

A Child of Prediction.

On the History, Ontology, and Computation of the Lennard-Jonesium

Keywords: molecular dynamics, simulation, computation, modeling, prediction

Abstract

The Lennard-Jones (LJ) fluid, named after mathematician-physicist-chemist Sir John Lennard-Jones (1894-1954), occupies a special place among fluids. It is an ideal entity, defined as the fluid whose particles interact according to the Lennard-Jones potential. This paper expounds the history of the LJ fluid to throw light on the tensions between theory and computational practice.

The paper argues for the following claims. Firstly, the computational approach—even prior to the computer—pragmatically aims at prediction, not truth. Secondly, computer simulation methods, especially “molecular dynamics” (MD), triggered a change in epistemology. Now, simulated model fluids became targets of investigation in their own right. The urge for prediction turned the LJ fluid into the most investigated fluid in engineering thermodynamics. Thirdly, MD took a huge upswing in the 1990s, due to exploratory options in simulation. We discuss how, under these conditions, predictive success might be fraught with problems of reproducibility.

Introduction

The Lennard-Jonesium, named after mathematician-physicist-chemist Sir John Lennard-Jones (LJ, 1894-1954)¹, occupies a special place among substances. It is an ideal entity, a child of molecular theory and the computer, and defined as that substance whose particles interact according to the LJ potential. This potential describes the pairwise repulsive (very small distance) and attracting (van der Waals) forces with a relatively simple and mathematically tractable expression.

¹ Born as John Edward Jones, he added the name of his wife to his surname when they married in 1925. He was knighted in 1946.

One might assume that this topic would be of interest only for some specialists from computational chemistry and physics. However, as a biography can tell the history of one person by involving a wider story of family and culture and thus can throw light on bigger transformations in society, the history of the Lennard-Jonesium exemplifies the dynamic relationship between prediction, theory, mathematization, and computer instrumentation. This history includes a computational turn prior to the computer and a new culture of prediction emerging around 1990, and it throws additional light on philosophical transformations that involve epistemology, methodology, and the social organization of science.²

The present paper discerns four phases in the creation of the Lennard-Jonesium. The story has the form of a drama in four acts. It opens with a prelude in front of the curtain that reminds the reader of the Laplacian program, a bold, mathematics-driven attempt to generalize Newtonian mechanics to all of physics. The incarnation of the rational-mechanical dream is the Laplacian demon that can predict everything from computing the dynamics of particles and forces, equipped with superhuman intelligence. Laplace was aware that applying this idea to the prediction of macroscopic phenomena from the interactions of the particles on the molecular scale was way beyond mathematical tractability at his time. However, it set the standard: In theory, the prediction of macroscopic phenomena can succeed based on the true mathematical form of interaction between particles on the molecular scale plus sufficiently powerful mathematical means.

Act 1 starts out with the renaissance of the Laplacian program. Over the second half of the 19th century, pioneers like Maxwell and Boltzmann developed statistical mechanics, an approach that treated thermodynamic phenomena by a statistical strategy based on distributions in ensembles of very many particles. Johannes Diderik van der Waals (in his 1873 dissertation) considered averaged interactions between particles in a given system.

² The transformations associated with simulation modeling have been intensely studied in philosophy, see for example Humphreys (2004), Winsberg (2010), Morrison (2015), Lenhard (2019), and also in history of science, see Galison (1997) for an early instance. The history of molecular dynamics has not yet received the attention it deserves, apart from some noteworthy work from practitioners (Rowlinson 2002, Battimelli et al. 2020, Ciccotti et al. 2022). In particular, the philosophical and historical analysis of thermodynamics engineering is practically new territory.

From there, a slow but steady flow of contributions searched for ways to analyze material properties and macroscopic phenomena via mathematical models of particles and their interactions. In the early 20th century, mathematically minded theoreticians, with John Lennard-Jones among them, set in motion a computational turn. Although this approach looks much like a revival of the (Laplacian) rational mechanics dream, it is importantly different. The new computational approach deliberately upgrades mathematical tractability. It specifies a mathematical structure that is not an idealized model of a theory but, rather, together with adjustable parameters is flexible enough so that predictions (more or less) match measured data. Thus, the hunt for the “true” potential was replaced by the ongoing elaboration of potentials that balance theoretical adequacy with mathematical tractability and empirical fit.

Act 2 deals with the unanticipated upheaval triggered by quantum theory. This theory provided a new fundament for phenomena on the molecular scale, but had a remarkably small effect on the computational approach to predicting macroscopic phenomena described above. Incorporating quantum theory left the mathematical treatment virtually unchanged. Lennard-Jones numerically investigated a family of potentials and chose one of the four adjustable parameters in accordance to quantum theoretical results. The computational approach achieved assuring successes in terms of matching a growing range of calculated properties to measured ones. Over the next two decades, this approach was elaborated, with the LJ potential as the most widely used way of describing the particle interactions, as it provided the best balance between theory, mathematical tractability and empirical fit. Significantly different from a rational program à la Laplace, the computational approach aimed at pragmatics rather than truth.

Act 3 welcomes the computer on the stage. Pioneering works in the 1950s and 1960s explored numerical simulation methods to solve Newton’s equation of motion for a large number of particles, called “molecular dynamics” (MD).³ Such methods gave mathematical tractability a new sense. Now, simulated model fluids became objects on their own, the prime

³ We leave aside Monte Carlo (MC) methods, the second main branch of computer-based molecular simulation. A similar story could be told about MC.

targets of investigation.⁴ In this context, the LJ substance acquired paradigmatic status in the field of MD – the (ideal) model substance⁵ whose definition is motivated by a computational method of prediction. In this sense, it is a child of prediction.

