used only DF at short range and only HF at long range. Split-range functionals are still an evolving research topic.

The theme of separating long-range, continuous \textit{vs.} short-range, discrete interactions runs throughout numerous other molecular-scale models. Models in this category include the ‘dressed’ ion theory, which posits that ions in solution always go in clad with strongly bound, first shell, water molecules so that their radius is larger than would be suggested from a perfect crystal (Fig. 4e). These larger radii appear in coupling to continuous water velocity fields when using the Stokes-Einstein equation for ionic diffusion coefficients.\textsuperscript{40} They should also appear when coupling to continuous ionic charge distributions in the primitive model of electrolytes to describe the volume fraction at which ion pairing will begin to cause steric problems.\textsuperscript{41} The Marcus theory of electron transport describes two separate, localized structural states of a charged molecule that interact with a continuously movable, long-range, Gaussian, field. Larger magnitude fluctuations in the solvent structure lead to broader Gaussians, which in turn are the cause of more frequent arrival at favorable conditions for the electron to jump. It is common practice in quantum calculations to explicitly model all atoms and electrons of a central molecule quantum-mechanically while representing the
entirety of the solvent with a continuous dielectric field.

The theories above are not perfect. They show issues precisely at the point where short- and long-range forces are crossing over. At high ionic concentrations, the dressed ion theory breaks down due to competition between ion-water and ion-ion pairing. When solvent molecules are strongly bound, the use of a continuous density field cannot fully capture their influence on thermodynamic properties. Even without strongly bound solvent, dielectric solvation models leave open the important question of whether electrons from the fully modeled molecule are more or less likely to ‘spill out’ into the surrounding solvent. Returning back to Aristotle’s objection to discrete objects, it is known that density based models don’t accurately capture the free energy of forming a empty cavity. Thousands of years on, we are still vexed by the question of how to understand the interface between material objects and vacuums.

**Liquid-State Theories**

The divide between short and long-range, discrete, and continuous distributions also plays a key role in the development of thermodynamic theories for gasses and liquids. In the 1860s, Boltzmann proposed his transport equation for the motion of gas density over space and time. The model employed the famous stoßzahlansatz, which states that the initial positions of molecules before each collision is chosen ‘at random.’ (Fig. 4a) In the original theory, the probability distribution over such random positions was often confused with their statistical averages – a point which lead to enormous confusion and controversy persisting even until 1960.

This history very nearly parallels the development of electronic density theories. After electromagnetism and gas dynamics had been worked out at the end of the 19th century, Gibbs’ treatise on statistical mechanics laid out the classical foundations of the relationship between statistics and dynamics of molecular systems. Nevertheless, there were contemporary arguments with Ehrenfest and others about the need for introducing statistical hypotheses into an exact dynamical theory. Early on, it had been hoped that an exact study of the motion of the molecules themselves could predict the appropriate ‘statistical ensemble’ by finding long-time limiting distributions. However, that hope was spoiled by the notice that initial conditions must be described statistically. The idea persists even at present, though it has been tempered by the recognition that sustaining nonequilibrium situations requires an infinite environment, which has to be represented in an essentially statistical way.

The resolution, according to Jaynes, is to understand the Boltzmann transport equation as governing the 1-particle probability distribution, $NP(r|C)$, rather than the mass density (or average) of the actual molecules, $n(r)$. It turns out that this switch in perspective from exact knowledge of all particle positions to probability distributions is one of the key ways of separating short and long-range effects. Two of the oldest and most widely known uses of this method are in the dielectric continuum theory dating from before Maxwell’s 1870 treatise, even to Sommerfeld (Fig. 4c), and the Debye model of ionic screening from 1923. For both, a spatial field $E(r - r_0)$, emanating from a discrete molecule at $r_0$, is put to a bulk thermodynamic system whose average properties are well-defined using, for example, $P(r|E)$ for the dipole density $\mu(r)$ at point $r$, due to a field, $E$ or $n(r; \phi)$ for the ion density.
at point \( r \) due to a voltage, \( \phi \). Treating \( \phi \) and \( E \) as weak perturbations and looping \( \mu(r) \) (or \( n(r) \)) back in as additional sources gives a self-consistent equation for the response of a continuum.

