“It would be very complicated, if not practically impossible, to reach the spinodal.”
Jan Wedekind, Guram Chkonia, Judith Wölk, Reinhard Strey, and David Reguera,
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What is Liquid? [in two dimensions]

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Abstract

We consider the practicalities of defining, simulating, and characterizing “Liquids” from a pedagogical standpoint based on atomistic computer simulations. For simplicity and clarity we study two-dimensional systems throughout. In addition to the infinite-ranged Lennard-Jones 12/6 potential we consider two shorter-ranged families of pair potentials. At zero pressure one of them includes just nearest neighbors. The other longer-ranged family includes twelve additional neighbors. We find that these further neighbors can help stabilize the liquid phase.

What about liquids? To implement Wikipedia’s definition of liquids as conforming to their container we begin by formulating and imposing smooth-container boundary conditions. To encourage conformation further we add a vertical gravitational field. Gravity helps stabilize the relatively vague liquid-gas interface. Gravity reduces the messiness associated with the curiously-named “spinodal” (tensile) portion of the phase diagram. Our simulations are mainly isothermal. We control the kinetic temperature with Nosé-Hoover thermostating, extracting or injecting heat so as to impose a mean kinetic temperature over time. Our simulations stabilizing density gradients and the temperature provide critical-point estimates fully consistent with previous efforts from free energy and Gibbs’ ensemble simulations. This agreement validates our approach.

Keywords: Liquids, Statistical Physics, Molecular Dynamics, Tension, Spinodals, Phase Equilibria
I. WHAT IS LIQUID [ IN TWO DIMENSIONS ]?

This work had its origin in the recent death of our colleague Douglas Henderson. Bill’s friendship with Doug dated back to the 1960s, their early years as scientists, working at the Lawrence Livermore Radiation Laboratory (Bill) and IBM’s Almaden Research Centre in San José (Doug). Bill and Carol visited Doug and RoseMarie’s homes south of San Francisco and, after the Loma Prieta earthquake of 17 October 1989, in Sandy Utah. These visits became more frequent following the Hoovers’ move to Ruby Valley Nevada in 2005.

All four of us have carried out research work devoted to a longstanding challenge of equilibrium statistical mechanics, a better understanding of liquid state structure. The Mayers’ virial series for gases and the Einstein and Debye models for ordered solids provide a relatively accurate understanding of matter’s simplest pair of phases. Liquids remain more mysterious. The question asked by Doug and John Barker in 1976 was a good one and remains so today. Bill adopted this same title as the basis for two publications, one in 1998, the second in 2014, the latter as part of the celebration of Doug’s 80th birthday.

II. VAN DER WAALS’ 1873 MODEL FOR GASES AND LIQUIDS

Though atomistic liquid structure remains mysterious, van der Waals provided us with his Nobel Prize winning macroscopic “equation of state”. This thermodynamic model describes both gases and liquids as well as the “critical” condition at which the two become indistinguishable. van der Waals chose two material properties, $a$ and $b$, to characterize the strengths of the attractive and repulsive contributions to the pressure and energy of fluids, both gaseous and liquid. For simplicity we adopt “reduced units” here, setting van der Waals’ material properties $a$, characterizing attraction, and $b$, characterizing repulsion, both equal to unity. Throughout this work we use reduced units, setting particle masses and Boltzmann’s constant both equal to unity in addition to the potential parameters and van der Waals’ $a$ and $b$. In two space dimensions, with kinetic energy $K = \sum (p_x^2 + p_y^2)/2 = NT$, van der Waals’ mechanical and thermal equations of state are:

$$ (P + \rho^2)(1 - \rho) = \rho T \ [ \text{Mechanical} ] ; \ e = T - \rho \ [ \text{Thermal} ] . $$

$P$, $\rho$, $T$, and $e$ — pressure, density, temperature, and internal energy — are the macroscopic thermodynamic variables linked together by van der Waals in his 1873 dissertation on The
Continuity of the Gas and Liquid States. For consistency with thermodynamics the resulting mechanical and thermal properties of these fluids are correlated by the second-derivative “Maxwell relation” that follows from the mixed partial derivatives of $A/T$ with respect to volume and temperature, $(\partial^2[A/T]/\partial V \partial T) = (\partial^2[A/T]/\partial T \partial V)$ where $A$ is Helmholtz’ free energy, $E - TS$ and $S$ is entropy:

$$(\partial[P/T]/\partial T) = (\partial[e/T^2]/\partial v) = (\rho/T)^2$$

for van der Waals.

According to van der Waals’ model and in accord with nature, the gas and liquid phases can only be distinguished at temperatures below a critical isotherm, on which the unstable minima and maxima of van der Waals’ pressure equation, a cubic in the density, coalesce. The “critical point” on this isotherm is the only location in the pressure-density plane where the isothermal slope and curvature simultaneously vanish:

$$(\partial P/\partial \rho)_T = 0 \quad \text{and} \quad (\partial^2 P/\partial \rho^2)_T = 0 \quad \rightarrow \quad \{ P_c = 1/27, \ \rho_c = 1/3, \ T_c = 8/27 \}.$$ 

At this critical point the two fluid states, gas and liquid, become indistinguishable. They also become hard to investigate as the vanishing first derivative implies infinite compressibility, $-d\ln V/dP$, and zero sound speed, as $c = \sqrt{(\partial P/\partial \rho)S} \propto \sqrt{(\partial P/\partial \rho)_T}$, where $S$ is entropy. This singular behavior of the pressure derivatives is reflected in the macroscopic nature of critical density fluctuations big enough to see. The fluctuations are observed visually as a milky “critical opalescence”.