Act 4 examines a twist internal to MD. Since the 1990s, MD grew into a widely used tool in both science and engineering for predicting the properties of materials. Both LJ potential and substance retained their prominent status. We argue that this upswing rests on the exploratory options that cheap and easily accessible computing power offers. These options go hand in hand with a new social organization of research and lead to a new culture of prediction.⁶ The section discusses how simulations, even those of the simple Lennard-Jonesium, acquire a bricolage character that might lead to philosophical problems, including problems with reproducibility.

Prelude: particles, forces, mathematics—the rational paradigm

One of the most often told stories about modern science is the success of Newton’s theory of gravitation. Core ingredients are the daring idealization of sun and planets into point masses, together with the invention of a mathematical way to investigate the resulting dynamics (differential calculus). Arguably, Newtonian mechanics gained in influence over the 18th century, culminating in the “Laplacian program” (Fox 1990) to unite all of physics under the

⁴ Tractability is a fundamental issue in philosophy of simulation since the pioneering Humphreys (1991). The autonomy of models is beautifully and influentially discussed in Morgan and Morrison (1998).

⁵ A remark on terminology. The name *Lennard-Jonesium* highlights how common the usage of the LJ substance is. This substance can occur in all three phases. However, in a thermodynamic sense, fluids are especially challenging, because they lack the order of crystals but are not as random as gases. Hence the focus of researchers is often on the *LJ fluid*.

⁶ Regarding the social organization, fostering an ongoing recent discussion about computational science, cf. [reference blinded], Wieber and Hocquet (2020), Hocquet and Wieber (2021).

perspective of particles that interact via forces—and to perfect the pertaining mathematical analysis.⁷ The well-known “Laplacian demon” illustrates how comprehensive the ambition is:

“We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed, if this intellect were also vast enough to submit these data to analysis, it would embrace in a single formula the movements of the greatest bodies of the universe and those of the tiniest atom; for such an intellect nothing would be uncertain and the future just like the past would be present before its eyes.” (Laplace 1902 <1814>, p. 4)

Laplace promises an all-encompassing predictive capability that not only rests on a deterministic viewpoint, but also requires an intelligence whose mathematical abilities are far superior to the human ones. Nevertheless, the position of mathematics is remarkable. Laplace rightly pointed out that actual prediction is beyond human powers. Where Newton had mastered the dynamics between two moving masses, technically solving the Newtonian equations of motion, the computing demon faces a task of indefinitely greater proportions. He would have to solve a far greater number of these equations, namely for all particles of the world. Although this situation looks discouraging for a being with the limited power of a human, Laplace’s point of view does not express humility toward the attempts of prediction. Quite on the contrary, Laplace expressed no doubts that the mathematical formulation captures reality. In the hands of Laplace and others, the integral and differential calculus had not only developed into a powerful and theoretically sophisticated tool. It had acquired metaphysical significance: The inner structure of physical reality was assumed to be of mathematical nature—it could be expressed in the language of calculus, in particular by particles and the forces acting between them, following relatively simple mathematical laws. We will refer to it as the rational standpoint or paradigm.⁸

⁷ Laplace’s *Traité de mécanique céleste* (1799-1825) brought the mathematical instrument of calculus and differential equations to full bloom and earned Laplace his fame.

⁸ This viewpoint has also been called rational mechanics. The status of rational mechanics is debated in history and philosophy of science. Truesdell counts as a chief proponent of rational mechanics (cf., e.g. 1968), whereas Wilson (2006) analyzes much of the rational picture to be a “facade”—to name but two rich contributions.

This standpoint envisions the research process in physics as deriving consequences (predicting phenomena) from mathematically formulated general laws. Empirical backing is of course important, but defenders of the rational standpoint typically are convinced that (more or less) simple and general laws rule physics because the mathematical cosmos of higher analysis (calculus) fits the real cosmos. Therefore, Laplace's demon does not so much highlight intractability, but rather the principled power of mathematization: it captures the laws and the strategies to their mathematical analysis, even if that does not deliver on the promise of prediction.

Laplace was one of the boldest figures regarding the mathematization of science. He tried to emulate the successes in astronomy in various other fields, including the phenomenon of capillarity. There, his program led to an impasse. Technically, a (differential) equation of motion determines the movement of a particle, mathematically speaking by simultaneously solving "Newton's equations" for all particles.⁹ Actually doing this, however, was out of the question. When Laplace studied capillarity, for instance, he resorted to continuum models, giving up the picture of discrete interacting particles.

In a way, the particles-and-forces picture had reached an impasse of mathematical tractability that forced scientists to take other routes, in which matter was treated as a continuum. Two generations of scientists accepted this state of the matter. While mathematization took an enormous upswing in the 19th century (in a way that Laplace had not foreseen), the labyrinth of myriad particles and forces ceased to be of primary interest (or of interest at all), given the success of continuum theories. Time for the curtain to open for Act 1 and a conceptual shift that eventually led to a renaissance of the particles-and-forces approach that included the invention and adoption of the LJ potential.