As was the case for electronic structure theory, the most concise description of this type of self-consistent loop is provided by a density functional equation for the Helmholtz free energy (with \( \beta = 1/k_B T \)),

\[
\beta A[E, \beta] = \inf_{\mu \in \{\mu\}} [-\log(\mu) - \beta E \cdot \mu] \approx -\ln \sum_{\mu \in \{\mu\}} g(\mu)e^{\beta E \cdot \mu}.
\]  

(5)

The curvature of \( A \) with changing applied field, \( E \), gives the response function which is related to the conventional dielectric. Consider first a case where \( \mu \) contains enough information to exactly assign a dipole to every one of \( N \) molecules. An example would be a single molecule with twice as many ways to create a small dipole as a large one, \( g(4) = 2 \) and \( g(2) = 4 \). Then \( g(\mu) \) is a product over counting factors. The free energy, \( A \), will have jump discontinuities in its slope as the field, \( E \) is varied because the solution jumps from one assignment \( (\mu = 2) \) to another \( (\mu = 4 \text{ at } 2E \geq \ln 2) \). Its graph is very much like Fig. \[\text{a}]. In a discrete function space, density functional theory equations yield solutions exhibiting the a discrete nature.

On the other hand, if \( g(\mu) \) varies continuously with \( \mu \) in some range of allowed average densities, then the solution will describe a smooth field free energy. Interestingly, starting from the first situation and computing

\[
S[\bar{\mu}, \beta] = -\beta \sup_E \left[ A[E, \beta] + \int E(r) \cdot \bar{\mu}(r)dr \right]
\]

(6)

leads to such a continuous version of \( \log g(\mu) \approx S(\mu) \) (in fact its concave hull). This concave function allows densities that are intermediate between discrete possibilities for the system’s state. Such intermediate densities could only be reached physically by averaging, so that \( \bar{\mu} \) is an average polarization over possible absolute assignments of dipoles to molecules, \( \mu \).

After the theory of self-consistent response to a long-range response theory had been
worked out, further development of liquid-state theory had to wait 40 years for developments in quantum-mechanical interpretation of light absorption and scattering experiments. Some early history is given in Ref.\textsuperscript{54} and Debye’s 1936 lecture\textsuperscript{55} in which he explains how electronic and dipole orientational polarization could be clearly distinguished from measurements of the dielectric capacitance of gasses along with the great advancements made in the 1920s (which Debye credits to von Lau in 1912) of using x-ray and electron scattering to confirm molecular structures already adduced by chemists from symmetry and chemical formulas alone. Thus, the long-range theory gave a comprehensive enough description of macroscopic electrical and density response that it could be used as a basis to experimentally determine local structure.

With statistical mechanics, quantum mechanics, and molecular structure in hand, liquid-state theories developed in the 1930s-50s through testing hypotheses about the partition function against experimental results for heat capacities. One of the earliest models was the ‘free volume’ (also known as cell model) theory, developed by Eyring and colleagues and independently by Lennard-Jones and Devonshire in 1937. The theory was put on a statistical mechanical basis by Kirkwood in 1950,\textsuperscript{56} as essentially expressing the free energy of a fluid in terms of the free energy of a solid composed of freely moving molecules trapped, one each, in cages exactly the size of the molecular volume, plus the free energy cost for trapping all the molecules in those cages in the first place. It competed\textsuperscript{57} with the ‘significant structure’ theory of liquids (also proffered by Eyring and colleagues\textsuperscript{58,59}). In the significant structure theory (Fig. 4f), the partition function for the fluid is described as an average of gas-like and solid-like partition functions to account for the difference in properties between highly ordered and more disordered regions (which contain vacancies).

**Scaled Particle vs Integral Equations**

Also around that time, a competition emerged between the scaled particle theory\textsuperscript{60} and the ‘integral equation’ approach based on (and now lumped together with) Percus and Yevick’s\textsuperscript{61} use of the Ornstein and Zernike’s 1914 integral equation for liquid structure. This connection was significant, since theories of the correlation function prior to 1958 applied the superposition approximation due to Kirkwood, Yvon, Born, and Green (ca. 1935).\textsuperscript{62,63}

The scaled particle theory approach takes the viewpoint that the number, sizes and shapes of molecules in a fluid are determined by integrating the work of ‘growing’ a new particle in the middle of a fluid. The key idea is that the chemical potential of a hydrophobic solute is equal to the work of forming a nanobubble in solvent. For simple hard spheres, the work is $PdV$, where $P = k_BTn_0G(d)$, $n_0$ is the bulk solvent density, and $G(d)$ (Fig. 4b), the density of solvent molecules on the surface of the solute at size $d$. Hence, knowing the contact density for any shape of solute molecule provides complete information on the chemical potentials of those molecules. This very local idea can be related to counting principles at very small sizes,\textsuperscript{64} and interpolated to macroscopic ideas about surface tension at very large sizes – creating a way to interpolate between the two scales.