For any temperature less than the critical temperature value $T_c = (8/27)$ van der Waals’ model gives two values of the density which can coexist at mechanical and thermal equilibrium. In addition to these “binodal” points there are two other density values on every subcritical isotherm and on some adiabats between which the van der Waals equation of state is mechanically unstable. These pairs of points form the high-density and low-density boundaries of unstable isothermal and adiabatic “spinodal regions”, within which at least one of the two van der Waals’ compressibilities is negative. Straightforward algebra shows that van der Waals’ adiabatic spinodal line [where $(\partial P/\partial \rho)_S$ vanishes] has the same form as the isothermal line, but at half the temperature:

$$T_{\text{isothermal}} = 2\rho(1 - \rho)^2 = 2T_{\text{adiabatic}}.$$ 

The van der Waals model’s “binodal” equilibrium coexistence curves and the “spinodal” curves of divergent compressibility are characteristic of many real macroscopic fluids and
common microscopic fluid models which include both attractive and repulsive pair forces. The best known microscopic model is Lennard-Jones’ 12/6 potential from the 1920s:

\[ \phi_{LJ}(r) = \left(\frac{1}{r}\right)^{12} - 2\left(\frac{1}{r}\right)^{6} \rightarrow \phi'(1) = 0 ; \phi(1) = -1 . \]

The van der Waals and Lennard-Jones phase diagrams are compared in Figure 1. Although van der Waals’ equation has no solid phase, a more sophisticated state-equation model, based on the known hard-disk equation of state, for disks of diameter \( \sigma \) and number density \( \rho = (N/V) \):

\[
\left(\frac{PV}{NkT}\right) = \left(\frac{PV}{NkT}\right)_{\text{disks}} - \rho \text{ with } B_2 = (\pi/2) \text{ and } \sigma \equiv 1 \text{ for disks ,}
\]

provides a three-phase equation of state analogous to van der Waals’ two-state solution. The critical parameters depend upon the reduced units chosen for the hard-disk model. With disk diameter \( \sigma \) and Boltzmann’s constant set equal to unity this model gives \( (P_c, \rho_c, T_c) = (0.019, 0.269, 0.216) \) with a dimensionless compressibility factor \( (PV/NkT) = 0.326 \), quite close to the value of \( (1/3) \) obtained by using a maximally truncated three-term virial expansion, \( (PV/NkT) = 1 + B_2\rho + B_3\rho^2 \).

It is evident from Figure 1 that pair potential models can provide a semi-quantitative understanding of the coexistence and coalescence of the less-dense gas and more-dense liquid phases of simple fluids, where both phases are formed from the same ingredients.

Understanding the details of the microscopic structure leading to this macroscopic behavior is an excellent illustration of the problem areas all four of us have enjoyed exploring. Before entering into the details of our own work let us consider the progressive steps leading from van der Waals equation in the late 1800s up to Barker and Henderson’s review a century later.

III. THEORIES AND MODELS OF THE LIQUID STATE

In the late nineteenth century critical-point experiments were carried out by heating a known quantity of liquid in a sealed tube with an obvious “meniscus”. That word, “meniscus”, comes from the Greek for “curved moon”. It is because the two phases interact with their container’s surface differently that the meniscus separating them is curved. Near the “critical point”, where gas and liquid become indistinguishable, dramatic density fluctuations broaden and destroy the meniscus separating the two coexisting phases.
FIG. 1: At the left is van der Waals’ phase diagram and at the right the two-dimensional Lennard-Jones analog. In the van der Waals case the isothermal and isentropic spinodal lines, where the corresponding compressibility diverges, are shown. In the Lennard-Jones case, with its solid phase, there is a triple point near $T = 0.4$ below which the gas and solid coexist. Between the triple-point temperature and the critical temperature (roughly 0.56) lower-density gas and higher-density liquid can coexist.

In 1882 Hannay declared “The formation of a meniscus is the only test of the liquid state”. That meniscus definition is superior to Wikipedia’s notion, “Liquid is a nearly incompressible fluid that conforms to the shape of its container”. Hannay was right. A liquid-gas interface, or meniscus, with the liquid the denser of the two fluid phases, is necessary to distinguish the one phase from the other. Wikipedia’s liquid definition would include dense fluids of hard disks or spheres. But neither of those hard-particle systems has the attractive forces necessary to stabilize a liquid phase.

By 1900, with the advent of Boltzmann and Gibbs’ statistical mechanics, atomistic models became important. Kinetic theory and lattice dynamics offered useful descriptions of gases and solids. Good structural models for liquids were absent. This lack soon motivated the construction of physical models of liquid structure. In 1930s London John Bernal simply added more and more ball-bearing particles to ball-and-stick or conglomerate balls-in-paint structures. Bernal found that the radial distributions of pairs of balls resembled those inferred from radiation experiments on real liquids. At about this same time Joel Hildebrand,
in Berkeley, immersed more than 100 gelatin balls in a fish tank, likewise finding that the distribution of the balls’ separations resembled the distributions of interparticle distances in liquid argon, scaled up by eight-or-so orders of magnitude. Bernal and Hildebrand were looking for bulk liquid structure, not the interfacial menisci stressed by Hannay.

John Barker devoted most of his working life to the understanding of liquids, publishing his only book, *Lattice Theories of the Liquid State* in 1963, just as it was becoming clear that lattices were not a proper starting point for “understanding”. Before he and Doug Henderson had discovered and implemented perturbation theory Barker had attempted to improve his understanding of liquids by extending “lattice theories”, like the Ising Model. That model, with its hole-particle symmetry, seems very distant to real liquids. Barker invented “tunnel models”, taking advantage of the mathematical simplicity of one-dimensional chains of particles, coupled with a symmetry-breaking description of the tunnel locations. In tunnel models for simple atoms one-third of the degrees of freedom are longitudinal and two-thirds are transverse to the tunnels. Barker’s collaboration with Doug in the 1960s, based on a perturbation theory of the Helmholtz free energy, was soon to provide a surprisingly useful predictive theory. The theory provided all the liquid thermodynamic properties based on known properties of hard spheres. This hard-sphere-based theory’s success is a bit puzzling because the underlying model is itself incapable of providing the two-fluid meniscus characteristic of real liquid-gas coexistence.