Act 1: Revival and a computational turn

In the later 19th century, pioneers like Maxwell and Boltzmann found ways to revive the particle-forces picture. They circumvented the complexities of very many interacting particles by probabilistic mathematics and thus created a branch of thermodynamics that became known as statistical mechanics or molecular thermodynamics. This yielded new interpretations of the phenomenological laws of thermodynamics. Regarding the substances

⁹ This solution is meant when Laplace talks about "a single formula" in the quote above.

that could be treated then by these theories, severe restrictions came from the fact that solutions of the probabilistic equations could only be found for the simplest cases, like gases modeled as hard spheres and ideal crystals.

Boltzmann praised the theory that all of physics comes down to the interaction of material particles:

“If this theory would hold good for all phenomena, we should be still a long way off (...) to know everything. But the difficulty to enumerate all the material points of the universe, and determining the law of mutual force for each pair, would be only a quantitative one; nature would be a difficult problem, but not a mystery for the human mind.” (Boltzmann 1895, p. 413)

Boltzmann clearly echoes Laplace, maybe with less metaphysical conviction, but with equally full trust in mathematization. Of course, he is also admitting the quantitative difficulty. The quantitative question is accessible because statistical mechanics provides a bridge between the theoretical forces and empirically measurable (macroscopic) properties.

In his PhD thesis, van der Waals took a different approach (van der Waals 1873): based on the picture of interacting particles, he developed a mean field theory based on suitable averaging, finally resulting in his famous equation of state which accounts both for repulsive and attractive interactions.

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (1)$$

The equation contains two adjustable parameters a and b accounting for these different interactions. If both are zero, the equation is the ideal gas law where no pairwise interaction occurs. We do not discuss here how van der Waals motivated the particular form of equation (1). One can see van der Waals’ work as a step toward the revival of the rational standpoint à la Laplace. With the correct mathematical description of how particles interact, thermodynamic properties can be computed “from below”.¹⁰

Another famous equation of state is the virial equation (Kamerlingh Onnes 1901/1902) that can be understood as a density expansion of the ideal gas law.

¹⁰ We would like to point out that we intentionally use the somewhat neutral term “particle” because the existence of atoms was still highly controversial at the time.

$$\frac{p v}{R T} = 1 + B \frac{1}{v} + C \frac{1}{v^2} \quad (2)$$

Like equation (1), the equation (2) refines the ideal gas law by adding parameters (we stopped after the second term; if $B, C = 0$, then (2) is the ideal gas law). Importantly, the second virial coefficient B is (indirectly) measurable and it is known from the theory of molecular thermodynamics that it is related mathematically to the pair potential by an integral. Hence, there is a bridge between empirical measurement and pair potentials, but passing it is not straightforward. One cannot derive or estimate the form of the potential (force) from theory and observation. The only feasible approach was indirect: first guess the form, integrate and then compare the compound to measured values. This approach utilizes two simplifying conditions: First, interactions are restricted to *pairwise* interactions, else the problem would be intractable. For the same reason, the *form* of the pair interaction potential must be mathematically convenient. Since the simplicity of mathematical laws is part-and-parcel of the rational standpoint, it is often open to interpretation whether authors are assuming a simple potential out of metaphysical principles or rather pragmatic opportunism.

The hopeful expectation in the line of the rational standpoint was that there this a true and general form of the potential so that different substances differ (only) by their characteristic parameters. “All were hoping, as Einstein [...] had been earlier, that the form of the intermolecular potential would be universal.” (Rowlinson 2002, p. 204) Bringing this expectation to the test first required a set of relevant data precise enough so that one could adjust the parameters—to then see how good a match could be achieved. In 1920, it was possible to get reasonably good data on transport properties, namely viscosity, thermal conductivity and diffusion coefficients of gases. The difficulty was to relate these properties to the pair potential, which involved solving complicated integrals. The theories of Chapman and Enskog, who derived it from Maxwell (Chapman) and Boltzmann (Enskog) gave a celebrated solution. This theoretical breakthrough is rightly admired, but in practice, it led to formidable integrals utterly intractable but in the simplest cases.

What we identify as a computational turn is a practice-oriented approach that ranks tractability higher. The complication, and the interest from a philosophical standpoint, comes from the fact that tractability is not in line with derivation from theory. One had to find a sort of compromise. The art of framing such a compromise has much to do with what later acquired the name *computational* sciences. The 1920s had no electronic computer in sight and taking a computational standpoint was highly unusual.

From such viewpoint, what could the function for describing the pair interactions between particles look like? It has to have at least two contributions, one for describing repulsion, which acts mainly at very small distances between the particles, and one for describing the attraction (namely the van der Waals forces), which is important at intermediate distances and fades out at larger distances. In the times well before the computer, which we are considering here, the range of functions which were mathematically tractable was rather limited; one had to rely on logarithmic tables and mechanical calculation devices. A convenient guess that was still tractable was a polynomial composed of two terms, one for the attractive and one for the repulsive part:

$$u(r) = \alpha r^{-n} - \beta r^{-m} \quad (3)$$

where u is the pair potential and r the distance between the two particles. This expression has four adjustable parameters, the exponents (n, m) , and the factors (α, β) .¹¹

This is the moment when our protagonist enters the stage, then a young colleague of Chapman's at Manchester: John E. Lennard-Jones. He took up the task, that means beating a path to integrate the potentials so that a meaningful empirical test could be done. In (1924), he showed how to computationally obtain the viscosity of a gas, in which the interactions are described by equation (3) for the case $m = 2$. Lennard-Jones was aware that the choice $m = 2$ for the second exponent was wrong, but made this choice nevertheless, because he had found a way to calculate the resulting viscosity. This shows the new value of tractability. The revival of the interacting-particles approach that now enfolded can be described as a dance between data, mathematical modeling, and computation.