On the other hand, the integral equation approach expresses the idea that long-range fluctuations in density are well described by a multivariate Gaussian distribution. If the probability distribution of the density, $n(r)$, was actually Gaussian, its probability would
be,

\[ P[n(r)] = P[n_0] \exp \left( -\frac{\beta}{2} \int drdr' (n(r) - n_0)G(r, r')(n(r') - n_0) \right) / Z[\beta G], \] (7)

where \( G(r, r') \equiv \text{const} \cdot \delta(r - r') - c(r - r')/\beta. \) In the RPA, \( -c(r)/\beta \) is energy for placing a pair of molecules at positions \( r \) and \( r'. \)

When they are not Gaussian distributed, the correlations in instantaneous densities, \( n(r) \), provide a means of estimating \( c \), the direct correlation function. \( \) This long-range idea has been used to show that \( G \) degenerates to the pairwise energy for very large separations \( (G(r) \to U(r) \text{ as } r \to \infty) \). For simple hard spheres, it can also be related to counting principles at short separations, since there the correlations must drop to -1, expressing perfect exclusion. Assuming limits both hold right up to the discrete boundary of a solute yields the mean spherical approximation (MSA, Fig. 4b).

These two theories thus express, in pure form, the divide between short-range and long-range viewpoints on molecular structure. Integral equation theories are most correct for describing continuum densities and smooth interactions. Theories that, like SPT, are based on occupancy probabilities of particles in well-defined local structures and geometries are most correct for describing short-range interactions that can contain large energies and discontinuous jumps.

Fig. 3b shows \( P(n|d) \), the probability that a randomly chosen sphere of radius \( d \) contains exactly \( n \) discrete water molecules. Each curve is marked by its value of \( d \) in nanometers. The free energy for creating an empty nanobubble of size \( d \) in water is shown in its counterpart, Fig. 3a. Both computations are very closely related, and easiest to do from the local picture of scaled particle theory. The cavity formation free energy (Fig. 3a) is, in principle, also able to be computed from a density functional based on relating the logarithm of Eq. 7 with the entropy. \( \) However, when the calculation is done in the usual density functional way the cavity formation free energy is surprisingly difficult to reproduce.

**Perturbation Theories**

Slowly but surely during the same time period as integral equation theories were being developed the method of molecular dynamics emerged. \( \) Its primary limitations of small, fixed, particle numbers, large numbers of parameters, finite sizes and short timescale simulations weigh heavy on the minds of its practitioners. \( \) Early models of water needed several iterations before reproducing densities, vaporization enthalpies and radial distribution functions from experiment. Initial radial distributions from experiment were wrong, and the models had to be corrected and then un-corrected to chase after them. \( \) Surprisingly, early calculations took the time and effort to calculate scattering functions and frequency-dependent dielectrics to compare to experiment. \( \) By contrast, the bulk of ‘modern’ simulations report only the data that can be readily calculated without building new software.

By checking data from integral equations against molecular dynamics and scattering experiments it was clear by 1976 that many powerful and predictive methods had been created to describe the theory of liquids. \( \) Nevertheless, there remained even then lingering questions about the applicability of integral methods to fluids where molecules contained
dipole moments, and the treatment of long-range electrostatics in MD. Some difficulties in modeling phase transitions and interfaces were anticipated, but it was hardly expected that bulk molecular dynamics methods themselves would stall and eventually break down when simulating liquid/vapor and liquid/solid surfaces.

It was also beginning to be recognized that there were two complementary approaches to the theory of fluid structure. The short-range viewpoint stated that the radial distribution function should be reproduced well at small intermolecular separations (small distance in real-space). This leads to good agreement with interaction energies and pressures so that the virial and energy routes to the equation of state work well. The long-range viewpoint instead emphasizes reproducing the structure factor at small wavevectors. Because of this, it favors using the compressibility route to the equation of state and leads to good agreement with fluctuation quantities.