IV. PROGRESS IN UNDERSTANDING FROM COMPUTER SIMULATIONS

Soon after World War II, in the 1950s, the advent of computers opened up completely new research opportunities. Alder, Jacobson, Wainwright, and Wood developed Monte Carlo and molecular dynamics simulation algorithms modeling equilibrium distributions of dozens or hundreds of hard particles in two and three space dimensions. They discovered and characterized the hard-disk and hard-sphere fluid-solid transitions. These melting-freezing transitions occur when the solid phases are expanded about ten percent in \((x, y)\) or \((x, y, z)\), corresponding to melting densities, relative to close-packed, of about \((4/5)\) (for disks) and \((3/4)\) (for spheres).

In 1958 Jerry Percus and George Yevick formulated an integral equation for the pair distribution function. Mike Wertheim solved the equation analytically for hard spheres
five years later. A numerical solution of the hard-disk analog appeared half a century later, in 2008. The analytic work for spheres gave an excellent approximation to the hard-sphere distributions from Monte Carlo and molecular dynamics simulations. These developments led to the successful refinements of perturbation theory reviewed by Barker and Henderson in 1976. Their approach was paralleled by several other dedicated scientists, among them Farid Abraham, Hans Andersen, Frank Canfield, David Chandler, Ali Mansoori, Jay Rasaiah, George Stell, and John Weeks.

V. BARKER AND HENDERSON’S DESCRIPTION OF “LIQUIDS”

After a decade working together Barker and Henderson addressed our title question from the standpoint of perturbation theory, in 1976. Rather than constructing physical many-body models they adopted the results of hard-particle computer simulations to develop and evaluate a perturbation theory based on the Percus-Yevick hard-sphere distribution function. They treated attractive forces as a perturbation added to a reference repulsive potential. The resulting free energy calculations related the thermodynamics of homogeneous liquids to hard-sphere fluid-phase properties. Helmholtz’ and Gibbs’ free energies can alternatively be found by integrating equation of state data taken from Monte Carlo or molecular dynamics simulations. With today’s computers brute-force simulation is the more practical and much-simpler approach.

Barker and Henderson summarized the state of the art of the 1970s perturbation work in their review. In its simplest form liquid perturbation theory is based on optimizing a reference-system’s hard core size by minimizing Helmholtz’ free energy at fixed values of the density and temperature. The success of this theory is surprising given that the reference hard-particle systems have no liquid phase. Bill Wood, at Los Alamos, pointed out that the hard-particle systems’ fluid-solid surface tension is negative. Thus drops of hard disks and spheres don’t form. Unlike models with attractive forces hard particles don’t form clusters.

VI. CONCEPTUAL DIFFICULTIES : LIQUIDS’ “SPINODAL REGION”

There is a tremendous literature on the “spinodal” region of the phase diagram. For van der Waals’ equation this is usually taken to be the mechanically-unstable region with
negative isothermal compressibility. In principle a negative compressibility, either isothermal or adiabatic, generates exponential growth of density fluctuations and so is ruled illegal in realistic fluid models. Thus the borders of a spinodal region for real fluids, if there were one, would be hard to access and describe.

The internet reveals that “spinodal” originated as a synonym for “cusp”. This explanation seems curiously incomplete (and mercifully absent from most textbooks) as no cusp is apparent in realistic phase diagrams like those of van der Waals or the Lennard-Jones potential. See again Figure 1. We consider a region with negative compressibility strange, artificial and “unstable”. Shamsundar and Lienhard explicitly object to the term “unstable”, citing the reality of nearby states of superheated liquids and supercooled gases, likewise nonequilibrium states not appearing in a conventional single-valued phase diagram. Any fluid under tension and subject to mechanical noise cannot persist unchanged for long. Solids do characteristically exhibit tensile strength but still can suffer shear instabilities. We will illustrate such models later in this work. There is as yet no accepted standard for bulk “liquid” structure, though not for lack of trying. Wedekind et alii described access to the spinodal regions well:

“It would be very complicated, if not practically impossible, to reach the spinodal.”

In the context of the usual single-component thermodynamics for a simple material like argon the spinodal region of the phase diagram corresponds, at least conceptually, if not in the laboratory, to a mix of a denser liquid and a less-dense gas. Because such a system isn’t homogeneous it is clear that a simple phase diagram or a model like van der Waals’ is an incomplete description. Simulations in this region lead to highly-complex evolving structures of transient rotating clusters or clumps of particles. The properties of nonequilibrium clusters are complex, involving surface tension and rotational contributions to the energy, making the characterization of “pressure” somewhat uncertain.

In our own effort to clarify the ambiguities of “spinodal states” for two-dimensional fluids we thought it prudent to consider three different initial conditions, all of them equally plausible a priori. With Lennard-Jones forces both the square lattice, sufficiently expanded to reach a density of 0.4, or a triangular lattice expanded to that same density, have energies exceeding that at the critical point and so cannot serve as models for a spinodal state
FIG. 2: Four snapshots in a “spinodal” evolution. The dynamics is Nosé-Hoover isothermal at the subcritical temperature $T = 0.5$. The initial condition, at the left, is a perfect square lattice of area 4000 containing 1600 Lennard-Jones particles. Fourth-order Runge-Kutta integration with $dt = 0.005$ to time 40. The instability of the lattice gives rise to coarsening, soon forming a percolating cluster spanning the volume. Boundary potentials quartic in $dx$ and $dy$ repel any particles with $|x|$ or $|y|$ exceeding $\sqrt{1000} = 31.623$.

using conservative mechanics. A simple way out of this energy problem is to consider isothermal molecular dynamics, starting and finishing at an imposed kinetic temperature less than critical and greater than that at the triple point. Such a choice lies somewhere in a nonequilibrium liquid range. In two space dimensions, the Lennard-Jones critical and triple-point temperatures are on the order of 0.56 and 0.4 according to Barker, Henderson, and Abraham. We have chosen the temperature 0.5 as our standard initial (and final, time-averaged) condition for our exploratory molecular dynamics simulations. See Figure 2 for a sample evolution from an unstable square lattice. An expanded triangular lattice provides a similar history. A third possibility, illustrated in Figure 3 is to divide up the system into cells with the structure in each cell chosen randomly. A special case of this choice takes a regular stress-free lattice with the number of randomly-located vacancies chosen to satisfy the desired density, 0.4 in our case, close to the Barker-Henderson-Abraham estimate of the critical density in Figure 1.