Argon can illustrate the point. This noble gas was an obvious candidate, because it is spherical and unpolar, hence, fairly easy to model; and it was the best available of all noble gases. The second virial coefficient had been measured by Kamerlingh Onnes and Crommelin at temperatures below 20°C (1910), and new data had been published by Holborn and Otto over a wide range of temperatures (Holborn and Otto 1924). Lennard-Jones took these data as the benchmark against which he put his pair potential to the test. The question was whether there were parameter values for the potential function with which the measured

¹¹ Equation (3) is often ascribed to Mie (1903), although he does not explicitly argue about a potential. Grüneisen (1912) works with the same function and notes problems with the virial coefficient becoming infinite, cf. Rowlinson (2002) for details.

data could be described. He realized that the problem was not well posed for the computational task because the data could not be used to uniquely determine the four parameters. Therefore, he changed the strategy and first made a guess for the two exponents, for which he used ($n = 13$, $m = 4$), hoping that this would give good results for Holborn and Otto's measurements (which, in fact, it did not). From there, Lennard-Jones computed the best choices for α and β . In a similar vein, Hassé and Cook (1929) calculated with an ($n = 8$, $m = 4$, or short: 8, 4) potential, settling on 4 as Lennard-Jones had done in (1924) and then simplifying the calculations with logarithmic tables by assuming 8, which is 4×2 . Only then they determined the remaining two parameters. This was again a move characteristic of the computational approach's relaxed relationship to theory.

It is important to note that the result inevitably is a sort of holistic achievement. How good the model matches the data depends on many factors: the choice of the parameters that were fixed a priori (which was partially guided by convenience, partially by intuition and relying on others), the training data that were used for the adjustment of the remaining parameters, their initial values and, finally, the technical quality of adjustment of the parameters (is an optimum found?). All this determined the outcome in a way that cannot be treated explicitly (which in fact still holds today for model development). Open to assessment is only the observed fit that holistically depends on all of the assumptions.

The primary success of researchers like Lennard-Jones consisted in showing that the computational approach was feasible at all. This opened the door for something like computational chemistry to become a viable research program. Obviously, restrictions regarding the acceptable mathematical forms applied that had nothing to do with physics. Further problems arose from the parameter fitting, the results of which depended on many factors, a fact which Lennard-Jones took very seriously. However, researchers quickly lost interest in the (13, 4) and (8, 4) potentials because of a revolutionary turn that is the subject of the following section.

Act 2: Grafting computational chemistry on a new fundament

Quantum theory counts as an exemplar of a scientific revolution and it changed the world view in important ways (Kuhn 1962). It propelled chemistry into the gaze of theoretical physicists and vice versa (Nye 1993, Gavroglu and Simoes 2012). Schrödinger's equation, published in 1926, became the starting point for quantum chemistry. Importantly, it has the

form of a wave equation, and hence looked familiar to many scientists. This equation entails the complete information about electronic structure, but it is extremely difficult to extract this information by analytical means, even in the simplest cases. An early great success was the work by Heitler and London (1927) who could derive the bond (its energy) between two hydrogen atoms from the Schrödinger equation. Theorists were enthusiastic and thought this first step proved that the job is done. Dirac's notorious quote, cited in virtually every portrayal of quantum chemistry, expresses the opinion:

“The underlying physical laws necessary for the mathematical theory of (. . .) the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble...”
(Dirac 1929, 714)

In a way, Dirac echoes Boltzmann and Laplace, including the expression of difficulty and the insufficient powers of human intelligence—notably for calculation not for theory development. However, if predictions of chemical relevance are taken as a benchmark, quantum chemistry has been a very protracted endeavor. Larger molecules (than Heitler and London's hydrogen) turned out to be much more difficult, if not out of reach—not to mention the Avogadro number (how many particles are needed to compute the thermodynamic properties of substances?). The Schrödinger equation and the classical models of particles and forces are fundamentally different. Despite the difference, the two approaches were combined with amazing ease.

The pioneer of quantum chemistry, Fritz London¹², was among the first who extracted quantitative mathematical relationships from the Schrödinger equation. In his 1930 paper, London argued that (under certain conditions) the dispersion energy (leading to attractive forces) decreases with r^{-6} with increasing distance r between the atoms. In a remarkably smooth move, Lennard-Jones adopted London's finding to the interactions between molecules and transferred it to describing interactions via potentials. He took up the exponent 6 from London's work and inserted it into the (n, m) potential introduced in Act 1. He¹³ then tried 9, 10, and 12 finding that $n = 12$ worked best, especially regarding the fit with the

¹² See the well-informed biography by Gavroglu (2005)

¹³ In his paper, Lennard-Jones acknowledges “help of Miss M. J. Littleton in the numerical calculations” (p. 474).

potential energy curve for helium obtained by Slater and Kirkwood (1931) with quantum methods (Lennard-Jones 1931).¹⁴ In other words, Lennard-Jones managed to swiftly graft the classical potentials onto the new quantum theory. The (12, 6) potential then became linked to the name of Lennard-Jones. The Lennard-Jones potential and the (12, 6) potential are mostly used synonymously today.