**Inherent structures**

Water proved to be a major challenge to molecular models because of its mixture of short-range hydrogen bonding and long-range dipole order. One successful physical picture of water was provided by the Stillinger-Weber ‘inherent structure’ model introduced in the early 1980s. It represented a cross between the ‘significant structure’ theory and the free volume theory. In it, molecules are fixed to volumes defined by their energetic basins, rather than by a rigid crystal lattice. Where the free volume theory had only one reference structure, the inherent structure (like the significant structure theory) had many. One for each basin. Each energetic basin looks, on an intermediate scale, like a distortion of one of the crystalline phases of ice. Thermodynamic quantities can be predicted using the energies and entropies associated to each basin – by virtue of the minimum energy structure and the number of thermal configurations mapping to that minimum.

![Figure 4: Hybrid discrete/continuum theories.](image)

(a) Boltzmann picture of scattering by one particle chosen ‘at random’ from the continuum. (b) Mean spherical approximation for the hard sphere fluid of diameter $\sigma$. $g(r)$ and $c(r)$ are known at $r << \sigma$ and $r >> \sigma$, but the central region is a guess. (c) Sommerfield conception of a dipole above a continuous polarizable medium. (d) Bohm-Pines conception of a quasiparticle (purple, central peak) and two long-range plasmons (blue). (e) Dressed ion, quasichemical, or Lorenz-Lorentz-Mossotti-Clausius cavity models of a discrete molecule in a continuum solvent. (f) Significant / inherent structure theory of a coexisting mixture of ordered and disordered regions making up an overall homogeneous phase.
Hybrid Theories in Liquid-State Structure

The Lennard-Jones fluid presented a challenge to the integral equation and SPT theories above because it contains both short-range repulsion and long-range attraction. At high densities, however, it was found that the radial distribution function was almost identical to the radial distribution for hard spheres (compare Fig. 3e and Fig. 4b). The transition from liquid to solid was also described fairly well using the hard-sphere model. On the other hand, at low densities the distribution function could be described by perturbation from the ideal gas. These two discoveries justify the use of a perturbation theory to calculate the effect of long-range interactions at very low and very high densities. A comparison of molecular dynamics with integral equation plus correction theories is shown in Figs. 3e,f.

At intermediate densities, however, a liquid-to-gas phase transition occurs that can be qualitatively understood, but not explained well as a perturbation from either limit. Instead, the integral equation method turns out to hold the best answer in the supercritical region. It is often encountered in the form of a perturbation theory from the critical point. It is no accident that the integral equation method works well here. Supercritical fluids are characterized by long-range correlations that can take maximum advantage of that theory. For the same reason, integral equations describe the compressibility well, but do poorly on the intermolecular energy.

This raises the question of whether there exists an inverse perturbation theory – deciding on the long-range shape of correlation functions first and then correcting them for packing interactions at short-range. This kind of correction would look like an adjustment to the solution of the Poisson-Boltzmann equation. This kind of approach has been presented in Refs. More recently, Remsing and Weeks introduced a general scheme for adding local corrections to long-range continuum theory based on a split-range Coulomb pair potential. In this theory, the long-range forces (from the long-range, smooth part of the potential) are used to compute a ‘starting’ density using RPA-like perturbation from a uniform fluid. Although it seems a lot like the molecular density functional method, this starting density remains smooth at the origin and should describe, for example, the ultrasoft restricted primitive model, which has no short-range Coulomb interactions. Next, the local structure is added by perturbatively creating a cavity at origin.

Counter to the historical development of exchange corrections to TF theory, the method of adding long-range perturbation on top of known short-range energies appeared before the works above. Widom’s potential distribution theory divides the chemical potential of a molecule into structural, cavity formation terms, and long-range solvent ordering contributions. Originally, the former were based on a local density approximation from the hard sphere fluid and the latter from a pairwise term that amounted to a van der Waals theory. Detailed molecular simulations have been used to compare the two approaches with exact simulations by brute force calculation of all the energetic contributions. Focusing on the short-range structure leads to a model whose first step is to form an empty cavity in solution (blue curve in Fig. 5aa, labeled ‘Packing’). Fig. 5aa shows the free energies of the next step (Na+ and Cl- ions) divided into ‘long-range’ and ‘inner-shell’ parts of the re-structuring. All points come from MD. If, instead, the long-range interaction between an ion and solvent occurs first, we are lead to couple the solvent to the smooth electric field of a Gaussian charge distribution. Fig. 5ab shows the free energy of that first step as a function of charge for a
(a) Ion solvation free energy components for the short-range (empty cavity first) model computed from an MD model of NaCl in SPC/E water. $R$ is the cavity radius, ‘HS’ denotes the cavity formation cost, ‘LR’ is the full ion-SPC/E water interaction after a cavity is present, and ‘IS’ is the free energy of removing the cavity constraint.