The two sample evolutions shown here are typical of the spinodal region. The equilib-
FIG. 3: Four snapshots in a “spinodal” evolution. The dynamics is Nosé-Hoover isothermal at the subcritical temperature $T = 0.5$. The initial condition was a perfect square lattice of 3600 sites in an area 4000 with 1600 of the sites, randomly chosen, containing Lennard-Jones particles. Boundary potentials quartic in $dx$ and $dy$ repel any particles with $|x|$ or $|y|$ exceeding $\sqrt{1000} = 31.623$.

The equilibrium phase diagram disallows states under tension. There is an initial exponential growth of density fluctuations, followed by a slower coarsening of clusters to form a percolating cluster spanning the entire volume. The details of the first exponentially unstable phase depend upon the initial conditions. The details of the second phase, with the nonequilibrium equilibration of growing clusters, are relatively easy to see but hard to predict, suggesting the exploration of alternative methods for characterizing liquids.

Gravity can take us in the direction of Hannay’s meniscus. The evolution of an initial state toward the formation of a meniscus can be visualized by adding a small gravitational field to the dynamics. With a field the liquid state lies below the vapour with which it equilibrates. The Figure 1 phase diagram for Lennard-Jones’ potential indicates that a liquid about six times denser than its vapour should be stable at a temperature of 0.5, well below the critical temperature of 0.56 and above the triple point temperature of 0.4. This suggests a feedback dynamics similar to the “Gibbs’ ensemble” algorithm, with particles transferred from interacting simulations with a common pressure and temperature. Feedback within a single simulation provides a less singular evolution. Let us turn to dynamics in the presence of an external gravitational field.
VII. IMPLEMENTING A “LIQUID” VISION WITH MOLECULAR DYNAMICS

In the present work we consider the need, and fill it, for a “meniscus” separating a “gas” from a “liquid” fluid. We stabilize and investigate the interfaces defining phase boundaries. To do this we first of all model the idea of a physical “container”, to which all the particles in our simulations must conform. To simulate the dynamics of such a manybody system we enclose it within a special fixed boundary, a smooth nearly-rigid container modeled with a quartic repulsive surface potential.

In keeping with the expected accuracy of a fourth-order Runge-Kutta integration of the motion equations we adopted one-sided quartic potentials to contain our simulations. We begin with both rectangular and circular “containers” for our molecular dynamics. The boundary potential energy in the circular case is $(dr^4/4)$ where $dr$ is the depth of penetration beyond a circular boundary of radius $r$. To reflect escaping particles in the rectangular case the boundary potentials are $(dx^4/4)$ and $(dy^4/4)$ imposed on the four sides of a rectangular container. $dx$ and $dy$ are the penetrations beyond the vertical and horizontal walls of a rectangular container. See Figures 4 and 5 for typical equilibrium snapshots of 400 Lennard-Jones particles with the density and kinetic temperature at a fluid state point well above the gas-liquid coexistence curve, $\rho = 0.4; \ T = 1 > T_C \approx 0.56$. The wild density fluctuations seen in these two equilibrium snapshots rightly suggest that time-averaging is needed to aid the analysis of the gas-liquid meniscus structure.

The Figures document that typical penetrations, beyond the quartic boundaries, are about one particle diameter, consistent with an energy-based estimate:

$$(dx^4/4) \approx (dy^4/4) \approx (dr^4/4) \approx T = 1 \rightarrow dr \approx 1.414.$$  

With these straightforward model boundary potentials providing a conforming container we next seek out a means for emphasizing and localizing the meniscus characteristic of the liquid state.

VIII. STABILIZING THE MENISCUS WITH GRAVITY

Barker and Henderson were satisfied with a formal semiquantitative perturbation theory based on a reference hard-core potential. We prefer a more physical approach, based on
FIG. 4: An equilibrium snapshot of 400 Lennard-Jones particles at $T = 1$ confined by square boundary potentials at $\pm \sqrt{250} = 15.811$. The density is 0.4. The simulation time $t = 100$ is adequate for equilibration. Here, and throughout, we use fourth-order Runge-Kutta integration with a timestep $dt = 0.005$.

FIG. 5: An equilibrium snapshot of 400 Lennard-Jones particles at $T = 1$ confined by a circular quartic boundary potential at $r = \sqrt{1000/\pi} = 17.841$. The snapshot was taken after 20,000 timesteps with $dt = 0.005$. The density is 0.4. The simulation time $t = 100$ is adequate for equilibration.
observations of phase equilibria. For us, a stable interface separating a liquid from its less-
dense gas is the necessary and defining aspect of liquid behavior. From the observational
standpoint to be sure one is viewing a liquid (as opposed to a gas or hard-particle fluid)
requires observing the interface separating the two varieties of simple fluids, the liquid and
the gas. This is easy to do by simulating a gas bubble surrounded by liquid or a liquid drop in
a dilute gas; but such clearcut observations become blurred nearer the “critical point” where
fluctuations are macroscopic. There the manybody dynamics is dominated by percolating
clusters of macroscopic size.

To encourage our particles’ conformation to their container with a visible meniscus we
include a second innovation, a constant vertical acceleration, $-g$ for each of our computa-
tional particles. This constant downward force is added to the pairwise forces from other
particles and to the boundary forces defining our containers:

$$F = F_{\text{pair}} + F_{\text{penetration}} + F_{\text{gravity}}.$$  

We harbor the optimistic assumption that such a combination of particle plus boundary plus
gravitational forces will accommodate not only a gas-liquid interface but also the liquid-solid
one. In 1977 Ladd and Woodcock demonstrated that sufficiently close to the triple point it
is possible to see both of these liquid interfaces simultaneously\textsuperscript{16}. At such a “triple point”
there are no thermodynamic “degrees of freedom”. All three phases coexist at the same
pressure and temperature. By adding gravity we provide our fluid systems with a pressure
gradient satisfying the continuum force balance, \((dP/dy) = -\rho g\) in the stationary state.
The pressure gradient \((dP/dy)\) forces the fluid to conform its shape to its container, and,
over a wide range of pressures, serves to localize and illustrate the gas-liquid and liquid-solid
interfaces.