Whereas quantum theory revolutionized physics, the computational approach was able to incorporate it without much ado. Due to the adjustable parameters, the mathematical form was flexible enough. The challenge in Lennard-Jones's (post-quantum) 1931 paper remained invariant: determine the best parameters for a concrete substance and then see how good the overall fit (for a range of data) actually gets. Around this challenge, a community of researchers formed, which shared a perception of what are relevant puzzles and methods to solve them.¹⁵ The quality of approximation steadily increased, be it a better fit or approximation to more diverse data. Beginning in the early 1930s, the LJ (12, 6) potential rose in prominence over more than two decades ("the Lennard-Jones era") and became the standard potential of the field that aimed at predicting properties of substances¹⁶ through mathematical analysis of particle-force models.

The almost encyclopedic book by Hirschfelder, Curtiss and Bird (1954, abbreviated as HCB) provides a compendium of what the "molecular theory of gases and fluids" had achieved by then. We would like to draw attention to the date and title. The date indicates that this ambitious summary has been written at the point in time just before digital computers became

¹⁴ Rowlinson 2002, p. 242 gives more details, including literature, on the parameters of the (12, 6) potential that Lennard-Jones used in 1931 to compute the second virial coefficient. Fischer and Wendland (2023) describe the history of intermolecular potentials up to 1971, with the LJ potential among them.

¹⁵ In other words, the computational approach became a normal science in the sense of Thomas Kuhn.

¹⁶ Important restrictions apply. Argon is spherical and nonpolar so that the van der Waals force is the only relevant attractive force. More complicated particles with more complicated interactions were still mostly out of reach. Therefore, predicting properties of substances means a limited range of properties for a limited range of substances. More complicated potentials than the LJ (12, 6) tried to capture additional types of interactions, such as those resulting from electrical dipole moments, i.e. the polarity of molecules.

available to a larger community. HCB tried to keep in balance a twofold commitment. The targets were the properties of real fluids and gases, i.e., something one can empirically measure. At the same time, the actors saw themselves as theorists, rather than empirically driven experimentalists.

HCB claimed to “survey the entire field from a unified viewpoint” (p. v) This unified viewpoint established the LJ potential at the top of the hierarchy, closest to reality. We argue that, at the same time, the crowning of the LJ (12,6) also marks the end of an epoch. We continue our small series of quotes that echo each other (and Laplace) with a passage from HCB’s preface.

“Equilibrium and non-equilibrium properties can be interrelated through the common link of the intermolecular force laws. In principle, these force laws can be obtained exactly from molecular quantum mechanics. Up to the present time, however, mathematical difficulties have restricted the success of this approach; nevertheless, a reasonably good qualitative picture of molecular interactions has been obtained. Hence it is customary to describe the interaction between two molecules in terms of simple empirical functions, the form of which is suggested from quantum mechanics. These functions contain several adjustable constants, which can be determined for various substances by analyzing experimental measurements of bulk properties by means of the corresponding statistical mechanical formulae. Therefore, the molecular approach gives a complete description of the bulk behavior in terms of a small number of constants characteristic of the substance under consideration.” (HCB 1954, p. v)

The expectation that a “complete description” is possible with only a “small number” of parameters testifies the still lasting influence of the rational picture. At the same time, and in conflict with the former point, HCB acknowledge the empirical character of the functions. Substances differ but share a common (mathematical) structure of their interaction potentials. Typically for the computational viewpoint, predictive capability rests on the mathematical form *combined with* adjustable parameters. However, to what extent this structure counts as theoretical or as pragmatic (flexible and tractable) remains open, even if not openly acknowledged.

The LJ (12, 6) potential counted as the crowning achievement because it offered a favorable balance of tractability and fit, a synthesis that could work with new data and attain a good

match in a manageable way.¹⁷ Remarkably, there still seems to remain a glimmer of the rational hope in HCB. Time and again, they mention the consensus that the LJ potential is close to reality. On the other hand, they also admit that no perfect fit can be expected, since the LJ potential is not the exact description (HCB 1954, p.167). Still, the LJ (12, 6) potential was the gold standard because of the good fit to transport properties. The point was that only more realistic functions can give more coherent values, but that these functions were generally intractable. Overall, HCB entertain an ambivalent position regarding how the LJ potential relates to reality. Sometimes they treat it as a (less than perfect) guess at the truth, sometimes as a mathematical tool.

Not long after HCB had documented and confirmed the leading role of LJ (12, 6), this status crumbled, mainly because a wider range of tractable potentials became available. The LJ (12, 6) worked good only for spherical particles without electrical moment, like argon. And even there, data of higher precision showed that the flexibility of the LJ (12, 6) reached its limits. Maitland et al. (1981) write from a very different vantage point when they look back and judge the former king: “It is now recognized that this procedure yields little more than a crude estimate of intermolecular forces.” (1981, p. 3) They go on and provide a hierarchy according to accuracy, with the highest class being prediction with accuracy equal to experiment. The LJ potential now appears at the bottom of the hierarchy. Such a damning verdict by a popular book at the time can only lead to one conclusion—the career of the LJ potential had reached its end by 1980. But this is not at all what happened. On the contrary, it remained extremely popular and enjoyed (and still enjoys) a new career.

Act 3: A child of prediction

¹⁷ In HCB, for a quantitative glimpse, the LJ potential has most entries in the index (55), apart from generic categories like intermolecular forces. Rank 2 goes to equation of state (44 entries). More importantly, sections with LJ (12, 6) are regularly concluding the chapters, presenting the cutting-edge work. The seminal book by Hill (1956) further confirms the case.