(b) Interaction free energy of SPC/E water with a Gaussian charge distribution, $Q \exp(-r^2/l^2)/(l\sqrt{\pi})^3$. Points correspond to simulation data, while lines assume a constant dielectric model. Adapted with permission from Ref. [87] Copyright 2016 American Chemical Society.

Both continuous and discrete approaches were combined by Matyushov [90] to study charge transfer and dipolar solvation. In that work, the dipole density response function to the electric field of a dipole is worked out in linear approximation. A sharp cutoff is used to set the field to zero inside the solute, resulting in a hybrid short/long range theory. The approach succeeds because the linear response theory is correct at long range, where the largest contributions to the solvation energy of a dipole originate.

**The Future: A Middle Way**

Early Eastern thought tends to place opposing ideas next to one another in an attempt to understand them as parts of a whole picture. Written around the beginning of the Middle ages, in 400 AD, the Lankavatara Sutra relates Buddha’s view that this unity applies to atoms and ‘the elements’ (which refer to something like the classical Greek elements), ‘even when closely examined until atoms are reached, it is [only the destruction of] external forms whereby the elements assume different appearances as short or long; but, in fact, nothing is destroyed in the elemental atoms. What is seen as ceased to exist is the external formation of the elements.’ Perhaps inspiring to Bohr sixteen centuries later, [91] the quote concludes, “I am neither for permanency nor for impermanency ... there is no rising of the elements, nor their disappearance, nor their continuation, nor their differentiation; there are no such things as the elements primary and secondary; because of discrimination there evolve the dualistic indications of perceived and perceiving; when it is recognised that because of discrimination there is a duality, the discussion concerning the existence and non-existence of the external world ceases because Mind-only is understood.” In the 1600s, just before Newton’s time,
Miyamoto Musashi wrote “Students of the Nito Ichi School of strategy should train from the start with the [short] sword and the long sword in either hand... The long sword should be wielded broadly and the companion sword closely.”

Of course, it is impossible to deduce scientific principles if we include any elements of mysticism in a theory. Nevertheless, the debate on the separation between short and long-range seems to permeate history. This idea that a meaningful understanding of collective phenomena should be sought by combining physical models appropriate to atomic and macroscopic length scales was taken up even recently by Laughlin, Pines, and co-workers. They state, “The search for the existence and universality of such rules, the proof or disproof of organizing principles appropriate to the mesoscopic domain, is called the middle way.”

On one account it is clearly possible to set the record straight. There are well-known ways of converting local structural theories into macroscopic predictions and as vice-versa. Bayes’ theorem states that, for three pieces of information, \(A\), \(B\), and \(C\),

\[
P(A|BC) = \frac{P(B|AC)P(A|C)}{P(B|C)}. \tag{8}
\]

If ‘C’ represents a set of fixed conditions for an experiment, ‘B’ represents the outcome of a measurement, and ‘A’ represents a detailed description of the underlying physical mechanism (for example complete atomic coordinates), then Bayes’ theorem explains how to assign a probability to atomic coordinates for any given measurement, ‘B’. Of course, in a reproducible experiment, \(C\) will completely determine \(B\), so \(B = B(C)\). Thus, the probability distribution over the coordinates is a function only of the experimental conditions, \(P(A|BC) = P(A|C)\). This summarizes the process of assigning a local structural theory from exactly reproducible experiments.

On the other hand, a local structural theory provides an obvious method for macroscopic prediction. Given a complete description, ‘A,’ simply follow the laws of motion when interacting with a macroscopic measuring device, ‘B.’ This would properly be expressed in the language above as \(P(B|AC) = P(B|A)\), since the experimental conditions are irrelevant. Bayes’ theorem then gives us a conundrum, \(P(B|C) = P(B|A)\), stating that every microscopic realization of an experiment must yield an identical macroscopic outcome.

The solution to the puzzle is to realize that unless an experiment is exactly reproducible, \(BC\) is always more informative than the conditions, \(C\), alone and \(P(A|BC) \neq P(A|C)\). This explains why studying exactly integrable dynamical systems is such a thorny issue, and is the central conceptual hurdle passed when transitioning from classical to quantum mechanics. Now identifying ‘B’ with a partial measurement that provides a coarse scale observation of some long-range properties, \(P(A|BC)\) describes a distribution over the short-range, atomistic, and discrete degrees of freedom. Because of experimental uncertainty, the exact location of those atoms is evidently subjective and unknowable (since it is based on measurement of \(B\)). Nevertheless, it can in many cases be known to a high degree of accuracy.