The phenomena of yield stress (for the solid) and surface tension (for the liquid) could
prevent shape conformation unless these properties can be overcome by gravitational or
rotational forces. We have chosen gravity as the simpler of these two choices. Finally, in
order to prescribe the overall temperature of our two-phase or three-phase systems we apply
Nosé-Hoover isothermal dynamics with a target temperature $T_{NH}$:

$$T_{NH} = \langle \langle K/N \rangle \rangle = \langle \langle p_x^2/2 \rangle + \langle p_y^2/2 \rangle \rangle.$$  

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The fundamental conceptual basis of our present work is conservative Hamiltonian molecular dynamics. We include the forces and potential energies from a constant gravitational field as well as those describing special containerized boundary conditions. For flexible control of the simulations, and to accelerate convergence, we generalize the underlying mechanics to include Nosé-Hoover control of temperature. Let us next outline the Nosé-Hoover control mechanism.

Molecular Dynamics with specified kinetic temperatures has made steady-state nonequilibrium simulations a standard method for simulating steady nonequilibrium flows of mass, momentum, and energy. In 1984 Nosé introduced his novel time-reversible Hamiltonian dynamics. He treated the kinetic temperature as an independent variable imposed on the dynamics. This is accomplished by augmenting the manybody motion equations with a time-reversible friction coefficient \( \zeta \). Hoover provided a simplified formulation of Nosé’s approach which has been widely adopted. We use it here:

\[
\begin{align*}
\dot{x} &= p_x ; \quad \dot{p}_x = F_x - \zeta p_x ; \quad \dot{y} = p_y ; \quad \dot{p}_y = F_y - \zeta p_y \\
\dot{\zeta} &= (1/N\tau^2)[\langle K \rangle - K(t)] \quad [\text{Nosé–Hoover Dynamics}] 
\end{align*}
\]

Here \( \langle K \rangle \) is the constant target value of the kinetic energy, imposed by \( \zeta \). In the two-dimensional systems we consider the kinetic temperature is \( T = (1/N)\sum(p_x^2 + p_y^2)/2 = (K/N) \), and the relaxation time \( \tau \) can be chosen as a typical collision time. For the current simulations we have chosen \( \tau = 1 \).

If it is desirable to accelerate convergence it is quite practical to begin with a higher imposed temperature and/or a higher gravitational field. It is perfectly feasible to specify analytic time dependences for these target temperatures and fields, \( T(t) \) and \( g(t) \), within the equations of motion.

For simplicity and clarity we restrict our investigations to two-dimensional systems. We look directly at coexisting phases, so as to avoid the need for free energy calculations. Corresponding implementations for three-dimensional systems are straightforward. This will be clear as we discuss the necessary diagnostics for analyzing the results of our computer simulations.
FIG. 6: Four Nosé-Hoover Lennard-Jones snapshots at times 12,500, 15,000, 17,500, and 20,000. Gravitational field 0.01 with 640 particles confined by a square boundary, quartic potentials at $|x| = 20$ and $|y| = 20$. Timestep 0.005 and $T = 0.5$. Fourth-order Runge-Kutta integration.

X. ISOTHERMAL LENNARD-JONES FLUIDS WITH GRAVITY

The simulations leading to Figures 4 and 5, when time-averaged, correspond to equilibrium homogeneous fluids due to the lack of any organizing field. Figures 6 and 7, which include gravity, illustrate very different situations incorporating menisci. They snapshot the evolving morphology of 640 Lennard-Jones particles in square and round containers of enclosed volume 1600, corresponding again to a near-critical density $\rho = 0.4$. In both these highly inhomogeneous systems the gravitational field strength is $g = 0.01$. The slightly subcritical kinetic temperature, $\langle (p_x^2 + p_y^2)/2 \rangle$, is 0.5, and the Nosé-Hoover relaxation time imposing it is unity. The underlying two-million-timestep simulations including all $(640 \times 639/2)$ Lennard-Jones interactions take a half day on a desktop computer. The two field-driven figures, with four sample snapshots from the last halves of the runs, both show a denser phase $\rho \approx 1$ below a lower-density gas phase $\rho \approx 0.1$. We will see in Figure 17 that time-averaging isothermal snapshots provides additional simplicity and considerable clarity.

Koch, Desai, and Abraham’s comprehensive spinodal work using the Lennard-Jones potential suggests a gas-liquid density ratio of roughly six at $T = 0.5$. In our earlier exploratory simulations the gravitational field strength obeyed a feedback differen-
FIG. 7: Four Nosé-Hoover Lennard-Jones snapshots at times 12,500, 15,000, 17,500, and 20,000.
Gravitational field 0.01 with 640 particles confined by a circular boundary at $r = \sqrt{x^2 + y^2} = \sqrt{1600/\pi} = 22.568$. Timestep $dt = 0.005$ and $T = 0.5$.

Partial equation based on generating our desired factor of six in the density difference,
$\dot{g} = 0.01[ N_{\text{gas}}(t) - (N/7) ]$. $N_{\text{gas}}$ is simply the number of particles with positive $y$ coordinates. Because the resulting fluctuating field strength was close to 0.01 we adopted the simpler and smoother approach of using a constant gravitational field for Figures 6 and 7. With cartesian coordinates $\{ q = (x, y), p = (p_x, p_y) \}$ the $4N + 1$ differential equations of motion are:

$$\{ \dot{q} = p ; \dot{p} = F - \zeta p \} ; \dot{\zeta} = (K/N) - 0.5 ; K \equiv \sum(p_x^2 + p_y^2)/2 .$$

The summed forces $F$ on each particle include pair forces, gravity, and the container forces. We add on the thermostat forces, $\{ -\zeta p \}$, assigned the task of imposing isothermal conditions throughout the container. The particle interactions are Lennard-Jones without any cutoff, with quartic boundary potentials on the sides of the square container and along the perimeter of the circular container.