The announced main player, the Lennard-Jonesium, or LJ fluid, has not yet appeared at all. This section is about how the LJ potential gave rise to the Lennard-Jonesium.¹⁸ On the surface, it appears to be a simple and not even comprehensive renaming, actually, however, this turn includes a fundamental shift in reference. The LJ potential is an expression intended to capture the pairwise molecular interactions in substances. From a guess at the truth, it morphed into an empirically effective potential whose flexibility and tractability granted widespread use (see Act 2). The LJ *fluid* is fundamentally different. It is *defined* as the fluid whose molecular interactions exactly follow the LJ potential. In other words, it is not a more-or-less adequate stepping-stone toward finding the true potential of some real fluid, but postulates a fluid that does not exist in reality. This redefinition entails a fundamental reorientation in terms of objects: *Ontology follows method*.

Such movement is not uncommon in science. There is a certain pragmatic tendency to follow what a method makes accessible. In a sense, it becomes convenient to study the LJ fluid. The current movement fits to a long history of scientific studies of idealized objects and models, starting with Galilei at the latest. However, what counts as idealized and accessible, depends on the historical conditions. The twist under investigation here happened at a peculiar time. When the research program into the LJ potential appeared to be jaded in the 1960s, the (electronic digital) computer re-defined what is mathematically feasible. Molecular simulation emerges, with the two main branches of Molecular Dynamics (MD) and Monte Carlo (MC). A telling and pioneering example is the work of Aneesur Rahman (1927-1987).¹⁹ He published a paper in 1964 that earned him the title of a founder of molecular dynamics. The first sentence of the paper states the approach.

¹⁸ Strictly speaking, the LJ potential can also describe solids, hence speaking of the LJ substance is more precise. In this article, we follow the actors' usage of LJ fluid where convenient.

¹⁹ Rahman was born in India, studied in Europe, and, in 1960, arrived at Argonne National Laboratory, where he stayed for 25 years. This laboratory was operated by the University of Chicago and the Department of Energy. It had started around Enrico Fermi's work on nuclear reactors in the Manhattan Project (Metallurgical Laboratory 1942) and became one of the US supercomputing centers in 1946. The lab was located in the Argonne Forest named after a forest and battlefield in France. That Rahman later worked on argon is coincidental.

“A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4 K and a density of 1.374 g cm^{-3} .”

This sentence already tells a lot. First of all, the subject of investigation is a system of many particles that interact with the LJ potential. This system cannot be investigated with analytical (and approximative) mathematical means. Rahman follows a radically different strategy, going through all particles, i.e., solving a large set Newton's equation of motion. Of course, the forces change as the particles move, which is described by the equations and handled in the algorithm by a discretization of time. In other words, the blunt strategy consisted in solving many equations (each single one classical) again and again. This option had not been available prior to the computer.

A second observation is that Rahman names brand and model of the computer and thus underlines the importance of instrumentation. Thirdly, the reference goes to liquid argon, a sort of success message since liquids are (in)famously difficult to describe as they are neither as ordered as crystals nor are they as random as gases. The paper shows that the simulation results are in good agreement with experimental values. Of course, the chosen parameter values are crucial, because they determine the model performance.

One could argue that solving Newton's equation of motion for many particles is straightforward and, thereby question the pioneering character of Rahman's work.²⁰ However, this move was not as simple as it looks on first view. Nobody else had thought of it before—much like with Alexander's sword dissolving the Gordian knot. Another pioneer of the time, French mathematician-computer physicist Loup Verlet, in his obituary to Rahman, tries to corroborate the founding role that is commonly ascribed to Rahman. “There was a mental

²⁰ More precisely, Alder and Wainwright (1959a, 1959b) had simulated a hard sphere model in a similar way. There, particles interact only by (pairwise) repulsion. Rahman arguably was not aware of these earlier publications. From 1964 onward, MD as a simulation program gained steam, with the LJ fluid as the primary target, see Verlet (1967, 1968), or Nicolas, Gubbins, Streett, and Tildesley 1979, among many others. MD built one element among several in the emerging scientific communities of computational physics and computational chemistry. For instance, the Journal of Computational Physics has been founded in 1966 by Bernie Alder.

barrier here: many-body systems don't have exact solutions.” (1987, p. 60) This barrier was set in mathematical concrete since Poincaré had shown that the three-body problem could not be solved. Verlet's argument coincides with what philosopher of science Gaston Bachelard has called “epistemological obstacle” (Bachelard 1938). He appreciates, for instance, what a great obstacle it was to pass from light by burning to the incandescent light. Moving from one conception of modeling to another might be of comparable difficulty.

The LJ fluid flourished because several factors were working together. In effect, Rahman drew together resources from theory and mathematical modeling, but also from algorithms and software as well as from computing technology (notably, the computer is named already in the abstract). Taken together, these factors enabled Rahman to deliver predictions, or answer a certain set of questions. Rahman's paper was influential mainly because he showed how straightforwardly MD can be put to work. This is underlined by Verlet: “if the easiness of MD with continuous potential had been realized, a number of people (including my own group) who were currently performing MC [Monte Carlo] computations would have switched to MD.” In other words, once the system was there, it looked straight-forward to everybody.

The predictive capability of MD is extraordinary. Rightfully, nobody questions Newton's equations of motion. Therefore, if you know the interaction potential and if you have a method to solve the equations, you get predictions of both the macroscopic and atomistic behavior of the system, complicated as it may be—much in the sense of Laplace. Honing the predictive capability, or the simple power, of the MD system (including computer software and hardware), was deemed so important that the field made a methodological turn. After this turn, the LJ fluid had become a primary target of investigation.²¹ It was used as a “model fluid” for computational studies that could serve as starting point for building theories and for gaining insights into thermophysical behavior, even without seeing a need of relating it to a specific real substance.