Density functional theory traditionally focuses on \(P(B|C)\), where ‘B’ is the average density of particles in a fluid and ‘C’ is the experiment where a bulk material is perturbed by placing an atom at the origin. However, with a minor shift in focus, \(P(B|A'C)\) can also be found, representing the average density under conditions where a particle is placed at the
origin and some atomic information, $A'$ is also known. The objective of such a density functional theory would be to more accurately know the long-range structure by including some explicit information on the short-range structure. The dual problem is to predict $P(A|B'C)$, the distribution over coordinates when we are provided with some known information on the long-range structure. In a complete generalization, we might focus instead on $P(AB|A'B'C)$, representing the average density and particle distribution under conditions where density and particle positions are known only in part. Bayes’ theorem shows us that this kind of generalization is just the result of weaving the primal and dual problems together, since (given the redundancies, $B' = B'(B)$ and $A' = A'(A)$), $P(A|A'B'C) = P(A|B'C)P(A|B'C)/P(A'|B'C)$, and $P(B|A'B'C) = P(B|A'C)/P(B'|A'C)$.

The arguments above can be repeated for each of the elements in Table 1—replacing SR with $A$ and LR with $B$. What emerges is a persistent pattern of logical controversy, where a problem can be apparently solved entirely from either perspective. In some areas, one of the other approach is more expedient. In every case, however, recognizing and using both sides has proved to be profitable. Comparing these two perspectives, we find that the discussion concerning the existence of long and short-range theories ceases, leaving only different ways to phrase probability distributions.

We have now arrived at a point in the history of molecular science where these two great foundations, short-range, discrete structures and long-range, continuum fields are at odds with one another. Molecular dynamical models are fundamentally limited by the world view that all forces must be computed from discrete particle locations. Computational methods treating continuum situations focus their attention on solving partial differential equations for situation-specific boundary conditions. Connecting the two, or even referring back to simple analytical models, requires time and effort that is seen as scientifically unproductive. What’s worse, it reminds us that many, lucidly detailed, broad-ranging, and general answers were already presented in the lengthy manuscripts which set forth those older, unfashionable models.

Indeed, local and continuum theories are hardly on speaking terms. In molecular dynamics, the mathematics of the Ewald method for using a Fourier-space sum to compute long-range interactions are widely considered esoteric numerical details. Much effort has been wasted debating different schemes for avoiding it by truncating and neglecting the long-range terms. On the positive side, the central issue of simulating charged particles in an infinite hall of mirrors has been addressed by a few works. Much greater effort has been devoted to adding increasingly detailed parameters, such as polarizability and advanced functional forms for conformation and dispersion energies, to those atomic models. Apparently, automating the parameterization process is unfundable. In the case of polarization and dispersion, the goal of these atomic parameters is, somewhat paradoxically, to more accurately model the long-range interactions. The problem of coupling molecular simulations to stochastic radiation fields has, apparently, never been considered as such. Instead, we can find comparisons of numerical time integration methods intended to enforce constant temperature on computed correlation functions. In PDE models, actual molecular information that should go into determining boundary conditions, like surface charge and slip length, are replaced by ‘fitting parameters’ that are, quite often, never compared with atomic models. Indeed, it is difficult to studies in the literature that even contain a model detailed enough to connect the two scales are few and far between.
We are also at a loss for combining models of different scales with one another. Of the many proposed methods for coupling quantum mechanical wavefunction calculations to continuous solvent, essentially all of them neglect explicit first-shell water structure. Rather than attempting to faithfully reproduce the underlying physics, models are compared by directly checking against experimentally measured energies – and no clear winner has emerged (nor can it). Similar remarks can be made for implicit solvent models coupling molecular mechanics to continuum. There is currently debate on the proper way to conceptualize the ‘stiffness’ parameter of solvent modes in Marcus theory.

In order to make progress, we must apparently work as if we had one hand tied behind our back. Used correctly, simulations provide a precise tool to answer a well-posed question within a known theory, or as a method of experimentation to discover ideas. However, when used absent a general theory, simply as a tool to reproduce or predict a benchmark set of experimental data, simulation is not capable of providing any detailed insight or understanding of molecular science.

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