Individual densities $\{ \rho_i \}$, at each particle or at any grid point $(x_g, y_g)$, can be defined, and evaluated numerically, with the help of Leon Lucy’s two-dimensional “smooth-particle” weight function\textsuperscript{17}. The weight function spreads the influence of each particle very smoothly (two continuous derivatives everywhere) in space. For example the “delta-function” density of each two-dimensional particle and of its properties (such as velocity, energy, and pressure
tensor) are likewise distributed smoothly within a circle of radius $h$. The weight function is maximum at the particle’s location and vanishes on and beyond its bounding circle. The corresponding density distribution in the differential neighborhood $rdrd\theta$ of a particle is

$$\rho(r, \theta) = \frac{5}{\pi h^2}(1 - 6z^2 + 8z^3 - 3z^4) \ ; \ z \equiv r/h.$$  

A reasonable choice of the range $h$ of Lucy’s weight function for most atomistic simulations is 2 or 3 particle diameters. We have chosen 2 throughout the present work.

The normalization prefactor in one dimension, $(5/4h)$ for $-h < dx < +h$, is replaced by $(5/\pi h^2)$ for normalization within a circular area with $\pi r^2 < \pi h^2$:

$$\int_0^h 2\pi r dr (5/\pi h^2)(1 - 6z^2 + 8z^3 - 3z^4) \equiv 1 \text{ where again } z \equiv (r/h).$$

Lucy’s smooth weight function is convenient for comparing the results of atomistic simulations to the predictions of continuum mechanics, as we shall presently demonstrate, when seeking interfaces identifying the liquid phase.

A simple example illustrates the usefulness and power of smooth-particle weighting. Consider a one-dimensional lattice of points at the integers so that the coarse-grained “density of points” is unity. Using Lucy’s smooth-particle weighting function normalized for one-dimensional distributions,

$$w(|dx| < h) = \frac{5}{4h}(1 - 6z^2 + 8z^3 - 3z^4) \text{ where } z \equiv |dx|h,$$

gives for the density at each integer point 1.0156 for a “smoothing length” $h = 2$ and 1.0031 for smoothing length $h = 3$. The local density in a one-dimensional system at the grid point $x_g$ is the summed-up contribution from nearby particles $\{x_i\}$ within a distance $h$ of the grid point:

$$\rho(x_g) \equiv \sum_i w(|x_i - x_g|).$$

Applying this same definition, in between the integers, at the various midpoints $\pm(1/2), \pm(3/2), \ldots$, the smoothed densities are 0.9863 and 0.9973 respectively for smoothing lengths of 2 and 3.

Likewise, carrying out a one-dimensional average over $x$ for a few hundred horizontal strips the $y$-dependent pressure and density, $\{ \langle P(y) \rangle \}, \{ \langle \rho(y) \rangle \}$ can be computed with one-dimensional weights including all particles within a vertical separation $|dy| < h$ of the gridpoint in question, where $h$ is the range of the Lucy function. The spatial and temporal
FIG. 8: Time-averaged density contours from 0.05 to 0.85 for 640 Lennard-Jones particles at $T = 0.5$ and overall density 0.4. The quartic square boundaries are located at $\pm 20$. Space and time averages, over the horizontal $x$ coordinate in space, and using the final two million timesteps in a four million timestep run, in time, provide the $\langle P \rangle (\langle \rho \rangle)$ profile giving the structure of the meniscus perpendicular to that interface.

Averaging process involves three distinct steps: At each timestep [1] Compute individual particle properties such as $\rho_i$ and $P_i$ using two-dimensional smoothing; [2] Convert the particle data into spatial averages for a $y$ grid using one-dimensional smoothing; [3] Combine the spatial values by averaging over as many as millions of timesteps.

Figures 8 and 9 show time-averaged pressure and density profiles for the two boundary conditions, square and circular. In both cases the wildly fluctuating configurations of the snapshots, time-averaged over the last half of a two-million timestep simulation, provide a smooth meniscus with a width of just a few particle diameters. The pressure and density, averaged over both time and $x$ indicate a horizontal isotherm rather than the van der Waals’ loop suggested by Barker, Henderson, and Abraham’s phase diagram of Figure 1.

Figure 10 compares the structures of the meniscus, pressure versus density, for a series of five values of the gravitational field from 0.01 to 0.05. The upper segment of each of the five traces corresponds to the high-density high-pressure region near the bottom of the container, which supports the entire weight of the 640 Lennard-Jones particles. The low-density low-pressure region near the bottom of the plot (where the five traces agree)
FIG. 9: Time-averaged density contours from 0.05 to 0.85 for 640 Lennard-Jones particles at $T = 0.5$ with overall density 0.4. The circular boundary potential begins at $r = \sqrt{(1600/\pi)} = 22.568$. Averages over the horizontal $x$ coordinate using two million timesteps provide the $\langle P \rangle(\langle \rho \rangle)$ profile giving the structure of the meniscus.

FIG. 10: Time-averaged pressure as a function of time-averaged density using the last half of two million Runge-Kutta timesteps for 640 Lennard-Jones particles in a $40 \times 40$ quartic box. Five separate curves are shown corresponding to field strengths 0.01, 0.02, 0.03, 0.04, and 0.05. The lower portions of the five curves correspond to the meniscus separating liquid from gas. The good agreement indicates very little dependence of the pressure-density correlation upon field strength. The simulation with $g = 0.01$ used the last half of a four-million-timestep run.
FIG. 11: Two families of pair potentials, $\phi^L_m = (2-r)^{2m} - 2(2-r)^m$ and $\phi^S_m = (2-r^2)^{2m} - 2(2-r^2)^m$.

In the stress-free triangular lattice the short-ranged potentials, $\{ \phi^S_m(r < \sqrt{2}) \}$, have a range $\sqrt{2}$ so that each particle only interacts with 6 nearest neighbors. In the longer-ranged case, with $\phi^L_m(r < 2)$, each particle interacts with 3 shells of 6 neighbors each.

describes the meniscus atop most of the fluid. The good agreement of all five indicates that the present introduction of gravity into critical-region simulations provides accurate unambiguous estimates of the subcritical isotherms without the need for free energies or a Maxwell construction. Contour plots, as in Figures 8 and 9 are probably the best diagnostic tool for the meniscus as the density near the centre of the container can be assessed and, when time-averaged, is guaranteed to obey the barometer formula, $dP(y)/dy = -\rho(y)g$.