Against this background, the interaction potential gains an axiomatic character in the following sense: the LJ fluid is *defined* by the LJ potential, much like a number is defined by the (Peano) axioms. In the classical (pre-axiomatic) opinion, a definition has to meet its target. The axiomatic viewpoint turns that around. The definition of the number one does not (cannot and should not) meet what the number one *is*, but rather the other way around: the number one is what the definition says. The axiomatic standpoint is a controversial topic in

²¹ Some publications even speak of the “Lennard-Jonesium”.

the philosophy of mathematics because it seems to exclude that mathematics deals with real objects (since it defines and thereby creates its objects). Famously, Russell complained against Peano's axiomatic account that this kind of definition lacks the sort of realism that is required when defining the numbers (Russell 1956, p. 9). Similarly, Frege (a longtime worker into the foundations of arithmetics) attacked Hilbert (in 1903) because Hilbert's axiomatic of geometry would obscure what is true and what is not (Frege 1984).

The axiomatic turn in MD, triggered by the methodology of simulation, comes with an epistemological intricacy. There is a fundamental difference between empirically effective potentials for a real substance like argon, where measured properties are the target of parameter adjustment, and the LJ fluid, where the LJ potential is simply right qua axiom. The epistemological tension becomes graspable when researchers gloss over this difference. For instance, Battimelli et al. see the novelty in Rahman's paper in that he stepped from highly idealized hard shells bumping into each other to particles with continuous interaction potentials (the LJ potential) that looked much closer to reality. However, looking closer to reality is not alone due to advancing theory. Therefore, one should take statements like the following with a grain of salt:

“Indeed, with molecular dynamics one can “calculate theory”, and hence simulate and predict the observable behavior of real systems (including chemical and biological systems), by using as input only the laws of physics and its fundamental constants.”
(Battimelli et al. 2020, p. 3)

That the input consists solely of laws of physics and fundamental constants sweeps under the carpet the role of adjustable parameters. The prediction for any real system is not only based on laws of physics and fundamental constants, but also on adjustable parameters. That the LJ potential, which is not derived from laws of physics anyway, was inadequate for finer questions was clear by then (see Act 2). Research into pair potentials that more precisely fit experimental data went on. For instance, the “BBMS” potential (named after the authors' initials) contains more adjustable parameters than the LJ (Bobetic and Barker 1970; Barker, Fisher, and Watts 1971; Maitland and Smith 1971). Based on extensive parameter adjustments, this potential is superior to LJ for matching data of argon.

Act 4: A new culture of prediction and an irony of reason

The popularity of the LJ potential has remained outstanding, quite unimpressed by the fact that it is neither outstanding regarding theoretical derivation nor empirical fit. The LJ fluid is the simplest test model for sounding out the scope and limitations of the simulation method. This status as the standard model ensures the popularity of the LJ fluid largely independent of empirical fit.

“We continue to work with the simplest atomic systems, in other words, with monatomic fluids based on the LJ potential, not only because we want to introduce the methodology gradually, but also because a lot of the actual qualitative (and even quantitative) behavior of many-body systems is already present in this simplest of models.” (Rapaport 1997, p. 42)

There are more reasons. One is that the LJ *fluid* is a well-researched substance that is taken as a reference point for further studies, in particular for creating models and theories of fluids (cf. Hansen and McDonald 2013). However, we argue that the popularity of the LJ *potential* is due to organization in two senses, a methodological and a social one. Firstly, most advanced potentials are put together from building blocks—and the LJ potential is the most common of these building blocks. Secondly, on the social side, modeling activity thrives on software packages that allow researchers to modify and explore potentials easily—with the LJ potential built in. Hence, both aspects reinforce each other. We address them in turn.

Thanks to the computer simulation method, using simple potentials for putting together complex ones is mathematically feasible and, even straightforward. If a dipolar substance is to be modeled, one can use the LJ potential for the van der Waals force and add simply a point dipole, and so on with all kinds of more complicated interactions, internal to a molecule or between molecules. From a computer perspective, this additive strategy still results in tractable models. This makes the building block strategy highly attractive. Since the LJ potential captures the types of interactions that are always present (namely repulsion and attraction by van der Waals forces) in a simple way (and in a way which is comprehensively known), most molecular modeling approaches use it as a basic building block. Depending on the adjustment of their parameters, they can be fitted to data of different type and to complex substances. Of course, parameter adjustment renders the building blocks highly interdependent, because parameters of one block are adjusted conditional on the parameterized behavior of other blocks. This turns the potentials, despite their additive nature, into somewhat holistic entities.

The second sense of organization refers to social organization. Working with software packages that run on easily available networked computers makes a difference. Back in the pioneering times of MD in the 1960s (Act 3), researchers in MD were identical with the producers of software. Typically, the software was tied to the location and eventually also to the computer available there, as well as to the narrow group of those who had created the program. Here is anecdotal evidence. When Rahman and Stillinger reported on their path-breaking simulation of water during a workshop at CECAM (1973, one year after publication of the paper), the other participants hoped to learn about Rahman's simulation and software. However, Rahman went through the program and output without a single line of commentary (Battimelli et al. 2020, chapter 5.1) In other words, competitors in molecular simulation had to build their own programs, i.e., had to command the entire expertise.