XI. TWO FINITE-RANGE POLYNOMIAL PAIR-POTENTIAL FAMILIES

In our exploratory work here we have emphasized Lennard-Jones’ 12/6 pair potential because its thermodynamic properties are familiar and well investigated\cite{119}. Lennard-Jones’ potential is the most thoroughly studied of the “realistic” potentials. We have sought to learn more by introducing two very different families of finite-ranged pair potentials. The longer-ranged family $\{ \phi^L_m(r < 2) \}$, includes three shells of neighbors, 18 in all, at zero stress, while the short-ranged potentials, $\{ \phi^S_m(r < \sqrt{2}) \}$ include only the six nearest neighbors. For all of these potentials we continue to adopt “reduced units” based on a well-depth of
FIG. 12: Cold curves for the triangular lattice with the potentials of Figure 11. The stress-free square lattices are mechanically unstable to shear. Because the wider bowls, extending to $r = 2$ include second and third neighbors at zero stress the densities exceed the narrow-bowl value $\sqrt{4/3} = 1.1547$.

unity at the particle-pair separation of unity. All the potentials have smooth minima of -1 at $r = 1$. In the Lennard-Jones case we entirely avoid cutoff corrections by including all $N(N-1)/2$ pairwise interactions. The finite-ranged polynomial potentials, with order-$N$ interactions, are much faster to analyze. In our exploratory molecular dynamics simulations we enclosed a few hundred particles in a box with quartic-potential very smooth boundaries and included a weak gravitational field. Our plan was to observe phase boundaries directly.

To generalize these exploratory simulations we introduced two related families of finite-range polynomial pair potentials. These polynomial potentials require simulation times of order $N$ rather than $N^2$ for the force calculations. Figures 11 and 12 show six of the specimen potentials along with eight of their static-lattice “cold curves”, calculated for perfect triangular lattices. For the range of densities shown all the shorter-ranged potentials, $\{ \phi^S_m \}$, have their minima at $r = 1$ with cold curve minima at a density $\sqrt{4/3} = 1.1547$ and a binding energy $e(\rho = 1.1547) = -3$. Because the longer-ranged potentials extend to a separation of 2 their lattices are slightly compressed from the “close-packed” density 1.1547. The binding energy is accordingly increased. See Figure 12.
FIG. 13: Coexisting densities for $\phi^L_3$ and $\phi^L_4$. Both cases closely reproduce Onsager’s two-dimensional Ising model power law dependence of the density difference, $\rho_{\text{Liquid}} - \rho_{\text{Gas}}$ on $T_c - T$.

The Mayers’ 1940 “Derby Hat” idea for the region above the meniscus’ disappearance appears in Figure 14. Each of the data shown here was generated with a million timesteps using $dt = 0.001$.

XII. GAS LIQUID COEXISTENCE AND THE MAYERS’ “DERBY HAT”

Figure 13 shows our estimates for the gas-liquid coexistence curves for two of the short-ranged potentials. These coexistence curves were obtained using an improved version of the “liquid-ribbon” method described by Farid Abraham in 1980, using 256 particles. Here we use conventional molecular dynamics ($N = 3600$, $dt = 0.001$, $t = 2000$), with a cell, elongated horizontally and with periodic boundaries at its top and bottom. Smooth particle averaging with Leon Lucy’s weight function then provides density and pressure profiles. The initial square-lattice configuration is quenched into the mechanically unstable region of the phase diagram using Nosé-Hoover dynamics. The system rapidly separates into vapour and liquid phases. The density profile is symmetrized prior to recording the values of the flat regions of the gas and liquid phases’ densities. The final configuration of each simulation becomes the starting point for the next-lower temperature simulation. The full set of eight coexisting density pairs is then correlated with their temperatures, as shown in Figure 13.

The coexistence data are then fitted to the scaling laws shown in the figure. For the variation of the density with temperature, $\Delta \rho(T)$, the exponents $1/7.5$ and $1/7.9$ resulted
FIG. 14: The Mayers’ 1940 idea, now obsolete, that a meniscus-free region of infinite compressibility (shaped like a “Derby Hat”) would be found atop the two-phase coexistence region, is illustrated here in red. Our simulations carried out above the critical temperature and with a small gravitational field show the presence of relatively large clusters of particles in the low-density upper portions of our containers, as shown in Figure 15.

for the 6/3 and 8/4 long-ranged ($r \leq 2$) potentials. Because these exponents approximate Onsager’s 1/8, found analytically for the two-dimensional Ising model, we repeated the scaling law fits using 1/8 for the exponent.

The law of “rectilinear diameters” (the mean of gas and liquid densities varies linearly with temperature) was adequate for the 6/3 potential while a quadratic fit was needed in the righthand plot of the 8/4 data. These choices enabled the vapour (red) and liquid (black) densities to be drawn in as continuous curves with critical temperatures of 0.685 and 0.503. We abandoned an effort to estimate the critical region for the 10/5 potential. The relatively weaker binding energy indicated that weeks of computer time might be required for an accurate assessment of that potential’s critical point.

In 1940, as described in Chapter 14 of their Statistical Mechanics text\textsuperscript{20}, Joseph and Maria Mayer argued from the standpoint of their statistical-mechanical cluster theory that there is a highly-complex “Derby-Hat” critical region atop the coexistence curve, as is shown in Figure 14. The red “Hat” region was thought to sit atop the two-phase region in which gas and liquid are separated by a meniscus. If this construction were correct, as has been recently championed by Woodcock and Khmelinskii\textsuperscript{21}, the meniscus should suddenly vanish at the same temperature but at a whole range of different densities, different by as much as ten percent according to the Mayers’ estimate in three space dimensions. Here the main difference seen above and below the apparent critical temperature of 0.685 for the $\phi_5^3$ potential is the concentration of large clusters in the vapour phase, visible in Figure 15.
FIG. 15: Sixteen snapshots of 400 particles with $\phi_L^L(r < 2)$ controlled by a gravitational field $g = 0.01$. The periodic width of the system is $\sqrt{800}$ and the spacing between the snapshots is 20,000 timesteps, corresponding to an elapsed time of 100. The lefthand columns, starting at lower left, correspond to subcritical temperatures of 0.61 to 0.68 and the righthand columns to supercritical temperatures from 0.69 to 0.76, finishing at the upper right. The laptop time for all these simulations is a few minutes.

These polynomial potentials avoid cutoff corrections. We briefly considered the usefulness of energy comparisons with the square lattice, but preliminary calculations revealed that lattice unstable to shears parallel to either the $x$ or the $y$ direction. By contrast, as is consistent with hexagonal symmetry, the triangular lattice has an isotropic shear modulus, a convenient property for modeling atomistic results with isotropic continuum mechanics.

Either type of potential choice, $(2 - r)^{12} - 2(2 - r)^{6}$ or $(2 - r)^{6} - 2(2 - r)^{3}$, can provide the same curvature at the potential minimum of unity $\phi'' = 72$ as does Lennard-Jones’
FIG. 16: $T = 0.5$ isotherms for Lennard-Jones’ potential and two families of polynomial potentials. The longer-ranged potentials, \( \{ \phi^L_m(r < 2) = (2 - r)^{2m} - 2(2 - r)^m \} \), with \( m = 3, 4, 5, \) and \( 6 \), appear to exhibit liquid phases while the nearest-neighbor shorter-ranged potentials, \( \{ \phi^L_m(r^2 < 2) = (2 - r^2)^{2m} - 2(2 - r^2)^m \} \), appear to go directly from the solid to the gas phase on heating, with no intermediate liquid phase. Approximately 500 simulations were carried out for these isotherms, all with \( dt = 0.001 \), one million timesteps, and Nosé-Hoover control of the temperature using \( \dot{\zeta} = 10[1 - (K_t/K_0)] \). These data have been smoothed slightly for clarity.

XIII. TIME-AVERAGED THERMOSTATED MOLECULAR DYNAMICS

Figure 14 showed equally-spaced snapshots of 400 longer-ranged \( \phi^L_3 \) particles in a gravitational field. The temperatures run from 0.61 in the lower left corner to 0.76 at the upper right. There are eight snapshots below the critical temperature and eight above. Although the fluctuations are large it is clear that the cooler subcritical configurations are qualitatively closer to a gas-liquid interface than the more diffuse supercritical configurations to the right. The fluctuations evident in the snapshots can largely be removed by time averaging. Figures 17 and 18 show density and pressure profiles with one million timesteps for each temperature. The eight subcritical isotherms show a relatively sharp transition to a lower density gas-phase plateau. Above the critical temperature the density follows the barometer formula with a decreasing density and pressure with altitude. The gravitational field organizes the fluid without noticeably perturbing the structure of the meniscus.
FIG. 17: 16 density profiles, subcritical in blue and supercritical in red, for 16 temperatures ranging from 0.61 to 0.76. The relatively sharp meniscus broadens noticeably at the critical temperature. Each profile is the average of two million Runge-Kutta timesteps with $dt = 0.005$. $N = 400$ in a square container, periodic at the sides, quartic at the bottom and top, with a gravitational field strength of 0.01.

FIG. 18: 16 pressure profiles, subcritical in blue and supercritical in red, for 16 temperatures ranging from 0.61 to 0.76. The dip in the subcritical plots corresponds to the surface tension’s negative contribution to the mean pressure, $P = (P_{xx} + P_{yy})/2$. These data, just as those in Figure 17 required a bit under one day of laptop time. $N = 400$ in a square container, periodic at the sides, quartic at the bottom and top, with a gravitational field strength of 0.01.
XIV. CONCLUDING REMARKS

We have explored the critical region for two varieties of polynomial pair potentials, finding that the shorter-ranged family can sublime directly from the solid phase to the gas, without the intervention of a liquid. The monotone isotherms of the shorter-ranged potentials, displayed in Figure 15 is consistent with this finding. The longer-ranged family, with second and third neighbor interactions form a liquid phase with a well-defined but fluctuating meniscus. Time-averaging the fluctuating profiles provides stable smooth estimates of the meniscus region separating the liquid and gas.

With the longer-ranged potential \((2 - r)^6 - 2(2 - r)^3\) a visual inspection of the heated liquid in the presence of a weak field reveals a complexity outside the normal range of thermodynamics. Clusters of particles abound, from dimers and trimers up to percolating clusters which stretch all the way across the simulation. In view of these fluctuating features time-averaging is necessarily required to visualize and stabilize a liquid-gas interface. And time averaging is not enough. In principle field-free time averaging would only produce a constant mean density everywhere!

In order to “see” the definite boundary between liquid and gas we have considered an innovative version of molecular dynamics, with a containerized region and a localizing gravitational field. This combination, when time-averaged, provides density and pressure profiles in which the phases are separated by a meniscus. For small field strengths these profiles resemble the Maxwell construction tie-line linking the two fluid phases below the critical point. This same technique is equally applicable using Monte Carlo simulations in the canonical ensemble. The presence of gravity provides a definite time-averaged interface, providing a distinction between the gas and liquid and addressing the “What is Liquid” directly, through Hannay’s interface. The complexities due to fluctuations moderated by surface tension can be overcome with gravity. It is rewarding to see the subcritical dip in the pressure (Figure 18) disappear at the estimated critical temperature as calculated independently with the liquid-ribbon technique. It is particularly interesting to see that attractions beyond the first neighbors are needed for the liquid phase.

Our goal here has been twofold. We have introduced a simulation technique which provides a time-averaged description of the meniscus, curved or flat, depending upon the boundary conditions, separating the two phases. We have also introduced two families of pair
potentials which are relatively short-ranged, thereby avoiding the complications associated with cutoffs, often employed in the case of Lennard-Jones simulations. Because the gravitational field generates a density gradient spanning a wide range of densities, including the critical density, the method developed here is relatively insensitive to the number of particles chosen and the overall volume of the simulation container.
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