“In the past, many simulation programs have been handed down from one research group to another and from one generation of students to the next. Indeed, with a trained eye, it is possible to trace many programs back to one of the handful of groups working in the field 20 years ago.” (Allen and Tildesley, 1987, p. vi)

This situation drastically changed around 1990 when cheap computing power became easily available to every researcher. From then on, users could easily download a number of software packages, run them, and fiddle around with them without having the expertise that would be necessary to create the software.²² This development is characterized by a soar in work aiming at refining and examining advanced potentials, based on existing building blocks (including the LJ potential as basic ingredient) that are suitably combined and parameterized. In this way, the mathematical (or computational) and the social organization of modeling foster the role of the LJ potential.

²² On the turn from experts to users in computational sciences, see also [blinded reference], Wieber and Hocquet (2020), Hocquet and Wieber (2021). We do not address the obvious challenges for the quality of the simulations related to this, and only cite a paper from the field of soft matter simulations in which practitioners warn about dangerous developments: “One does not become theorist by buying chalk, an experimentalist by buying a microscope, or a computational scientist by downloading software.” (Wong-ekkabut and Karttunen 2016, p. 2535).

This type of organization brought a striking upswing to MD as Image 1 displays (cf. also Maginn and Elliott 2010). A similar upswing happened in neighboring fields, like in density functional theory, a popular theory in computational quantum chemistry.

[Locate figure 1 here.]

Figure 1. The relative share of papers on MD (dotted line), resp. density functional theory (DFT), in all papers appearing in the databank Scopus. In absolute numbers, publications per year went up from below hundred in 1975 to nearly 20,000 in 2020, both MD and DFT. MD shows an additional “tooth” that arguably depicts the hype around nano (apparently swiftly ending 2005-2010).

The 1990s turn motivated our distinction between Acts 3 and 4. It signals a transformation to a new “culture of prediction” (Johnson and Lenhard 2011) that works with the computer but differs in computing technology, epistemology and social organization. In particular, working with mainframe computers goes hand in hand with a central organization that controls the (costly) access to the machines. Since the 1990s, easily accessible, cheap, and networked computers became available. With them, an exploratory mode evolved in which modelers can sound out model behavior by varying parameters, thus thriving on the flexibility of models. This kind of exploration was present already in Lennard-Jones’ work (testing different choices of exponents), but could become highly attractive to many only when models are responsive and computation is cheap.

The exploratory mode has philosophical ramifications that are worth exploring.

Parameterization is a key ingredient of the exploratory mode that balances various and partly unknown factors (and errors). Only after parameterization, the model produces predictions that are candidates for matching with data.²³ Additionally, models are employed and parameterized by different actors and groups who implement them on different hardware, using different software packages, compilers, evaluation routines, etc. As a result, the models acquire a bricolage character. At the same time, the models are disciplined by the orientation at prediction that guides the adjustment process. During this process, the various (bricolage) differences are compensated by (parameter) adjustments.

²³ The significance of parameterization has been discussed by Parker (2014) for the case of climate modeling and by Hasse and Lenhard (2017) as “Boon and Bane” for simulation in a more general setting.

We explore two philosophical consequences of the bricolage character. Firstly, assessing the merits of the mathematical structure (separate from adjustments) can get elusive. Is the predictive capability based on the structure or rather on the adjustments? The more exploratory (adjustment-friendly) the specification process, the less the structure is responsible for the predictions.²⁴ Consequently, well-seasoned philosophical arguments are getting under pressure. One is the no-miracles argument for scientific realism: If a model would not represent something real, its predictive power would be a miracle. Each step of adjustment seems to diminish the (potential) miracle a little. Another instance is structural realism. In a recent paper, Patton (2023) has aptly pointed out how structural realism draws on predictive success.²⁵ However, convincing cases rest on how clearly the mathematical structure can be discerned. Cases like molecular simulation present a challenge, because one can study the role of mathematical structure only together with (not separate from) parameterization.²⁶

The second consequence concerns the worries about reproducibility that have long arrived in the computational science community. In general, practitioners are well aware that they obtain their results with the help of hardware, software, and modeling approaches of significant variety. Under these conditions, reproducibility is hard to attain. Furthermore, molecular dynamics contains a stochastic element so that reproducibility is meant in a statistical sense, anyhow. In the rising awareness to the problem of reproducibility, the LJ fluid plays a special role because the model is relatively simple and defined in a precise mathematical way. However, recent studies have found inconsistencies in published simulation results on the LJ fluid. In short, the simulations are less reproducible than anticipated (Stephan et al. 2019).

Is reproducibility a matter of stricter standardization and control, i.e., a matter of aligning practice with standards known in principle? In principle, the problems are known, but in practice, so the widely shared opinion in computer science and simulation, it is regularly

²⁴ An extreme example would be deep neural networks that work with a very generic structure but millions of parameters.

²⁵ One example is Bokulich's (2017) analysis that predictive success suggests that at least some isomorphism holds between (idealized) model and world.

²⁶ We suggest the need for a more systematic philosophical investigation.

impossible to fully specify all elements. If so, the bricolage status is inherent even to models that are so seemingly well-defined as the LJ fluid, when it comes to extracting information from them by computational methods. This analysis fosters established claims about the epistemology of simulation, namely that simulation is not simply computation of a given theoretical model, but requires a separate process that connects the theoretical model with an executable simulation.²⁷ The problem, or challenge, of reproducibility indicates how far-reaching and sometimes surprising the consequences of this epistemology are.

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²⁷ Humphreys (2004) concluded with heralding a new epistemology. Winsberg (2010) and Lenhard (2019), among others further developed this epistemology.

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Figure 1:

