Hard-sphere fluids with chemical self potentials

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Abstract

Existence, uniqueness and stability of solutions is studied for a set of nonlinear fixed point equations which define self-consistent hydrostatic equilibria of a classical continuum fluid that is confined inside a container $\Lambda \subset \mathbb{R}^3$ and in contact with either a heat and a matter reservoir, or just a heat reservoir. The local thermodynamics is furnished by the statistical mechanics of a system of hard balls, in the approximation of Carnahan-Starling. The fluid’s local chemical potential per particle at $r \in \Lambda$ is the sum of the matter reservoir’s contribution and a self contribution $-(V \ast \rho)(r)$, where $\rho$ is the fluid density function and $V$ a non-negative linear combination of the Newton kernel $V_N(|r|) = -|r|^{-1}$, the Yukawa kernel $V_Y(|r|) = -|r|^{-1}e^{-\kappa |r|}$, and a van der Waals kernel $V_W(|r|) = -(1 + \kappa^2 |r|^2)^{-3}$. The fixed point equations involving the Yukawa and Newton kernels are equivalent to semilinear elliptic PDEs of second order with a nonlinear, nonlocal boundary condition. We prove the existence of a grand canonical phase transition, and of a petit canonical phase transition which is embedded in the former. The proofs suggest that, except for boundary layers, the grand canonical transition is of the type “all gas $\leftrightarrow$ all liquid” while the petit canonical one is of the type “all vapor $\leftrightarrow$ liquid drop with vapor atmosphere.” The latter proof in particular suggests the existence of solutions with interface structure which compromise between the all-liquid and all-gas density solutions.

KEYWORDS:
Nonlinear analysis: fixed point problems, integral and partial differential equations; Classical fluids: liquid vs. gas phase transition, liquid drops, liquid-vapor interface; Particle systems: hard sphere-, Yukawa-, Newton-, and van der Waals-interactions; Statistical mechanics: petit- and grand-canonical ensembles, van-der-Waals limit.
1 INTRODUCTION

The interface between physically coexisting thermodynamic (locally) pure phases poses a challenging array of problems in statistical mechanics which fall somewhere inbetween the micro- and macroscopic realms. The large scale (macroscopic) geometry of the interface can be successfully modeled as a sharp *Gibbs interface*, computed from some constrained principle of minimum surface area (Wulf shape); this generalizes to the dynamical domain in form of motion by mean curvature and related principles. The transversal structure of the interface, which obviously is not resolved when the interface is modeled as a Gibbs interface, is the hard problem that lives at the fringe of the macro-world and for which there is no definitive answer yet.

To get a hand on the transversal structure it is customary to invoke a van der Waals (for fluids) or Weiss (for magnets) mean-field approximation which allows one to study both the large scale geometry and the transversal interface structure. While this approximation overly simplifies the problem, it is far from being understood completely and continues to attract the attention of mathematical physicists.\[1\] [2] [7] [9] [10] [12] For the liquid-vapor interface at equilibrium, which is the motivation for this paper, the van der Waals type models emerge in Kac\[27\] type scaling limits from the statistical mechanics of systems of interacting microscopic particles, with particle densities resolved on the long distance scale of the attractive part, $V_A$, of the particle interaction $V_R + V_A$, while the short distance repulsive part $V_R$ is absorbed into the local thermodynamics.\[54\] [41] [33]

The local thermodynamics of an $N$-body system with repulsive pair interaction $V_R$ is given by a pure phase, defined in the thermodynamic limit of a macroscopically spatially uniform system in thermal equilibrium with a heat reservoir at reciprocal temperature $\beta \in \mathbb{R}^+$ and a matter reservoir at logarithmic fugacity (i.e., chemical potential per particle : temperature ratio) $\gamma \in \mathbb{R}$, characterized by a position-independent pressure : temperature ratio $p = \varphi(\beta, \gamma)$ and particle density $\eta = \partial_\gamma \varphi(\beta, \gamma)$ at all points of differentiability of $\gamma \mapsto \varphi(\beta, \gamma)$. On general thermodynamic grounds, $(\beta, \gamma) \mapsto \varphi(\beta, \gamma)$ is strictly positive, increasing in $\gamma \in \mathbb{R}$, and convex in $\beta \in \mathbb{R}^+$ and $\gamma$. By convexity, $\gamma \mapsto \varphi(\beta, \gamma)$ is differentiable a.e., but the models from physics are expected to be better behaved and feature only finitely many points of non-differentiability, at $\gamma_1(\beta), \gamma_2(\beta), \ldots$, say. At such a $\gamma_k(\beta)$ typically two different pure phases are equally likely, one of them denser than the other, and one needs to select the one which furnishes the local thermodynamics.

In this paper the local thermodynamics is chosen to represent a continuum formed
by many identical hard microscopic balls, known (in a fluid state) as a hard-sphere fluid and more generally as a hard-sphere system. A hard-sphere system is characterized by a $\beta$-independent pressure : temperature ratio, i.e. $\varphi(\beta, \gamma) = \varphi_\bullet(\gamma)$. We will write $\varphi_\bullet'(\gamma)$ for $\partial_{\gamma} \varphi_\bullet(\gamma)$. The function $\varphi_\bullet(\gamma)$ has a point of non-differentiability at $\gamma_{fs}$ associated with a fluid-versus-solid transition. Here we are interested in studying the fluid phases, but for our investigations we do need to have control over this singularity.

Physically, a hard-sphere fluid may model the short distance repulsion between the spherical atoms in a noble gas or between neutrons in a neutron fluid. Over somewhat larger distances $r$ any two such atoms or neutrons also feel attractive forces $-\nabla V_A$, the van der Waals (Jr.) force in the case of atoms, which is due to self-induced dipole-dipole interactions associated with their first excited configurations, and the Yukawa force in the case of neutrons, which is explained in terms of the pion exchange of the strong nuclear forces. When the number of atoms or neutrons becomes too large, as in (helium) brown dwarf stars or in neutron stars, Newtonian gravity has to be added. We choose the $V_A$ interaction to mimic any of these physical systems. More precisely, writing $\alpha V$ for $V_A$, we let $\alpha V$ stand for any non-negative-linear combination of the form

$$\alpha V(r) = A_W V_w(r) + A_V V_v(r) + A_N V_N(r),$$

(1)

where

$$V_w(r) = -(1 + \kappa^2 r^2)^{-3},$$

(2)

$$V_v(r) = -e^{-\kappa r}/r,$$

(3)

$$V_N(r) = -1/r,$$

(4)

are integral kernels of strictly negative definite compact operators on $L^2(\Lambda)$ for any bounded $\Lambda \subset \mathbb{R}^3$, and where $A_w \in \{0, \alpha_w\}$, $A_V \in \{0, \alpha_v\}$, and $A_N \in \{0, \alpha_N\}$, while $\alpha_w$, $\alpha_v$, and $\alpha_N$ are strictly positive coupling constant : temperature ratios. In the van der Waals approximation the effect of $\alpha V$ on the system is accounted for by adding to the externally generated chemical potential per particle : temperature ratio $\gamma$ the chemical self potential per particle : temperature ratio at $r$, given by $-(\alpha V \ast \eta)_\Lambda(r)$, where

$$ (V \ast \eta)_\Lambda(r) = \int_{\Lambda} V(|r - \tilde{r}|) \eta(\tilde{r}) d^3 \tilde{r}. $$

(5)
We refer to \((V_N * \eta)_\lambda(r)\) as the \textit{Newton –}, to \((V_Y * \eta)_\lambda(r)\) as the \textit{Yukawa –}, and to \((V_W * \eta)_\lambda(r)\) as the \textit{van der Waals potential of \eta at \(r\)}.

In his original study, van der Waals\cite{53} assumed boundary effects to be negligible and the density function \(\eta(r)\) to be spatially uniform, i.e. \(\eta(r) \equiv \eta\). These assumptions can be rigorously correct only in the infinite volume limit\cite{35} when the fluid fills all space \(\mathbb{R}^3\) uniformly, with gravity “switched off;” note that \(V_W(| \cdot |) \in L^1(\mathbb{R}^3)\) and \(V_N(| \cdot |) \in L^1_{\text{loc}}(\mathbb{R}^3)\) merely. When \(A_N = 0\) and the constant function \(\eta(r) \equiv \eta\) is substituted in \((5)\) with \(\Lambda = \mathbb{R}^3\), then \(- (V * \eta)_{\mathbb{R}^3} = \eta \|V(| \cdot |)\|_{L^1(\mathbb{R}^3)}\) is a constant function, too. Setting \(\|V(| \cdot |)\|_{L^1(\mathbb{R}^3)} =: \|V\|_1\) for short, the van der Waals densities \(\eta_{\text{vdW}}\) are then computed from the van der Waals fixed point equation\cite{4}:

\[
\eta = \phi'(\gamma + \alpha \|V\|_1 \eta).
\] (6)

In \((\alpha, \gamma)\)-parameter space there are disjoint, open two-dimensional domains where the algebraic equation \((6)\) has one or three solutions in the fluid density regime, respectively (see also sections IV & V); these regions are separated by a closed one-dimensional subset featuring two solutions of \((6)\), except for one point (the critical point) at which only one solution exists. Constant (large enough) \(\alpha\) sections and constant (intermediate size) \(\gamma\) sections through the fluid solution manifold over the \((\alpha, \gamma)\) half plane each produce an \(S\)-shaped curve associated with the famous “van der Waals loop.” In the region with three fluid density solutions, the largest solution is interpreted as the liquid density phase, the smallest as the gas (a.k.a. vapor) density phase of the fluid, and the intermediate density solution as a thermodynamically unstable artifact of the model. The liquid and the gas density solutions are each stable fixed points of \((6)\) under iteration, the intermediate density solution is not. However, thermodynamically the liquid and gas density solutions are simultaneously stable only along the \textit{gas \\& liquid coexistence curve} \(\alpha \mapsto \gamma = \gamma_{\text{vdW}}(\alpha)\) of the model, determined by Maxwell’s equal-areas construction,\cite{37} rigorously vindicated in Ref.\cite{55}, while away from this curve (still in the three-solutions region) thermodynamically only one of these two solutions is stable, the other one at most metastable. Here, thermodynamic stability and metastability are understood with \(\alpha\) and \(\gamma\) fixed, and explained below.

\footnote{In textbooks (e.g. \cite{23, 38}) one usually finds discussions of \((6)\) with \(\phi'(\gamma)\) replaced by van der Waals’ \(\phi'_{\text{vdW}}(\gamma)\) which corresponds to a system of many hard rods on a line. While for systems of hard balls it gives quantitatively wrong answers, qualitatively they reproduce those obtained with the correct \(\phi'_{\text{vdW}}(\gamma)\). Also, usually a value for \(\|V\|_{L^1}\) is given without specifying \(V\).}
More interesting than (6) is the nonlinear fixed point problem
\[ \eta(r) = \psi^\prime(\gamma - (\alpha V \ast \eta)_{R^3}(r)) \] (7)
in the positive cone of the non-separable Banach space \( C_0^0(R^3) \) of bounded continuous functions \( \eta(r), r \in R^3 \). If \( V \in L^1(R^3) \), then (7) can be solved with the Ansatz \( \eta(r) \equiv \bar{\eta} \), which leads back to the algebraic fixed point equation (6). Yet, for a hard-sphere fluid with \( V(|r|) = V_y(|r|) \), whenever \( (\alpha, \gamma) \) is a point on the gas & liquid coexistence curve of locally uniform phases computed from (6), then (modulo translations and rotations) a unique monotonic planar interface solution \( \eta(r) \equiv \bar{\eta}(x) \) exists, where \( x \in R^3 \) is a cartesian coordinate of \( R^3 \). This can be shown by adapting the ODE arguments on p. 40-41 of Ref. [42], which are available because \( (-\Delta + \kappa^2)V_y(|r|) = -4\pi\delta(r) \). A monotonic planar interface solution illustrates the physical phenomenon of coexistence of the liquid and the gas density phases; they have been extensively studied in one dimensional models. [52 42 7 12]

Furthermore, using the equivalent radial ODE problem obtained with the help of 
\[ (-\Delta + \kappa^2)V_y(|r|) = -4\pi\delta(r) \], Mironescu \[39\] has shown that solutions in \( R^3 \) with spherical droplet / bubble geometry exist; these solutions do not exist exactly on the gas & liquid coexistence curve for the uniform phases, yet are nearby. Such ODE arguments are not available for a hard-sphere fluid with \( V(|r|) \neq V_w(|r|) \), and the existence and classification of the non-constant solutions in \( R^3 \) of (7) in this case is largely unexplored territory. We also note that since \( V_y(|r|) \neq L^1(R^3) \), the fixed point problem (7) is not well defined in \( R^3 \) as it stands with \( V_y \ast \phi \) given by (5); however, replacing \( V_y \ast \phi \) by \( \phi \) and stipulating the familiar Poisson equation \( \Delta \phi = 4\pi\eta \), solutions in \( R^3 \) for the related PDE problem \( \Delta \phi = 4\pi\psi^\prime(\gamma - \alpha\phi) \) do exist; it is easy to numerically compute radial solutions, which have applications in planetary science. [51 32]

To summarize, non-uniform van der Waals fluid theory furnishes an accessible model to study the structure of non-uniform density functions \( \eta(r) \) of a hard-sphere fluid in \( R^3 \). Evidently, boundary effects are absent in \( R^3 \). Moreover, for \( V = V_y \) and \( V = V_N \) simple ODE techniques greatly facilitate the computation of solutions in \( R^3 \).

Beside the structure of interfaces, their fluctuations are of interest. Unfortunately, in unbounded space \( R^3 \) all interface solutions are thermodynamically neither stable nor metastable and interface fluctuations diverge. [42 43 44] even though droplets may be quite long-lived in dynamical calculations with the Alan–Cahn and related evolution equations. To obtain finite fluctuations one needs to stabilize the interfaces.
An intuitively obvious way to obtain a stable fluid interface is to enclose the fluid inside a container \( \Lambda \) (with either wetting, non-wetting, or neutral mechanical boundary conditions) and to replace the thermodynamic contact condition of prescribed logarithmic fugacity \( \gamma \) by the stricter one of prescribed amount of matter \( \int_\Lambda \eta(\mathbf{r})d^3r = N \). When \( \Lambda \) is macroscopic and \( N \) halfway inbetween the values of \( |\Lambda|\bar{\eta} \) for the large and small fluid density values \( \bar{\eta} \) solving (6), then there is too much matter in the container to be all vapor, and too little to be all liquid. In this case the system must find a compromise structure: either a drop of liquid surrounded by vapor or a bubble of vapor inside liquid, depending on the mechanical boundary conditions. It is reassuring to find this scenario confirmed numerically for \( V = V_w \) and neutral mechanical boundary conditions, and in particle simulations of many hard balls with attractive \(-r^{-6}\) interactions. Interestingly enough, in Ref.[33] it was found numerically that the thermodynamic transition from the vapor state to the liquid-drop state is not gradual but occurs at a petit-canonical first-order phase transition which is embedded in the grand-canonical first order phase transition between vapor and liquid. To rigorously prove this empirical picture correct is an interesting mathematical problem which is still largely open.

To make a modest contribution toward its solution we here continue our previous study where we numerically evaluated the fixed point problem

\[
\eta(\mathbf{r}) = \varphi^\prime(\gamma - (\alpha V \star \eta)_A(\mathbf{r}))
\]

for a cohesive “hard-sphere continuum” inside a container \( \Lambda \subset \mathbb{R}^3 \) with neutral boundary. In this paper we study the existence, uniqueness, structure, and stability of fluid solutions to (8) with rigorous analysis. Stability is defined as follows.

The stability of solutions of (8) for the thermodynamic contact conditions “heat and matter reservoirs” is determined by the functional

\[
\mathcal{P}_{\alpha,\gamma}[\eta] = \int_\Lambda \varphi^\prime(\gamma - (\alpha V \star \eta)_A(\mathbf{r}))d^3r + \frac{1}{2} \int_\Lambda \int_\Lambda \alpha V(|\mathbf{r} - \tilde{\mathbf{r}}|)\eta(\mathbf{r})\eta(\tilde{\mathbf{r}})d^3r d^3\tilde{\mathbf{r}},
\]

which we rigorously derived from the grand-canonical ensemble in Ref.[33]. Solutions of (8) are critical points of (9) in the positive cone of the separable Banach space \( C^0_b(\Lambda) \). A solution \( \eta_\Lambda \) of (8) is globally \( \mathcal{P} \) stable if \( \mathcal{P}_{\alpha,\gamma}^{\Lambda}[\eta_\Lambda] = P_\Lambda(\alpha, \gamma) \), where

\[
P_\Lambda(\alpha, \gamma) := \max_\eta \{\mathcal{P}_{\alpha,\gamma}^{\Lambda}[\eta]\};
\]
global maximizers are denoted $\eta_\Lambda^{GC}(r)$, their dependence on $\alpha, \gamma$ implied. A solution $\eta_\Lambda$ of (8) is locally $\cal P$ stable if

$$\mathcal{P}_{\alpha,\gamma}''(\sigma, \sigma)|_{\eta_\Lambda} < 0$$

for all $\sigma \neq 0$ such that $0 \leq \eta_\Lambda + \sigma \in C_0^0(\Lambda)$. Here,

$$\mathcal{P}_{\alpha,\gamma}''(\sigma, \sigma)|_{\eta_\Lambda} = \frac{1}{2} \int_\Lambda \varphi''(\gamma - (\alpha V \ast \eta_\Lambda)(r)) (\alpha V \ast \sigma)^2(\eta_\Lambda(r)) d^3r$$

is the diagonal part of the second Gâteaux derivative of $\mathcal{P}_\Lambda$ at $\eta_\Lambda$. A solution $\eta_\Lambda$ of (8) satisfying (11) but not (10) is called $\cal P$ metastable. If $\mathcal{P}_{\alpha,\gamma}''(\sigma, \sigma)|_{\eta_\Lambda} > 0$ (= 0) for at least one $\sigma$, then $\eta_\Lambda$ is called $\cal P$ unstable (locally $\cal P$ indifferent).

In Ref. [33] we also explained that stability of solutions of (8) for a given amount of matter in thermodynamic contact with a “heat reservoir” at inverse temperature $\beta (\propto \alpha)$ is defined in terms of the following thermodynamic free energy functional. For each density function $\eta \in C_0^0(\Lambda)$ we define:

(i) its amount of matter in $\Lambda$,

$$N_\Lambda[\eta] = \int_\Lambda \eta(r) d^3r;$$

(ii) its energy : temperature ratio,

$$\mathcal{E}_\alpha[\eta] = \frac{3}{2} N_\Lambda[\eta] + \frac{1}{2} \int_\Lambda \int_\Lambda (|r - \tilde{r}|) \eta(r) \eta(\tilde{r}) d^3r d^3\tilde{r};$$

(iii) its (strictly) classical entropy,

$$\mathcal{S}_\Lambda[\eta] = \frac{5}{2} N_\Lambda[\eta] - \int_\Lambda \eta(r) \ln \eta(r) d^3r - \int_\Lambda \eta(r) \int_0^{\eta(r)} (p_\bullet(\eta) - \eta) / \eta^2 d\eta d^3r,$$

where $p_\bullet(\eta)$ is the hard-sphere pressure : temperature ratio as function of $\eta$;

(iv) its free energy : temperature ratio,

$$\mathcal{F}_\alpha[\eta] = \mathcal{E}_\alpha[\eta] - \mathcal{S}_\Lambda[\eta].$$

$^{2}$“GC” stands for grand canonical because those densities comprise the support of the grand canonical measure in the van der Waals limit.
The thermodynamic free energy : temperature ratio \( F_\Lambda (\alpha, N) \) is then given by

\[
F_\Lambda (\alpha, N) = \min_{\eta} \{ \mathcal{F}_\Lambda^\Lambda [\eta] \mid \mathcal{N}_\Lambda^\Lambda [\eta] = N \}.
\]

Solutions of (8) which saturate (17) are called globally \( \mathcal{F} \) stable and denoted \( \exists \eta^{\text{PC}}_\Lambda (r) \), their dependence on \( \alpha, N \) implied. Local \( \mathcal{F} \) stability etc. is defined in terms of the diagonal part of the second Gâteaux derivative of \( \mathcal{F}_\Lambda^\Lambda \),

\[
\mathcal{F}_\Lambda^\Lambda''(\sigma, \sigma) \bigg|_{\eta_\Lambda} = -\frac{1}{2} \int_\Lambda s''_\Lambda(\eta_\Lambda(r)) \sigma^2(r) \, d^3r + \frac{1}{2} \int_\Lambda \int_\Lambda \alpha V(|r - \tilde{r}|) \sigma(r) \sigma(\tilde{r}) \, d^3r \, d^3\tilde{r} \tag{18}
\]

where \( s_\Lambda(\eta) \) is defined by \( S_\Lambda^\Lambda[\eta] = \int_\Lambda s_\Lambda(\eta(r)) \, d^3r \). Variation is to be carried out under the constraint \( \int_\Lambda \sigma d^3r = 0 \) so that the \( \eta_\Lambda \)-disturbances preserve the number of particles.

We close this introduction by re-emphasizing that our study of the finite volume fixed point problem (8) is not motivated by trying to understand so-called finite-size corrections to dominant infinite volume results. Rather it is motivated by the physical phenomenon of stable interface solutions in finite containers holding a fixed amount of fluid. What makes such a study difficult are the following two points: (i) boundary layer effects are as big as interface effects, and one has to separate these in the analysis; (ii) one has to rule out competing solutions which take values in the crystal regime, and this leaves little wiggle room in parameter space. To level the ground we first study the simpler problem when the amount of fluid is controlled by a matter reservoir before turning to the problem with a fixed amount of fluid.

The rest of this article is structured as follows:

- In section II we define the Carnahan–Starling approximation to the fluid part and the Speedy approximation to the solid part of the function \( \gamma \mapsto \varphi_\bullet(\gamma) \).
- In section III we identify a parameter region in the \( (\alpha, \gamma) \) (half) space in which all solutions of (8) take values exclusively in the fluid density range.
- In section IV we identify a region in which fluid solutions are unique.
- In section V we identify a region where various fluid solutions exists.
- In section VI we study the thermodynamic stability of the fluid solutions in contact with heat-plus-matter reservoirs. We prove the existence of a vapor \( \leftrightarrow \) liquid phase transition in the finite-volume grand-canonical ensemble.

\(^{3\text{PC}} \) stands for petit canonical because those densities comprise the support of the petit canonical measure in the van der Waals limit.
In section VII we address the thermodynamic stability of the fluid solutions in contact only with a heat reservoir and also explain the relationship with the infinite-volume Lebowitz-Penrose results. We prove the existence of a petit-canonical finite-volume phase transition between the vapor state and a state for which we present evidence that it is of liquid-drop type.

Appendix A supplies some explicit evaluations valid for spherical geometry.

Appendix B lists the nonlinear partial differential equations associated with our fixed point integral equations.

Appendix C provides a “dictionary” to translate our dimensionless notation into conventional dimensional notation used in the physics literature.

Appendix D contains a brief list of (minor) errata for our previous papers on the subject, Ref.[29] and Ref.[33].

2 THERMODYNAMICS OF HARD SPHERE SYSTEMS

Numerical simulations of the dynamics of many identical hard balls indicate a thermodynamically stable fluid phase only when the dimensionless density (the volume fraction) \( \bar{\eta} \) stays below \( \bar{\eta}_f^c \approx 0.49 \), with numerical errors reportedly less than 1%. Numerical simulations also indicate a thermodynamically stable solid phase above \( \bar{\eta}_s^c \approx 0.54 \) all the way up to \( \bar{\eta}_{f_{cc}}^c = \pi \sqrt{2}/6 \approx 0.7405 \), the fcc crystal close packing fraction, although the system may “jam” into a glassy structure. The interval \((\bar{\eta}_f^c, \bar{\eta}_s^c)\) is interpreted as furnishing the coexistence of both fluid and solid phases. In the absence of empirical evidence for any further phase transition of the hard-sphere system, one may thus assume that the map \( \gamma \mapsto p = \wp_\bullet(\gamma) \) for a hard-sphere system is a positive, increasing, convex function over \( \mathbb{R} \), which is asymptotic to a straight line with slope equal to \( \bar{\eta}_{f_{cc}}^c \) when \( \gamma \uparrow \infty \). Moreover, the map \( \gamma \mapsto p = \wp_\bullet(\gamma) \) has a kink at \( \gamma = \gamma_{fs} \) but otherwise is locally real analytic, such that away from the kink we have \( \bar{\eta} = \wp_\bullet'(\gamma) \). At \( \gamma = \gamma_{fs} \) the left-derivative \( \lim_{\gamma \uparrow \gamma_{fs}} \wp_\bullet'(\gamma) = \bar{\eta}_{fs} \), and the right-derivative \( \lim_{\gamma \downarrow \gamma_{fs}} \wp_\bullet'(\gamma) = \bar{\eta}_{fs}^c \). Unfortunately, no manageable formula is known for the exact \( \wp_\bullet(\gamma) \), but convenient formulas for very accurate approximations to \( \wp_\bullet(\gamma) \) are known.

For the fluid regime \( \gamma \in (-\infty, \gamma_{fs}] \) we resort to a formula by Carnahan and Starling, whose numerological manipulations have led to a simple approximation
\( \varphi_{CS}(\gamma) \) to \( \varphi_{\bullet}(\gamma)|_{\gamma \leq \gamma_{fs}} =: \varphi_{\bullet}(\gamma) \) which remarkably accurately fits the empirical data obtained in computer simulations. Graphs of the function \( \varphi_{CS}(\gamma) \) and its derivative \( \varphi'_{CS}(\gamma) \) are displayed in Figs. 1 & 2 of Ref. [33].

**Definition 2.1:** The Carnahan-Starling approximation to \( \varphi_{\bullet}(\gamma) \) is defined by the map \( \gamma \mapsto p = \varphi_{CS}(\gamma) \), given by the parameter representation \( p = g_{1}(\eta) \) and \( \gamma = g_{2}(\eta) \), with \[ g_{1}(\eta) = \frac{\eta + \eta^{2} + \eta^{3} - \eta^{4}}{(1 - \eta)^{3}} \] \[ g_{2}(\eta) = \ln \eta + \frac{8\eta - 9\eta^{2} + 3\eta^{3}}{(1 - \eta)^{3}}. \] where \( \eta \) is a real parameter in the interval \( 0 < \eta \leq \eta_{fs}^\infty \approx 0.49 \). This gives \( \gamma_{fs} = g_{2}(\eta_{fs}^\infty) \approx 15.208 \) as right limit for the domain of definition \( (-\infty, \gamma_{fs}) \) of \( \varphi_{CS}(\gamma) \).

**Remark:** Note that (19) and (20) are related by a thermodynamic identity for a system of many identical hard balls,

\[ \eta g'_{2}(\eta) = g'_{1}(\eta). \]

Indeed, (20) is obtained from (19) by integrating (21) and conveniently choosing the integration constant. As a consequence we have that \( \varphi'_{CS}(\gamma) = g_{2}^{-1}(\gamma) = \eta \) is a dimensionless particle density — as already implied by the stipulated notation. □

**Remark:** Formally (19) and (20) are well defined for all \( \eta \in (0, 1) \), and one may want to study this mathematical model in its own right. Whenever we use \( \varphi_{CS}(\gamma) \) as defined for all \( \eta \in (0, 1) \) we will refer to it as the Carnahan-Starling model, to distinguish this mathematical model from the actual hard-sphere physics. □

For the solid regime \( \gamma \in [\gamma_{fs}, \infty) \) we resort to Speedy’s effective approximation \( \varphi_{sp}(\gamma) \) to \( \varphi_{\bullet}(\gamma)|_{\gamma \geq \gamma_{fs}} =: \varphi_{\bullet}(\gamma) \), whose leading term is determined theoretically while

\[ g_{1}(\eta) = \frac{\eta + \eta^{2} + \eta^{3} - \eta^{4}}{(1 - \eta)^{3}} \] \[ g_{2}(\eta) = \ln \eta + \frac{8\eta - 9\eta^{2} + 3\eta^{3}}{(1 - \eta)^{3}}. \]
the other terms invoke a Padé approximation to fit the numerical simulation data.

**Definition 2.2:** The Speedy approximation to \( \varphi_\bullet(\gamma) \) is defined by the map \( \gamma \mapsto p = \varphi_{Sp}(\gamma) \), given by the parameter representation \( p = g_3(\overline{\eta}) \) and \( \gamma = g_4(\overline{\eta}) \), with

\[
g_3(\overline{\eta}) = 3\frac{\overline{\eta}_{fcc}^{ep}}{1 - \overline{\eta}/\overline{\eta}_{fcc}^{ep}} + \frac{b - \overline{\eta}/\overline{\eta}_{fcc}^{ep}}{c - \overline{\eta}/\overline{\eta}_{fcc}^{ep}},
\]

with \( a = 0.5921 \), \( b = 0.7072 \), \( c = 0.601 \), and

\[
g_4(\overline{\eta}) = \gamma_{fs} + \int_{\gamma_{fs}}^{\overline{\eta}} \frac{g_3'(x)}{x} dx
\]

where \( \overline{\eta} \) ranges in the interval 0.54 \( \approx \overline{\eta}_{fs} \leq \overline{\eta} < \overline{\eta}_{fcc}^{ep} \approx 0.7402 \). Note that both \( g_3(\overline{\eta}) \) and \( g_4(\overline{\eta}) \) are monotonic increasing on \((\gamma_{fs}, \overline{\eta}_{fs})\), diverging \( \uparrow \infty \) for \( \overline{\eta} \uparrow \overline{\eta}_{fcc}^{ep} \).

Speedy’s paper features formula (23), while (24) follows from postulating the thermodynamic relation \( \overline{\eta}g'_4(\overline{\eta}) = g'_3(\overline{\eta}) \) for \( \overline{\eta}_{fs} < \overline{\eta} < \overline{\eta}_{fcc}^{ep} \); as a consequence, \( \varphi'_\bullet(\gamma) = g^{-1}_4(\gamma) \) for \( \gamma > \gamma_{fs} \). The integration constant is chosen such that \( \gamma_{fs} = g_4(\overline{\eta}_{fs}) \approx 15.208 \) is the left limit for the domain of definition \([\gamma_{fs}, \infty)\) of \( \varphi_{Sp}(\gamma) \).

To summarize, we stipulate the following:

**Convention 2.3:** In the remainder of the paper, for \( \gamma \leq \gamma_{fs} \), i.e. in the fluid phase, we take \( \varphi_\bullet(\gamma) := \varphi_{CS}(\gamma) \equiv (g_1 \circ g_2^{-1})(\gamma) \), with \( g_1 \) and \( g_2 \) given by (19) and (20) in Definition 2.1. For \( \gamma \geq \gamma_{fs} \), i.e. in the solid phase, we take \( \varphi_\bullet(\gamma) := \varphi_{Sp}(\gamma) \equiv (g_3 \circ g_4^{-1})(\gamma) \), with \( g_3 \) and \( g_4 \) given by (23) and (24) in Definition 2.2.

In the next two figures we display the hard-sphere pressure : temperature ratio (Fig.1) and the hard-sphere chemical potential per particle : temperature ratio (Fig.2), both as functions of \( \overline{\eta} \). The second figure in particular will be very helpful to consult when reading our proofs in the ensuing sections.

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\[5\] Speedy reports that his formula agrees to within less than half the reported error with the results of Alder et al.\[3\], which are given by their formula (1), an asymptotic expansion in powers of \( \overline{\eta}_{fcc}^{ep} - \overline{\eta} \), viz.

\[
g_3(\overline{\eta}) = \overline{\eta}_{fcc}^{ep} \left[ 3\frac{1}{1 - \overline{\eta}/\overline{\eta}_{fcc}^{ep}} + K_0 + K_1(1 - \overline{\eta}/\overline{\eta}_{fcc}^{ep}) + O((\overline{\eta}_{fcc}^{ep} - \overline{\eta})^2) \right],
\]

with \( K_0 \approx -3.44 \) and \( K_1 \approx 1 \) taken from table III in Ref.\[3\].
Fig. 1. Equation of state $p$ vs. $\eta$ for a classical hard-balls continuum. Displayed are fluid branch $(0 < \eta < 0.49)$ and solid branch $(0.54 < \eta < 0.74)$ together with the coexistence line $(0.49 \leq \eta \leq 0.54; \text{dotted})$ and the fcc crystal close packing limit (broken vertical line at $\eta = 0.74019$).

Fig. 2. Chemical-potential-per-particle : temperature ratio $\gamma$ vs. volume fraction $\eta$ for a classical hard-balls continuum. Displayed are fluid branch $(0 < \eta < 0.49)$ and solid branch $(0.54 < \eta < 0.74)$ together with the coexistence line $(0.49 \leq \eta \leq 0.54; \text{dotted})$ and the fcc crystal close packing limit (broken vertical line at $\eta = 0.74019$).
We end this subsection by emphasizing that we do need to know what we stipulated about $\varphi_\bullet(\gamma)$ for the solid phase even though in this paper we are studying only fluid solutions. In particular, “all the hard work” in our paper is caused by the following dilemma: to prove a first-order phase transition between two different stable fluid solutions one must find suitable $(\alpha, \gamma)$ pairs for which (8) has at least three all-fluid solutions, but one also must rule out any other globally stable solution which takes solid values somewhere in the container. Clearly, a sufficient though not necessary condition for the absence of a globally stable solution which takes solid values somewhere is the complete absence of any solution taking non-fluid values somewhere. This sufficient condition is simpler to implement, but is of course also more restrictive.

The space-uniform van der Waals theory gives a good indication of the difficulties ahead. Recall that the space-uniform solutions to the van der Waals problem (6) for given $(\alpha, \gamma)$ and $\|V\|_1 < \infty$ can be graphically determined as the abscissa values of the intersection points of the graph displayed in the second figure with the straight line $\eta \mapsto \gamma + \alpha \|V\|_1 \eta$. The $(\alpha, \gamma)$ pairs for which a phase transition in the fluid regime occurs while no solid solution exists at all lie in the $(\alpha, \gamma)$ domain which corresponds graphically to the family of straight lines $\eta \mapsto \gamma + \alpha \|V\|_1 \eta$ which have three intersections with the fluid branch but no intersection with the solid branch in the second figure Inspection of the second figure makes it obvious that this leaves us with only very little “room to wiggle” in $(\alpha, \gamma)$ space, so that we need to develop delicate analytical estimates to accomplish our feat of proving the grand canonical gas vs. liquid transition and the petit canonical vapor vs. drop transition within the non-uniform van der Waals model for a hard-sphere fluid with chemical self-potential confined to a container.

3 LOCATING THE FLUID SOLUTIONS IN $(\alpha, \gamma)$ HALF SPACE

In this section we give some sufficient and some necessary a priori conditions concerning the existence of solutions $\eta$ of (8) which do not take values outside the fluid regime, i.e. for which $\gamma - (\alpha V * \eta)_\Lambda < \gamma_{\text{fs}}$. We shall write $V * \eta$ for either $(V * \eta)_\Lambda$ or $(V * \eta)_{\mathbb{R}^3}$ whenever it is clear from the context what we mean. We set $\|V * 1\|_{C_0^\alpha(\Lambda)} = \Phi_{\Lambda}$, where $\| \cdot \|_{C_0^\alpha(\Lambda)}$ denotes the uniform (supremum) norm for $C_0^\alpha(\Lambda)$;
notice that $\Phi_{\mathbb{R}^3} = \|V\|_1$. We also introduce the notation $B_\xi = \{\eta : \|\eta\|_{C^0_b(\Lambda)} \leq \xi\}$ for the closed ball of radius $\xi$ in $C^0_b(\Lambda)$.

We begin with some sufficient conditions for existence.

**Proposition 3.1:** Assume that the inequality
\[ \gamma + \alpha \Phi_\Lambda \eta - g_\Lambda(\eta) \leq 0 \]  
(25)
is satisfied for at least one $\eta \in (0, \eta_{\infty})$, so that the algebraic fixed point equation
\[ \eta = g_\Lambda^{-1}(\gamma + \alpha \Phi_\Lambda \eta) \]  
(26)
has at least one solution $\eta \in (0, \eta_{\infty})$. Let $\eta_\Lambda^{\min}$ be the minimal and $\eta_\Lambda^{\max}$ the maximal solution in $[0, \eta_{\infty}]$ of (25). Then in the truncated positive cone $C^0_b(\Lambda) \cap \overline{B}_{\eta_{\infty}}$, there exists a pointwise minimal and a pointwise maximal fluid solution of (8), denoted $\eta_\Lambda^{\min}(r)$ and $\eta_\Lambda^{\max}(r)$, respectively. In particular, the iteration sequences $\{\eta^{(n)}\}_{n=0}^\infty$ defined by
\[ \eta^{(n+1)} = g_\Lambda^{-1}(\gamma - \alpha V \star \eta^{(n)}) \]  
(27)
with starting densities $\eta^{(0)} = \eta_\Lambda^{\min}$ and $\eta^{(0)} = g_\Lambda^{-1}(\gamma)$, respectively, both converge pointwise to the minimal solution $\eta_\Lambda^{\min}(r)$, the former monotone downward and the latter monotone upward. Starting the iteration map (27) with $\eta^{(0)} = \eta_\Lambda^{\max}$ yields a sequence which converges pointwise monotone downward to the maximal solution $\eta_\Lambda^{\max}(r)$.

**Remarks:** (a) Since, by hypothesis, (25) is satisfied, and since $g_\Lambda$ is continuous with $\lim_{\eta \downarrow 0} g_\Lambda(\eta) = -\infty$, the straight line $\eta \mapsto \gamma + \alpha \Phi_\Lambda \eta$ intersects the curve $\eta \mapsto g_\Lambda(\eta)$ at least once (and at most three times) in $(0, \eta_{\infty})$. Therefore a maximal point of intersection $\eta_\Lambda^{\max} \leq \eta_{\infty}$ does exist. (b) Proposition 3.1 does not state that $\eta_\Lambda^{\max}$ is the maximal solution in $C^0_b(\Lambda) \cap \overline{B}_{\eta_{\infty}}$; however, $\eta_\Lambda^{\min}$ is automatically the minimal solution in $C^0_b(\Lambda) \cap \overline{B}_{\eta_{\infty}}$. (c) Maximal and minimal solution, $\eta_\Lambda^{\max}$ and $\eta_\Lambda^{\min}$, may coincide.

To prove Proposition 3.1, all we need to know about $V$ is $V \in L^1(\Lambda)$ and $V < 0$.

**Proof of Proposition 3.1:** Consider first the case $\eta^{(0)} = \eta_\Lambda^{\max}$. Since $\gamma \mapsto g_\Lambda^{-1}(\gamma)$ is strictly monotonic increasing, and since $-(V * 1)(r) \leq \|V * 1\|_{C^0_b(\Lambda)} = \Phi_\Lambda$, but with $-(V * 1)(r) \neq \Phi_\Lambda$, the iteration (27) yields $\eta^{(n)}(r) \leq \eta^{(n-1)}(r)$ $\forall n \in \mathbb{N}$, and even $\eta^{(n+1)}(r) < \eta^{(n)}(r)$ $\forall n \in \mathbb{N}$ and all $r \in \Lambda$. Since
\[ g_\Lambda^{-1}(\gamma - \alpha V \star \eta) \geq g_\Lambda^{-1}(\gamma) > 0, \]  
(28)
the iterates are bounded below by a positive number. Hence, the iterates converge pointwise down to a strictly positive function $\eta^m_{M}$, which clearly is entirely fluid. By the $C^0_b(\Lambda)$ continuity of the operator $g_z^{-1}(\gamma - \alpha V \ast \cdot)$, the function $\eta^m_{\eta_{M}}$ solves (8).

As in Ref.[6] it can be shown that $\eta < \eta^m_{M}$ is any solution of (8), then by the monotonic increase of $g_z^{-1}(\gamma - \alpha V \ast \cdot)$ and by the fact that $\eta^m_{\eta_{M}}$ is a strict supersolution for (8), we can conclude that $g_z^{-1}(\gamma - \alpha V \ast \cdot)$ maps $[\eta, \eta^m_{\eta_{M}}]$ into itself. Therefore, $\eta \leq \eta^m_{\eta_{M}}$, and this proves that $\eta^m_{\eta_{M}}$ is the pointwise maximal solution in $C^0_{b,+} \cap \overline{A_{\eta_{M}}}$. By essentially the same arguments, starting the iteration with $\eta^{(0)} = \eta_{M}$ yields a monotone downward converging sequence of iterates with limit $\eta^m_{\eta_{M}}$, and $\eta^m_{\eta_{M}}$ is the pointwise maximal solution in $C^0_{b,+} \cap \overline{A_{\eta_{M}}}$. Next consider the case $\eta^{(0)} = g_z^{-1}(\gamma)$. Using again the strict monotonic increase of $\gamma \mapsto g_z^{-1}(\gamma)$, this time combined with the positivity of $-(V \ast 1)(r)$, we conclude that the sequence (27) iterates pointwise monotone upward. By (28) all iterates are strictly positive. Moreover, by induction it follows that, if $\eta^{(n)} < \eta^m_{\eta_{M}}$, then

$$
\eta^{(n+1)} = g_z^{-1}(\gamma - \alpha V \ast \eta^{(n)}) < g_z^{-1}(\gamma + \alpha \Phi \eta_{\Lambda}) = \eta^m_{\eta_{M}}.
$$

Clearly, $\eta^{(0)} < \eta^m_{\eta_{M}}$, so the sequence is bounded above by $\eta^m_{\eta_{M}}$. It now follows that it converges pointwise to a strictly positive solution $\eta^m_{\eta_{M}} \leq \eta^m_{\eta_{M}}$ of (8), and also that this solution is entirely fluid. Moreover, similarly as for the maximal solution it now follows that $\eta^m_{\eta_{M}}$ is the pointwise minimal solution in $C^0_{b,+} \cap \overline{A_{\eta_{M}}}$, hence in $C^0_{b,+} \cap \overline{A_{\eta_{M}}}$.

Lastly, the proof that $\eta^m_{\eta_{M}} = \eta^m_{\eta_{M}}$ is a minor variation on the proof of Corollary 4.5 in section IV.

By a slight sharpening of (25) we can improve Proposition 3.1 to the following.

**Proposition 3.2:** Assume that

$$
\gamma - \gamma_{ls} + \alpha \Phi \eta_{ls} \leq 0.
$$

Then (28) is satisfied for $\overline{\eta} = \eta_{ls}^\alpha$, so Proposition 3.1 applies. Now the pointwise maximal fluid solution $\eta^m_{\eta_{M}}$ of (8) in $C^0_{b,+} \cap \overline{A_{\eta_{M}}}$ is in fact the pointwise maximal fluid solution in $C^0_{b,+} \cap \overline{A_{\eta_{M}}}$.

**Proof of Proposition 3.2:** Since $\gamma_{ls} = g_z(\eta_{ls}^\alpha)$, (30) implies that (28) is satisfied by $\overline{\eta} = \eta_{ls}^\alpha$, so all conclusions in Proposition 3.1 apply.
To show that the pointwise maximal solution in $C_{b,+}^0 \cap B_{\pi_{\Lambda}}$, we notice that $\pi_{\Lambda}^\leq$ is a strict supersolution a.e. for (8). This implies that the sequence $\{\eta^{(n)}\}_{n=0}^\infty$ defined by (27) with initial value $\eta^{(0)} = \pi_{\Lambda}^\leq$ iterates pointwise monotonically downward, strictly monotonically a.e., to the pointwise maximal solution in $C_{b,+}^0 \cap B_{\pi_{\Lambda}^\leq}$ of (8). We show that this solution is in $C_{b,+}^0 \cap B_{\pi_{\Lambda}^M}$, and so, a fortiori, it is also the pointwise maximal solution in $C_{b,+}^0 \cap B_{\pi_{\Lambda}^M}$.

By (30), $\pi_{\Lambda}^\leq$ is a supersolution for (26). Therefore, either $\eta_{\Lambda}^\leq$ is itself the largest fixed point in $[0, \pi_{\Lambda}^\leq]$ of (26), or else the sequence $\{\eta^{(n)}\}_{n=0}^\infty$ defined by $\eta^{(n+1)} = g_2^{-1}(\gamma + \alpha \Phi_{\Lambda}^\leq \eta^{(n)})$ (31) with initial value $\eta^{(0)} = \pi_{\Lambda}^\leq$ iterates strictly monotonically downward to the largest fixed point in $[0, \pi_{\Lambda}^\leq)$ of (26), which in either case is $\pi_{\Lambda}^M$. Moreover, with $\eta^{(0)} = \eta_{\Lambda}^\leq = \eta^{(0)}$, for each $n > 0$ we have

$$\eta^{(n)} \leq \pi^{(n)}$$

because $\eta^{(n_0)} \leq \pi^{(n_0)}$ for some $n_0 \geq 0$ implies that

$$\eta^{(n_0+1)} = g_2^{-1}(\gamma - \alpha V \ast \eta^{(n_0)}) \leq g_2^{-1}(\gamma + \alpha \Phi_{\Lambda} \pi^{(n_0)}) = \pi^{(n_0+1)}.$$

We conclude that

$$\eta_{\Lambda}^M := \lim_{n \to \infty} \eta^{(n)} \leq \lim_{n \to \infty} \pi^{(n)} = \pi_{\Lambda}^M.$$ (34)

Hence, $\eta_{\Lambda}^M = \eta_{\Lambda}^M$, so $\eta_{\Lambda}^M$ is the pointwise maximal solution in $C_{b,+}^0 \cap B_{\pi_{\Lambda}^M}$. ■

**Remark:** For our $V$, the dominance can be sharpened from "$\leq$" to "$< \text{ a.e.}"" by noting that obviously $\eta^{(1)} < \pi^{(1)}$ a.e.

If we consider the extension of (8) to all $\gamma \in \mathbb{R}$, with $\phi^\prime_*(\cdot) = \phi^\prime_{CS}(\cdot) = g_2^{-1}(\cdot)$ for $\cdot \leq \gamma_{\Lambda}$ with $\phi^\prime_*$ meaning left derivative, and with $\phi^\prime_*(\cdot) = g_1^{-1}(\cdot)$ when $\cdot > \gamma_{\Lambda}$, with $\phi^\prime_*$ now meaning right derivative, covering fluid and solid branch as explained in Convention 2.3, then the existence results of Propositions 3.1 and 3.2 can be complemented by a result about the non-existence of solutions to the so extended (8) which are not fluid somewhere in $\Lambda$.

**Proposition 3.3:** If the inequality

$$\gamma - \gamma_{\Lambda} + \alpha \Phi_{\Lambda} \pi_{f,cc}^p \leq 0,$$ (35)

then...
holds, then the extended fixed point problem (8) does not have any solution that takes values outside the hard-sphere fluid regime somewhere in Λ.

Proof of Proposition 3.3: Since $\eta \leq \eta_{\text{fcc}}$ and since $g_4(\eta) > \gamma_{\text{fs}}$ for all $\eta \in (\eta_{\text{fcc}}, \eta_{\text{fcc}})$, we conclude that (35) implies for all $\eta \in (\eta_{\text{fcc}}, \eta_{\text{fcc}})$ that

$$\gamma + \alpha \Phi_{\text{L}} \eta < g_4(\eta).$$

(36)

Now suppose a solution $\eta$ of the extended (8) would exist which in some open subdomain $\Lambda_s$ of $\Lambda$ is solid. Then, clearly, $\eta > \eta_{\text{fs}} \leq \|\eta\|_{C^0_b(\Lambda)} \leq \eta_{\text{fcc}}$, and since $\gamma \mapsto g_4^{-1}(\gamma)$ is increasing, we conclude that in the solid region (i.e., in $\Lambda_s$) we have

$$\|\eta\|_{C^0_b(\Lambda)} \leq g_4^{-1}(\gamma + \alpha \Phi_{\text{L}} \eta) \|\eta\|_{C^0_b(\Lambda)}.$$ (37)

as a consequence of the extended (8). But by applying $g_4$ to both sides of (37), this leads to a contradiction with (36). Hence, no solution of the extended (8) can exist which somewhere in $\Lambda$ is not a hard-sphere fluid.

The next result requires $V \in L^1(\mathbb{R}^3)$. It relates the algebraic fixed point problem (6) for constant solutions in $\mathbb{R}^3$ of (7) to the problem (8) in bounded $\Lambda \subset \mathbb{R}^3$.

Proposition 3.4: Let $\alpha \|V\|_1 = A_W (\pi^2/4\kappa^2) + A_V (4\pi/\kappa^2)$. Suppose the algebraic fixed point problem (6) has a solution $\eta_{\text{vdw}} \leq \eta < \eta_{\text{fs}}$, so that $\eta_{\text{vdw}}$ satisfies

$$\eta = g_4^{-1}(\gamma + \alpha \|V\|_1 \eta).$$ (38)

Then for all domains $\Lambda \subset \mathbb{R}^3$ the fixed point problem (8) with $\alpha V = A_W V_W + A_V V_Y$ and $\varphi_*(\gamma)$ given in Definition 2.1 has a hard-sphere fluid solution.

Proof of Proposition 3.4: By subadditivity of the norm, we have

$$\alpha \|V * 1\|_{C^0_b(\Lambda)} \leq A_W \|V_W * 1\|_{C^0_b(\Lambda)} + A_V \|V_Y * 1\|_{C^0_b(\Lambda)}.$$ (39)

Since $V_w(|\cdot|) \in L^1(\mathbb{R}^3)$ and $V_Y(|\cdot|) \in L^1(\mathbb{R}^3)$, we have

$$\|V_w * 1\|_{C^0_b(\Lambda)} \leq \|V_w * 1\|_{C^0_b(\mathbb{R}^3)} = \frac{\pi^2}{4\kappa^2},$$ (40)

$$\|V_Y * 1\|_{C^0_b(\Lambda)} \leq \|V_Y * 1\|_{C^0_b(\mathbb{R}^3)} = \frac{4\pi}{\kappa^2}.$$ (41)
With (39), (40), and (41), we thus have
\[ \alpha \|V * 1\|_{C^0_b(\Lambda)} \leq A_w \frac{\pi^2}{4 \varepsilon^d} + A_y \frac{4 \pi}{\varepsilon^2} = \|V\|_1, \]  
valid for all \( \Lambda \subset \mathbb{R}^3 \). Hence, if (38) has a solution \( \pi_{vdw} \leq \pi_{fs} \), then by (42) this \( \pi_{vdw} \) is a supersolution for (26), and Proposition 3.1 now concludes the proof. \[ \square \]

We turn to the necessary conditions for the existence of fluid solutions.

**Proposition 3.5:** If the inequality
\[ \gamma - \gamma_{fs} + \alpha \Phi_{\Lambda} \varphi'(\gamma) \geq 0, \]  
holds, then the extended (8) does not have a hard-sphere fluid solution.

**Proof of Proposition 3.5:** Since \( V < 0 \) and \( \alpha > 0 \), and since \( \varphi'(\gamma) > 0 \), it follows directly from (8) that any solution \( \eta \) of the extended (8) satisfies the lower estimate
\[ \eta(r) > \varphi'(\gamma) \]  
for all \( r \in \Lambda \). Convoluting (44) with \( -V > 0 \) and multiplying by \( \alpha \) yields
\[ -(\alpha V * \eta)(r) > -(\alpha V * 1)(r) \varphi'(\gamma) \]  
for all \( r \in \Lambda \), from which it follows that
\[ \gamma + \|\alpha V * \eta\|_{C^0_b(\Lambda)} > \gamma + \alpha \Phi_{\Lambda} \varphi'(\gamma). \]  
If (43) holds, then from (46) it follows that \( \gamma + \|\alpha V * \eta\|_{C^0_b(\Lambda)} > \gamma_{fs} \), and so \( \|\eta\|_{C^0_b(\Lambda)} > \pi_{fs} \). Therefore, violation of (43) is a necessary condition for the existence of an all fluid solution of (8). \[ \square \]

We conclude this section with an obvious non-existence result.

**Proposition 2.6:** If the inequality
\[ \gamma - \gamma_{fs} > 0, \]  
holds, then the extended (8) does not have a solution which is fluid somewhere in \( \Lambda \).

**Proof of Proposition 2.6:** Trivial. \[ \square \]

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We now locate a connected region in \((\alpha, \gamma)\) space in which there exists a unique fluid solution for each pair of \((\alpha, \gamma)\) parameter values. The pertinent unique fluid solution need not be the unique solution per se, yet any other solution of (8) would necessarily take nonfluid values somewhere in \(\Lambda\).

Our existence and uniqueness results are based on the following theorem, for which much less is assumed about \(\wp\) than stipulated in Convention 2.3.

**Lemma 4.1** Consider (8) for a map \(\gamma \mapsto \wp(\gamma)\) of class \(C^2(\gamma)\) which is strictly positive, increasing, and convex, and for which

\[
K(\gamma) := \sup_{\gamma \in (-\infty, \tilde{\gamma})} \wp''(\gamma) < \infty. \tag{48}
\]

Assume \(\gamma (< \tilde{\gamma})\) and \(\alpha (> 0)\) are such that the operator \(\wp'(\gamma - \alpha V \ast \cdot)\) maps \(C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\) into itself, where \(\overline{B}_{\tilde{\eta}} = \{\eta : \|\eta\|_{C^0_{b}(\Lambda)} \leq \tilde{\eta}\}\) is a ball of radius \(\tilde{\eta} = \wp'(\tilde{\gamma})\). Assume furthermore that

\[
K(\gamma) \alpha \Phi_{\Lambda} < 1, \tag{49}
\]

with \(\Phi_{\Lambda} = \|V \ast 1\|_{C^0_{b}(\Lambda)}\), as defined above Proposition 3.1. Then there exists a unique solution \(\eta \in C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\) of (8). In particular, the iteration sequence \((27)\), starting with any \(\eta(0) \in C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\), converges strongly in \(C^0_{b}(\Lambda)\) to the unique solution.

**Remark:** Lemma 4.1 improves over Theorem 6.4 of Ref. [33], where uniqueness and strong \(L^1\) convergence are established under the same condition (49).

**Proof of Lemma 4.1:** By hypothesis, the operator \(\wp'(\gamma - \alpha V \ast \cdot)\) maps the \(\|\cdot\|_{C^0_{b}(\Lambda)}\) closed set \(C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\) into itself. This implies that \(\gamma - \alpha V \ast \eta \leq \tilde{\gamma}\) for any \(\eta \in C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\). This together with (48) in turn implies that \(\wp''(\gamma - \alpha V \ast \eta) \leq K(\gamma)\) for any \(\eta \in C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\).

Consider now two sequences \(\{\eta^{(n)}_i\} \subset C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\) for \(i = 1, 2\), defined by (27), with \(\eta^{(0)}_1 \neq \eta^{(0)}_2\) on a fat set. Set \(- (V \ast \eta^{(n)}_i)(\mathbf{r}) = \phi^{(n)}_i(\mathbf{r})\). Pick any \(1 < q < \infty\). Then, by the fact that \(\wp''(\gamma - \alpha V \ast \eta) \leq K(\gamma)\) for any \(\eta \in C^0_{b,+} \cap \overline{B}_{\tilde{\eta}}\), we estimate

\[
\left\|\eta^{(n+1)}_2 - \eta^{(n+1)}_1\right\|_{L^q(\Lambda)}^q = \int_\Lambda \left|\wp' \left(\gamma + \alpha \phi^{(n)}_2(\mathbf{r})\right) - \wp' \left(\gamma + \alpha \phi^{(n)}_1(\mathbf{r})\right)\right|^q \text{d}^3 \mathbf{r}.
\]
Combining (50) and (51) gives, after taking the $q$th root,

$$\left\| \eta_2^{(n+1)} - \eta_1^{(n+1)} \right\|_{L^q(\Lambda)} \leq K(\tilde{\gamma}) \alpha \left\| (-V)^{q'} * 1 \right\|_{L^{q'/q}(\Lambda)}^{1/q'} \left\| \eta_2^{(n)} - \eta_1^{(n)} \right\|_{L^q(\Lambda)}$$

for all $q \in (1, \infty)$. By taking $q \to \infty$, and noting that here ess sup = sup, we get

$$\left\| \eta_1^{(n+1)} - \eta_2^{(n+1)} \right\|_{C^0_b(\Lambda)} \leq K(\tilde{\gamma}) \left\| \alpha V * 1 \right\|_{C^0_b(\Lambda)} \left\| \eta_1^{(n)} - \eta_2^{(n)} \right\|_{C^0_b(\Lambda)}$$

By hypothesis (49), we have $K(\tilde{\gamma})\alpha \left\| V * 1 \right\|_{C^0_b(\Lambda)} < 1$, whence from (53) we conclude that the map $\eta \mapsto \varphi'(\gamma - \alpha V * \eta)$ is a $C^0_b$ contraction map in the closed truncated cone $C^0_{b,+} \cap \overline{B_\eta}$. We now apply the contraction mapping principle and conclude that a unique fixed point of $\eta \mapsto \varphi'(\gamma - \alpha V * \eta)$ exists in $C^0_{b,+} \cap \overline{B_\eta}$. In addition, the proof of the contraction mapping principle implies the $C^0_b$ convergence of the iteration sequence for any initial density $\eta^{(0)} \in C^0_{b,+} \cap \overline{B_\eta}$.

We now return to our $\varphi_\bullet(\gamma)$ given by Convention 2.3. In our first application of Lemma 4.1 we set $\tilde{\gamma} = \gamma_0$ ($\approx 15.208$). The following input from Ref. [33] capitalizes on
the fact that the graph of $\eta \mapsto g_2(\eta)$ has a unique inflection point at $\eta = \eta_0 \approx 0.130$.

**Lemma 4.2:** The regular global maximum $K(\gamma_a)$ of $\varphi''(\gamma)$ over the set $(-\infty, \gamma_a)$ occurs at $\gamma_1 \approx -0.67$ at which $\eta_1 \equiv g_2^{-1}(\gamma_1) \approx 0.130$ and $\varphi''(\gamma_1) = K(\gamma_a) \approx 0.047$.

We are now in the position to state the following Corollary of Lemma 4.1.

**Corollary 4.3:** Let the parameters $(\alpha, \gamma)$ satisfy the bound (25), and let $\alpha$ satisfy the inequality $\|\alpha V \ast 1\|_{C_0^b(\Lambda)} < 21.20$. Then there exists a unique fluid solution of (8).

**Proof:** By hypothesis, the parameters $(\alpha, \gamma)$ satisfy (25). This implies that the operator $\varphi'(\gamma - \alpha V \ast \cdot)$ maps $C^0_{b,+} \cap \overline{B}_{\eta_a}$ into itself. Next, using Lemma 4.2 and $1/0.047 \approx 21.20$, we conclude that $\|\alpha V \ast 1\|_{C_0^b(\Lambda)} < 21.20$ implies (49). Lemma 4.1 now guarantees us a unique solution in $C^0_{b,+} \cap \overline{B}_{\eta_a}$ of (8).

It is interesting to compare (49) to the sharp criterion for uniqueness, irrespective of $\gamma$, of a solution $\eta < \eta_{\text{inf}}$ to the associated algebraic fixed point problem (26). Geometrically, this criterion for uniqueness is that the slope of the straight line $\eta \mapsto \gamma + \alpha \Phi_A \eta$ may not surpass the smallest derivative of the curve $\eta \mapsto g_2(\eta)$, or $\alpha \Phi_A \leq g_2'(\eta_0)$, with $\eta_0 \approx 0.130$ defined in Lemma 4.2. From the definition of $\varphi''(\gamma)$ we then see that this criterion is precisely $K(\gamma_a) \alpha \Phi_A \leq 1$, with $K(\gamma_a) = \varphi''(\gamma_1) \approx 0.047$ given in Lemma 4.2. Thus, (49) is the direct analog of the geometric criterion that governs the associated algebraic fixed point problem (26), except for the case of equality $K(\gamma_a) \alpha \Phi_A = 1$, about which the contraction mapping principle is silent.

If $K(\gamma_a) \alpha \Phi_A > 1$, then there exist values of $\gamma$ for which (26) has either two or three solutions. In that case we can still arrive at a uniqueness theorem for (26) under the condition on $\gamma$ that it be not too large. Similarly, if (49) is violated, Lemma 4.1 still gives a uniqueness result for (8) by appropriately restricting $\gamma$ from above. For this second application of our Lemma 4.1 we introduce the following.

**Definition 4.4:** Given $\Lambda$, for each $\alpha$ we define $\gamma_\Lambda(\alpha)$ to be the largest upper bound on $\gamma$ such that for each $\gamma < \gamma_\Lambda(\alpha)$ there exists a unique positive solution $\eta(\alpha, \gamma)$ of (26).

**Remarks:** (a) Since $g_2'(\eta) > 0$ and $g_2((0, \eta_{\text{inf}}]) = (-\infty, \gamma_a]$, clearly $\gamma_\Lambda > -\infty$; (b) $\gamma_\Lambda(\alpha)$ has a discontinuity when $\alpha \Phi_A (\gamma_a) = 1$.

**Corollary 4.5:** Let $\alpha$ satisfy $K(\gamma_a) \alpha \Phi_A > 1$, and let $\gamma < \gamma_\Lambda(\alpha)$. Then $\eta(\alpha, \gamma) < \eta_1$, and (8) has a unique fluid solution $\eta_\Lambda \in C^0_{b,+} \cap \overline{B}_{\eta_a}$; in fact, $\eta_\Lambda \in C^0_{b,+} \cap \overline{B}_{\eta_\Lambda}$.
Moreover, the iteration sequence defined by \( \eta^{(n+1)} = \varphi_{CS}^{\gamma - \alpha V \ast \eta^{(n)}} \), starting with any \( \eta^{(0)} \in C_{b,+}^{0} \cap \overline{B}_{\eta}^{\gamma_{0}} \), converges in supnorm to this unique fixed point.

Proof: Since \( K(\gamma_{0})\alpha \Phi_{\Lambda} > 1 \), by definition of \( \gamma_{0} \) we see that \( \bar{\eta}(\alpha, \gamma) < \eta_{t} \). Therefore all \( \eta \in [\bar{\eta}_{t}, \eta_{t}] \) are supersolutions for (26), and thus strict supersolutions for (8). By the type of argument presented in the proof of Proposition 3.2 we conclude that no fluid solution of (8) exists which is somewhere larger than \( \eta(\alpha, \gamma) \).

Now pick any \( \eta \in C_{b,+}^{0} \cap \overline{B}_{\eta(\alpha, \gamma)} \). Since \( \gamma < \gamma_{0}(\alpha) \), \( (g_{2}^{-1})'(\gamma) > 0 \), \( V < 0 \), we have

\[
\left\| g_{2}^{-1}(\gamma - \alpha V \ast \eta) \right\|_{C_{b}^{0}(\Lambda)} \leq g_{2}^{-1}\left( \gamma + \alpha \Phi_{\Lambda} \left\| \eta \right\|_{C_{b}^{0}(\Lambda)} \right) \\
\leq g_{2}^{-1}(\gamma + \alpha \Phi_{\Lambda} \bar{\eta}(\alpha, \gamma)) = \bar{\eta}(\alpha, \gamma) .
\]

Therefore, the operator \( g_{2}^{-1}(\gamma - \alpha V \ast \cdot) \) maps \( C_{b,+}^{0} \cap \overline{B}_{\eta(\alpha, \gamma)} \) into itself.

We observe that \( g_{2}^{\prime}(\bar{\eta}(\alpha, \gamma)) > \alpha \Phi_{\Lambda} \) so that \( \bar{\eta}(\alpha, \gamma) \) is a stable fixed point of (26). The stability of \( \bar{\eta}(\alpha, \gamma) \) and the convexity of \( g_{2}^{-1}(\nu) \) for \( \nu < \gamma + \alpha \Phi_{\Lambda} \bar{\eta}(\alpha, \gamma) \) implies that

\[
K(\gamma_{0})\alpha \Phi_{\Lambda} < 1 ,
\]

where

\[
K(\gamma_{0}) := \sup_{\gamma, \nu}\left\{ (g_{2}^{-1})'(\gamma + \nu) : \gamma \in (- \infty, \gamma_{0}(\alpha)) \wedge \nu \leq \alpha \Phi_{\Lambda} \bar{\eta}(\alpha, \gamma) \right\} .
\]

We now can apply Lemma 4.1 to \( \eta \in C_{b,+}^{0} \cap \overline{B}_{\eta(\alpha, \gamma)} \). The proof is complete.

5 A \((\alpha, \gamma)\) REGION WITH SEVERAL FLUID SOLUTIONS

When \( V \in L^{1}(\mathbb{R}^{3}) \), it is readily shown that there is a connected region in \((\alpha, \gamma)\) parameter space in which the van der Waals’ algebraic fixed point equation (6) for constant density functions in \( \mathbb{R}^{3} \) has three solutions inside the fluid regime, \( \eta_{caw} < \eta_{caw}^{\mu} < \eta_{caw}^{\mu} \leq \eta_{caw} \), so these solutions satisfy (58). The smallest and the largest ones are stable under iterations while the intermediate one is unstable. Intuitively one expects that when \( \Lambda \subset \mathbb{R}^{3} \) is a container of macroscopic proportions, and \( \kappa^{-1} \) and \( \kappa^{-1} \) are molecular distances, then for most \((\alpha, \gamma)\) in the three fluid solutions region for the algebraic (58) our nonlinear integral equation (8) should also have a
small and a large fluid solution which are stable under iterations, while the unstable solution $\eta_{vdW}^u$ of (38) should be replaced by an interface type solution of (8) which is unstable under iterations. Numerical integrations of (8) with $V = V_w$ for a ball domain $\Lambda = B_R$ with moderately large $R = 50/\kappa$ support this expectation. A rigorous proof is desirable.

In this section we use monotone iteration techniques with sub- and supersolutions to show that at least part of this multiplicity region for the algebraic equation (38) corresponds to a multiplicity region of the integral equation (8) — for certain sufficiently small $\Lambda$. We will prove that at least three hard-sphere fluid solutions exist in some region of $(\alpha, \gamma)$ parameter space, two of them stable under iteration and one unstable. We will not show that exactly three fluid solutions exist; in fact, it might not be true that exactly three fluid solutions of (8) exist whenever it has at least three fluid solutions.

Recall that the starting function $\eta^{(0)} = g^{-1}_2(\gamma)$ is a subsolution for (8) in any $\Lambda$, and it launches an iteration sequence which converges upward toward the pointwise minimal solution; see Proposition 3.1. We also know from Proposition 3.4 that when $\eta_{vdW}^{a} \leq \eta_{a}$, then any starting function $\eta^{(0)} \in [\eta_{vdW}^{a}, \eta_{a}]$ is a supersolution for (8) in any $\Lambda$, and it launches an iteration sequence which converges downward toward the pointwise maximal fluid solution. One can rule out that the pointwise maximal solution coincides with the pointwise minimal solution if a sufficiently large subsolution of (8) in $\Lambda$ is available from which the iteration $\eta^{(n+1)} = \varphi_{\cdot}(\gamma - \alpha V \ast \eta^{(n)})$ converges upward toward a fluid solution which is larger than the pointwise minimal solution to (8).

Constructing suitable subsolutions that imply a $(\alpha, \gamma)$ region of multiple hard-sphere fluid solutions is a very difficult business, yet much easier for the Carnahan–Starling model. We will take advantage of this fact and, until further notice, first discuss (8) with $\varphi_{\cdot}(\gamma)$ replaced by $\varphi_{CS}(\gamma)$ for all $\gamma \in \mathbb{R}$, viz.

$$\eta(r) = \varphi'_{CS}(\gamma - (\alpha V \ast \eta)(r)).$$

Subsequently we seek those solutions which nowhere in $\Lambda$ surpass $\eta_{a}^{\leq}$. We emphasize that our multiplicity results for the Carnahan–Starling model in general have no bearing on the hard-sphere fluid; however, there will be a small sliver in $(\alpha, \gamma)$ space for which our Carnahan–Starling multiplicity results yield multiple hard-sphere fluid solutions.
So recall that \( \varphi'_{CS}(\cdot) = g^{-1}_2(\cdot) \) and consider the algebraic fixed point problem

\[
\overline{\eta} = g^{-1}_2(\gamma + \alpha \tau \overline{\eta})
\]  

(58)

for \( \gamma \in \mathbb{R} \) and \( \alpha \in \mathbb{R}_+ \), where \( \tau \in \mathbb{R}_+ \). Multiplicity of solutions of (58) can only occur if \( \alpha \) is large enough, namely (recalling Lemma 4.2 and Corollary 4.3) if

\[
\alpha \tau > \min_{\eta \in (0,1)} g'_{2}(\eta) = g'_{2}(\eta_1) \approx 21.20.
\]  

(59)

In addition, \( \gamma \) needs to satisfy \( \gamma \in (\hat{\gamma}^{\text{alg}}_{CS}(\alpha \tau), \check{\gamma}^{\text{alg}}_{CS}(\alpha \tau)) \), with upper and lower interval limits given by

\[
\hat{\gamma}^{\text{alg}}_{CS}(\alpha \tau) = g_2(\overline{\eta}_>) - \alpha \tau \overline{\eta}_>,
\]  

(60)

\[
\check{\gamma}^{\text{alg}}_{CS}(\alpha \tau) = g_2(\overline{\eta}_<) - \alpha \tau \overline{\eta}_<,
\]  

(61)

where \( \overline{\eta}_< < \overline{\eta}_> \) are the two distinct solutions to the equation

\[
\alpha \tau = g'_2(\overline{\eta}),
\]  

(62)

which exist only when (59) is satisfied, in which case \( \overline{\eta}_< < \overline{\eta}_< \) is a decreasing, and \( \overline{\eta}_> > \overline{\eta}_< \) an increasing function of \( \alpha \tau \). While it does not seem feasible to write down closed form expressions of the functions \( \alpha \tau \mapsto \overline{\eta}_< \) and \( \alpha \tau \mapsto \overline{\eta}_> \), their asymptotics for \( \alpha \tau \approx g'_{2}(\eta_\wedge) \) (recall (59)) and \( \alpha \tau \gg g'_{2}(\eta_\wedge) \) can easily be worked out, which gives us

\[
\hat{\gamma}^{\text{alg}}_{CS}(\alpha \tau) \approx \begin{cases} 
g_2(\overline{\eta}_1) - \overline{\eta}_1 \alpha \tau; & \alpha \tau \approx g'_2(\overline{\eta}_1) 
- \ln(\alpha \tau) - 1 + O(1/\alpha \tau); & \alpha \tau \gg g'_2(\overline{\eta}_1) 
\end{cases}
\]  

(63)

\[
\check{\gamma}^{\text{alg}}_{CS}(\alpha \tau) \approx \begin{cases} 
g_2(\overline{\eta}_1) - g'_2(\overline{\eta}_1) - 2 g'_2(\overline{\eta}_1) \alpha \tau + \frac{1}{2} g''_2(\overline{\eta}_1) [\alpha \tau - g'_2(\overline{\eta}_1)]^{1/2}; & \alpha \tau \approx g'_2(\overline{\eta}_1) 
- \frac{2}{3} \alpha \tau + O(1/\alpha \tau); & \alpha \tau \gg g'_2(\overline{\eta}_1) 
\end{cases}
\]  

(64)

where we used the identity \( g'_2(\overline{\eta}_1) = \overline{\eta}_1 g''_2(\overline{\eta}_1) \) to simplify. Numerically, \( g'''_{2}(\overline{\eta}_1) \approx 1235.22 \).

So the algebraic fixed point equation (58) has three solutions for all \( (\alpha, \gamma) \in \Theta^{\text{alg}}_{CS}(\tau) \), where \( \Theta^{\text{alg}}_{CS}(\tau) \equiv \{ (\alpha, \gamma) : \alpha \tau > g'_2(\overline{\eta}_1) \land \hat{\gamma}^{\text{alg}}_{CS}(\alpha \tau) < \gamma < \check{\gamma}^{\text{alg}}_{CS}(\alpha \tau) \} \). Note that the boundary \( \partial \Theta^{\text{alg}}_{CS}(\tau) \) is given by two functions of \( \alpha \) which depend on \( \alpha \) only through the product \( \alpha \tau \). Hence, for (58), triple solution regions in the \( (\alpha, \gamma) \) half plane for any two different \( \tau = \tau_1 \) and \( \tau = \tau_2 \) differ from each other only by some scaling along the \( \alpha \) axis, viz. they are affine similar. Since for fixed \( \tau \) the upper
boundary curve \( \hat{\gamma}_\text{alg}^{\text{CS}}(\alpha \tau) \) diverges to \(-\infty\) logarithmically while the lower boundary curve \( \check{\gamma}_\text{alg}^{\text{CS}}(\alpha \tau) \) does so linearly when \( \alpha \) becomes large, it follows that any pair of triple domains \( \Theta_\text{alg}^{\text{CS}}(\tau_1) \) and \( \Theta_\text{alg}^{\text{CS}}(\tau_2) \) has a non-empty intersection.

We next identify functionals of \( V \) which can be substituted for \( \tau \) to construct sub- and supersolutions for (57). Since both our van der Waals kernel \( V_W(|r|) \) and the Yukawa kernel \( V_Y(|r|) \) are monotonic increasing negative functions of \( |r| = r \), for \( \alpha V = A_W V_W + A_V V_Y \) and any container \( \Lambda \) with diameter \( \varnothing(\Lambda) \), we have

\[
V(|r - r'|) \leq V(\varnothing(\Lambda)) \quad \forall \, r, r' \in \Lambda.
\]

We define the abbreviation

\[
\Psi_\Lambda := -V(\varnothing(\Lambda))|\Lambda|.
\]

Subsolutions for (57) can be constructed by setting \( \tau = \Psi_\Lambda \), supersolutions by setting \( \tau = \Phi_\Lambda \) or \( \tau = \|V\|_1 \). Note that for bounded \( \Lambda \subset \mathbb{R}^3 \) we have the chain of inequalities

\[
\Psi_\Lambda < \Phi_\Lambda < \Phi_{\varnothing^3} = \|V\|_1.
\]

Since our findings about the triple algebraic solutions domain for (58) imply in particular that for any bounded domain \( \Lambda \subset \mathbb{R}^3 \) we have \( \Theta_\text{alg}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda) \neq \emptyset \) and also \( \Theta_\text{alg}^{\text{CS}}(\|V\|_1) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda) \neq \emptyset \), one can now show, with the help of monotone iterations and the mountain pass lemma, that for each \((\alpha, \gamma) \in \Theta_\text{alg}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda)\) and each \((\alpha, \gamma) \in \Theta_\text{alg}^{\text{CS}}(\|V\|_1) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda)\) the fixed point equation (57) has at least three solutions in \( C_0^b(\Lambda) \), which are ordered. However, for physically interesting domains \( \Lambda \) the sets \( \Theta_\text{alg}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda) \) and \( \Theta_\text{alg}^{\text{CS}}(\|V\|_1) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda) \) are generally very bad approximations to the full set of such \((\alpha, \gamma)\) points. The reason is that for physically interesting, i.e. macroscopic domains \( \Lambda \), the ratio \( \Psi_\Lambda / \Phi_\Lambda \) is tiny, converging to zero as \( \Lambda \uparrow \mathbb{R}^3 \). Worse, \( \Theta_\text{alg}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_\text{alg}^{\text{CS}}(\Psi_\Lambda) \) may even be a totally useless estimate of the three hard-sphere fluid solutions regime of (8), in the sense that the largest solution of (57) obtained by this method may always take values outside the physical range of hard-sphere fluid densities.

The following variation on our strategy yields more desirable multiplicity results. For bounded \( \Lambda \subset \mathbb{R}^3 \), let \( \zeta \Lambda \subset \Lambda \) denote a rescaling of \( \Lambda \) into \( \Lambda \) by a factor \( \zeta \leq 1 \), so that \( \varnothing(\zeta \Lambda) = \zeta \varnothing(\Lambda) \) and \( |\zeta \Lambda| = \zeta^3 |\Lambda| \). Then for \( \alpha V = A_W V_W + A_V V_Y \) the map \( \zeta \mapsto \Psi_{\zeta \Lambda} = -3^3 V(\zeta \varnothing(\Lambda))|\Lambda| \) takes a global maximum at \( \zeta = \hat{\zeta} \) (which might not be unique; it is unique when \( V = V_w \) or \( V = V_y \)). We always mean the largest \( \hat{\zeta} \).
Suppose now that \( \Lambda \) is a container domain of macroscopic proportions, and that \( \kappa^{-1} \) and \( \tau^{-1} \) are molecular distances. Then \( \xi \ll 1 \), and \( \forall \xi > \xi \) we have the ordering
\[
\Psi_\Lambda \ll \Psi_{\xi \Lambda} < \Phi_{\xi \Lambda} < \Phi_{\xi \Lambda} < \Phi_{\xi \Lambda} = \| V \|_1.
\]

For spherical macroscopic \( \Lambda \) (see Appendix A), and with \( \kappa = \tau = 1/2 \), we have \( \Phi_{\Lambda} \approx 50\Psi_{\xi \Lambda} \), while the first inequality separates two quantities “a universe apart.”

**Proposition 5.1:** Let \( \alpha V = A_w V_w + A_v V_v \). Let \( \overline{\Lambda} \subset \mathbb{R}^3 \) be a container for which \( \zeta \overline{\Lambda} \subset \overline{\Lambda} \). Then for each \( \xi \in [\xi, 1] \) and \( (\alpha, \gamma) \in \Theta^{\text{alg}}_{\text{CS}}(\Phi_{\xi \Lambda}) \cap \Theta^{\text{alg}}_{\text{CS}}(\Psi_{\xi \Lambda}) \) the equation
\[
\eta(r) = \varphi'_{\text{CS}}(\gamma - (\alpha V \ast \eta)(r))
\]
has at least three distinct solutions in \( C^0_b(\zeta \overline{\Lambda}) \). In particular, \( (69) \) has a pointwise minimal and a pointwise maximal solution, both of which are stable under iteration, and a third, unstable solution which is sandwiched inbetween.

**Proof:** For each \( (\alpha, \gamma) \in \Theta^{\text{alg}}_{\text{CS}}(\Phi_{\xi \Lambda}) \cap \Theta^{\text{alg}}_{\text{CS}}(\Psi_{\xi \Lambda}) \) the algebraic fixed point equation \( (58) \) has three solutions for \( \tau = \Phi_{\xi \Lambda} \) and for \( \tau = \Psi_{\xi \Lambda} \), denoted \( \overline{\eta}_{\xi \Lambda}^m < \overline{\eta}_{\xi \Lambda}^u < \overline{\eta}_{\xi \Lambda}^{\text{M}} \) and \( \overline{\eta}_{\xi \Lambda}^m < \overline{\eta}_{\xi \Lambda}^u < \overline{\eta}_{\xi \Lambda}^{\text{M}} \), respectively (suppressing their dependence on \( (\alpha, \gamma) \) from being displayed). Moreover, since \( \Psi_{\xi \Lambda} < \Phi_{\xi \Lambda} \), we have \( \overline{\eta}_{\xi \Lambda}^m < \overline{\eta}_{\xi \Lambda}^u \) and \( \overline{\eta}_{\xi \Lambda}^m < \overline{\eta}_{\xi \Lambda}^{\text{M}} \); the ordering of the unstable solutions is \( \overline{\eta}_{\xi \Lambda}^u > \overline{\eta}_{\xi \Lambda}^{\text{M}} \), but this is irrelevant for our arguments.

Now consider the iteration \( \eta^{(n+1)} = \varphi'_{\text{CS}}(\gamma - (\alpha V \ast \eta^{(n)})_{\xi \Lambda}) \) in \( C^0_b(\zeta \overline{\Lambda}) \cap \overline{B_1} \), with
\[
\eta^{(0)}_\mu(r) = \varphi'_{\text{CS}}(\gamma - \overline{\eta}_{\xi \Lambda}^u \int_{\xi \Lambda} \alpha V(|r - \tilde{r}|) d^3\tilde{r}) \quad \forall r \in \zeta \overline{\Lambda}
\]
and either \( \mu = m \) or \( M \). It is easily verified that \( \eta^{(0)}_\mu(r) \) is a subsolution of \( (69) \). Since \( \varphi'_{\text{CS}}(\gamma) > 0 \) and \( \varphi'_{\text{CS}}(\gamma) < 1 \), each \( \eta^{(0)}_\mu(r) \) launches a monotonic increasing sequence \( \{\eta^{(n)}_\mu\}_{n=0}^\infty \in C^0_b(\zeta \overline{\Lambda}) \cap \overline{B_1} \) which converges pointwise to some solution \( \eta^\mu(r) \) of \( (69) \).

Moreover, we have \( \eta^c(r) < \eta^c_M(r) \). To verify this claim, we note on the one hand that in Proposition 3.4 we already showed that the constant function \( r \mapsto \overline{\eta}_{\xi \Lambda}^m \) is a supersolution of \( (69) \) for any \( \zeta \Lambda \) (recall, this follows from \( -(V \ast 1)_\Lambda \leq \Phi_{\Lambda} \) for any \( \Lambda \)), so that with \( \overline{\eta}_{\xi \Lambda}^m < \overline{\eta}_{\xi \Lambda}^c \) we find \( \eta^{(0)}_m(r) < \overline{\eta}_{\xi \Lambda}^c \), and now we conclude as in the proof of Proposition 3.1 that \( \eta^c(r) < \overline{\eta}_{\xi \Lambda}^m \); incidentally, \( \overline{\eta}_{\xi \Lambda}^m < \overline{\eta}_{\xi \Lambda}^c \). On the other hand, \( \eta^{(0)}_M(r) > \overline{\eta}_{\xi \Lambda}^c \forall r \in \zeta \Lambda \), and since the iteration \( \{\eta^{(n)}_M\}_{n=0}^\infty \) is monotone upwards, it follows that \( \eta^c_M(r) > \eta^{(0)}_M(r) \forall r \in \zeta \Lambda \). In addition, \( \eta^{(0)}_M(r) > \eta^{(0)}_M(r) \forall r \in \zeta \Lambda \), so the strict
monotonic increase of the iterations now guarantees that \( \eta_M^c(r) \geq \eta_m^c(r) \forall r \in \zeta \Lambda \), and since \( \eta_m^c(r) > \eta_M^c(r) \forall r \in \zeta \Lambda \), it even follows that \( \eta_M^c(r) > \eta_m^c(r) \forall r \in \zeta \Lambda \).

Standard results about monotone iterations in ordered Banach spaces show that \( \eta_m^c(r) \) and \( \eta_M^c(r) \) are stable under iterations, and also locally \( \mathcal{P} \) stable; see Proposition 3.1 in Ref. [6]. The existence of a third, unstable (under iterations and in \( \mathcal{P} \) sense) solution sandwiched between \( \eta_m^c(r) \) and \( \eta_M^c(r) \) now follows, via the mountain pass lemma, from the local \( \mathcal{P} \) stability of \( \eta_m^c(r) \) and \( \eta_M^c(r) \) and the strong \( C^0_b(\Lambda) \) differentiability of the functional \( \mathcal{P}_\alpha^\gamma \eta \).

Lastly, \( a \) forteriori the unstable solution sandwiched between \( \eta_m^c(r) \) and \( \eta_M^c(r) \) is also sandwiched between the pointwise smallest and the pointwise largest solutions, \( \eta_m^c(r) \) and \( \eta_M^c(r) \), of (69), obtained by the iteration \( \eta^{(n+1)} = \varphi_{CS} \gamma - (\alpha V \star \eta^{(n)})_\Lambda \) from, respectively, \( \eta^{(0)} \equiv \varphi_{CS} \gamma \) and any \( \eta^{(0)} \equiv \pi^{(0)} > \pi^{(0)}_\Lambda ; \) cf., Proposition 3.1 with \( (0, \pi^{(0)}_\Lambda] \) replaced by \( (0, \pi^{(0)}_\Lambda^M] \) or by \( (0, 1) \), and which are stable under iterations. [5, 6]

Our proof of Proposition 5.1 reveals the ordering

\[
\varphi_{CS} ' \gamma < \eta_m^c(r) \leq \eta_m^c(r) < \eta_m^c(r) \leq \eta_M^c(r) < \pi^{(0)}_\Lambda.
\]

Our next proposition shows that the first “\( \leq \)" actually is an identity.

**Proposition 5.2:** Under the hypotheses of Proposition 5.1, we have

\[
\eta_m^c(r) \equiv \eta_m^c(r)
\]

**Proof of Proposition 5.2:** An obvious variation on the proof of Corollary 4.5.

**Remark:** We surmise that also \( \eta_m^c(r) \equiv \eta_M^c(r) \) but have not been able to prove it.
good enough to find a subset of \( \Theta_{\text{alg}}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_{\text{alg}}^{\text{CS}}(\Psi_\Lambda) \) which satisfies our wishes, and it’s even more hopeless to naively seek an admissible subset of \( \Theta_{\text{alg}}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_{\text{alg}}^{\text{CS}}(\Psi_\Lambda) \)

However, if we shrink the size of \( \Lambda \) by choosing a suitable \( \zeta \in (\hat{\zeta}, 1) \), then we can find a subset of \( \Theta_{\text{alg}}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_{\text{alg}}^{\text{CS}}(\Psi_\Lambda) \) for which at least three solutions of (69) take values only in the hard-sphere fluid regime, i.e. for which \( \eta^M_\zeta \leq \eta^\infty_\Lambda \approx 0.49 \). So we impose the restriction \( \eta^M_\zeta \leq \eta^\infty_\Lambda \) on \( \Theta_{\text{alg}}^{\text{CS}}(\Phi_\Lambda) \cap \Theta_{\text{alg}}^{\text{CS}}(\Psi_\Lambda) \) and seek admissible \( \zeta \).

To analyze the effect of this restriction we impose it on \( \Theta_{\text{alg}}^{\text{CS}}(\tau) \). Let \( \Theta_{\text{alg}}^{\text{CS}}(\tau) \) denote the \( (\alpha, \gamma) \) domain featuring three solutions of (58) in the hard-sphere fluid regime. Recalling the proof of Proposition 3.2, it is readily verified that \( \Theta_{\text{alg}}^{\text{CS}}(\tau) \) is given by \( \Theta_{\text{alg}}^{\text{CS}}(\tau) \equiv \{(\alpha, \gamma) : g_2'(\eta_\zeta^\infty) < \alpha \tau < g_2'(\eta_\zeta^\infty) \land \tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau) < \gamma < \tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau)\}, \) where

\[
\tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau) = \tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau), \tag{73}
\]

\[
\tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau) = \min\{\tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau), \gamma_{\text{fs}}^{\text{CS}}(\alpha \tau)\}, \tag{74}
\]

with

\[
\gamma_{\text{fs}}^{\text{CS}}(\alpha \tau) = \gamma_{\text{fs}} - \bar{\eta}_{\text{fs}}^\infty \alpha \tau. \tag{75}
\]

We note that the two boundary curves \( \tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau) \) and \( \tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \tau) \) intersect at the endpoints of the allowed \( \alpha \tau \) interval, i.e. at \( \alpha \tau = g_2'(\eta_\zeta^\infty) \) and \( \alpha \tau = g_2'(\eta_\zeta^\infty) \). So also the boundary \( \partial\Theta_{\text{alg}}^{\text{CS}}(\tau) \) is given by two functions of \( \alpha \) which depend on \( \alpha \) only through the product \( \alpha \tau \), and this implies for (58) that also triple hard-sphere fluid solution regions in the \( (\alpha, \gamma) \) half plane for any two different \( \tau = \tau_1 \) and \( \tau = \tau_2 \) differ from each other only by some scaling along the \( \alpha \) axis, i.e. once again these triple regions are affine similar. However, distinct from the set \( \Theta_{\text{alg}}^{\text{CS}}(\tau) \), the set \( \Theta_{\text{alg}}^{\text{CS}}(\tau) \) is bounded, and since it is also bounded away from \( \alpha \tau = 0 \), if \( \tau_1 \) and \( \tau_2 \) differ by too much then \( \Theta_{\text{alg}}^{\text{CS}}(\tau_1) \cap \Theta_{\text{alg}}^{\text{CS}}(\tau_2) = \emptyset \).

Thus, to carry out our construction of subsolutions presented in the proof of Proposition 5.1 we need to limit the size of \( \zeta \Lambda \) to make sure that \( \Theta_{\text{alg}}^{\text{CS}}(\Psi_{\zeta \Lambda}) / \Theta_{\text{alg}}^{\text{CS}}(\Phi_{\zeta \Lambda}) \) is not too small. Since \( \Lambda \) is supposed to be a macroscopic container domain, this means that \( \zeta > \hat{\zeta} \) has to be chosen sufficiently small. Recall that the maximum of \( \Psi_{\zeta \Lambda} \) then occurs for one or more \( \zeta \ll 1 \), and we stipulated that we mean the largest \( \zeta \) in case \( \zeta \) is not unique. We can precisely, though only implicitly characterize the range of scaled domains \( \zeta \Lambda \) for which our construction of subsolutions presented in the proof of Proposition 5.1 can be carried out. Namely, the intersection \( \Theta_{\text{alg}}^{\text{CS}}(\Psi_{\zeta \Lambda}) \cap \Theta_{\text{alg}}^{\text{CS}}(\Phi_{\zeta \Lambda}) \neq \emptyset \) for all \( \zeta \in [\hat{\zeta}, \zeta] \), where \( \zeta > \hat{\zeta} \) is the unique \( \zeta \) value for which the lower boundary of \( \Theta_{\text{alg}}^{\text{CS}}(\Psi_{\zeta \Lambda}) \) only touches the upper boundary of \( \Theta_{\text{alg}}^{\text{CS}}(\Phi_{\zeta \Lambda}) \) (possibly more than once), determined by

\[
\tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \Psi_{\zeta \Lambda}) = \tilde{\gamma}_{\text{alg}}^{\text{CS}}(\alpha \Phi_{\zeta \Lambda}), \tag{76}
\]
\[ \partial_\beta \hat{\gamma}_\beta^{\text{alg}}(\alpha) = \partial_\beta \hat{\gamma}_\beta^{\text{alg}}(\alpha \Phi_{\Lambda}). \] (77)

The upshot is:

**Proposition 5.3:** Let \( \varsigma \in [\varsigma, \zeta] \) and \( (\alpha, \gamma) \in \Theta_{\varsigma}^{\text{alg}}(\Psi_{\varsigma \Lambda}) \cap \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \). Then

\[ \eta(r) = \varphi_{\varsigma}^{\prime}(\gamma - (\alpha V * \eta)_{\varsigma \Lambda}(r)) \] (78)

has at least three ordered solutions in \( C^0_b(\varsigma \Lambda) \cap B_{\eta_{\varsigma <}} \), two of which can be computed by iterating with r.h.s. (78), starting from (70) with \( \mu = m \) and \( \mu = M \), respectively.

**Remark:** It is helpful to have a geometric illustration of the situation. Recall that \( \Theta_{\varsigma}^{\text{alg}}(\tau) \) is the bounded domain in \( (\alpha, \gamma) \) half space determined by (73), (74), (75) for which the algebraic fixed point equation (58) has exactly three solutions in the hard-sphere fluid regime. For the various \( \tau > 0 \) values associated with \( \Lambda \) which we have encountered in this section, all the domains \( \Theta_{\varsigma}^{\text{alg}}(\tau) \) are located in the negative \( \gamma \) half of \( (\alpha, \gamma) \) half space. They have roughly the shape of a receding moon crescent, being affine similar to each other by horizontal scaling (along the \( \alpha \) axis). The domains we have encountered are arranged as follows: \( \Theta_{\varsigma}^{\text{alg}}(\|V\|_1) \) is the leftmost domain, followed by \( \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \), then \( \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \), and finally \( \Theta_{\varsigma}^{\text{alg}}(\Psi_{\varsigma \Lambda}) \). For macroscopic \( \Lambda \) we have \( \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \cap \Theta_{\varsigma}^{\text{alg}}(\Psi_{\varsigma \Lambda}) \neq \emptyset \), in fact \( \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \approx \Theta_{\varsigma}^{\text{alg}}(\|V\|_1) \), and we have \( \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \cap \Theta_{\varsigma}^{\text{alg}}(\Psi_{\varsigma \Lambda}) \neq \emptyset \) for all \( \varsigma \in [\varsigma, \zeta] \); however, \( \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \cap \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) = \emptyset \), and there is much space inbetween.

For general macroscopic domains \( \Lambda \) it is not easy to come up with good explicit estimates on \( \zeta \), but in our section on spherical domains we will see that \( \zeta \Lambda \) is not exactly what one would call a macroscopic domain. So Proposition 5.3 falls far short of our ideal goal, which is to construct suitable subsolutions in macroscopic \( \Lambda \) which imply that for most if not all \( (\alpha, \gamma) \in \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \) equation (8) has (at least) three solutions whose range is in \( (0, \eta_{\varsigma <}) \). On the other hand, with the help of variational arguments we will be able to show that for a significant fraction of pairs \( (\alpha, \gamma) \in \Theta_{\varsigma}^{\text{alg}}(\Phi_{\varsigma \Lambda}) \) the fixed point equation (8) has at least three solutions whose range is in \( (0, \eta_{\varsigma <}) \), indeed. These arguments invoke our functional \( P^{\Lambda}_{\alpha, \gamma}[\eta] \) given in (9).

### 6 \( \mathcal{P} \) STABILITY AND THE GAS ↔ LIQUID PHASE TRANSITION

Consider first \( V \in L^1(\mathbb{R}^3) \) and recall that \( \Theta_{\varsigma}^{\text{alg}}(\|V\|_1) \) is the bounded domain in \( (\alpha, \gamma) \) half space determined by (73), (74), (75) with \( \tau = \|V\|_1 \) for which the algebraic...
fixed point equation \[ (6) \] has exactly three solutions in the hard-sphere fluid regime which are spatially uniform solutions of \[ (7) \]. This triplicity region of uniform hard-sphere fluid solutions contains a phase transition curve \( \gamma = \gamma_{vdW}^W(\alpha) \) along which the mean pressure functional \( \Pi_{\alpha,\gamma}(\eta) := \lim_{\Lambda \to \mathbb{R}^3} |\Lambda|^{-1} P_{\alpha,\gamma}^\Lambda[\eta] \) has an uncountable family of global maximizers for each \((\alpha, \gamma) = (\alpha, \gamma_{vdW}^W(\alpha))\) — the variational problem for \( \Pi_{\alpha,\gamma}(\eta) \) is degenerate! Amongst its global maximizers are a small \((\eta_{vdW}^m, m)\) and a large \((\eta_{vdW}^M, M)\) spatially uniform solution of \( (7) \). For spatially uniform density functions \( \eta \), the functional \( \Pi_{\alpha,\gamma}(\eta) \) takes the simple form

\[
\Pi_{\alpha,\gamma}(\eta) = \varphi \left( \gamma + \alpha \| V \|_1 \eta \right) - \frac{1}{2} \alpha \| V \|_1 \eta^2,
\]

and it is an elementary exercise to show that \( (6) \) is the Euler–Lagrange equation for

\[
\pi_{\alpha,\gamma}(\eta) := \sup_{\eta} \{ \Pi_{\alpha,\gamma}(\eta) \}.
\]

Van der Waals \( ^{53} \) interpreted the existence of two global maximizers of \( (79) \) as a phase transition between a uniform gas and a uniform liquid phase of the hard-sphere fluid; however, since \( (7) \) also has uncountably many interface type solutions which maximize \( \Pi_{\alpha,\gamma}(\eta) \), eventually the uniform solutions were interpreted as pure-, the interface type solutions as mixed phases describing the physical coexistence of locally pure phases.

Our goal in this section is to prove the finite volume analog of this gas ↔ liquid phase transition when the fluid is confined in a macroscopic container \( \Lambda \) and in contact with both heat and matter reservoirs. Of course, the analogy can go only so far: with our neutral mechanical boundary conditions there are no spatially uniform solutions to \( (8) \), so that the thermodynamic notion of a “pure phase” cannot apply in the strict sense of its original definition. Yet, empirically \( ^{33} \) (and intuitively) finite size distortions of the spatially uniform pure phases are limited to boundary layer effects near the container walls, so that in a macroscopic container which is connected to a matter reservoir the pure phases of the infinite volume thermodynamic formalism are approximately achieved in most of the container’s interior by quasi-uniform density functions. On the other hand, interface type solutions will not maximize \( P_{\alpha,\gamma}^\Lambda[\eta] \), for the formation of an interface comes at the price of an “interface penalty” which becomes negligible only in the thermodynamic (infinite volume) limit. To be sure, we have not been able to verify all those details. What we have been able to prove is stated in our
Theorem 6.1: Let $\Lambda$ be a convex container of macroscopic proportions, i.e. $\varnothing(\Lambda) \gg 1$ and $\varnothing(\Lambda)/|\Lambda|^{1/3} = O(1)$. Let $V \in L^1(\mathbb{R}^3)$. Then for a subset of $\Theta^{\text{sh}}_*([|V|])$ at least three ordered hard-sphere fluid solutions of (8) exist, (at least) two of which are locally $\mathcal{P}$ stable. The extension of this subset of $\Theta^{\text{sh}}_*([|V|])$ to the open set $\Theta_{\Lambda}^{\text{sh}}$ of (at least) triplicity of hard-sphere fluid solutions of (8) contains a phase transition curve along which (at least) two distinct hard-sphere fluid solutions maximize $\mathcal{P}_{\Lambda,\gamma}^\Lambda[\eta]$ globally. The transition is of first order in the sense of Ehrenfest, i.e. the partial derivatives of $(\alpha, \gamma) \mapsto \mathcal{P}_{\Lambda}(\alpha, \gamma)$ are discontinuous across this grand canonical phase transition curve.

Proof of Theorem 6.1: For the proof we adopt the line of reasoning of Ref.[29] where a canonical phase transition is proved for $V$ given by a class of regularizations of $V_N$ and $\varnothing$ given by the perfect gas law. Yet many more technical estimates are needed for the current proof, which makes it somewhat long, and so we begin with its outline.

In the first part of the proof we establish the multiplicity of solutions claimed in Theorem 6.1. We use Propositions 3.1 and 3.4 according to which a pointwise smallest hard-sphere fluid solution $\eta_m^\Lambda(r)$ of (8) exists when $(\alpha, \gamma) \in \Theta_{\Lambda}^{\text{sh}}([|V|])$, and that $\eta_m^\Lambda(r)$ is locally $\mathcal{P}$ stable (see Prop.3.1 in Ref.[6], and also below). Also by Propositions 3.1 and 3.4, a locally $\mathcal{P}$ stable pointwise largest hard-sphere fluid solution $\eta_M^\Lambda(r)$ of (8) exists, but Proposition 3.1 left open the possibility that $\eta_m^\Lambda(r)$ and $\eta_M^\Lambda(r)$ are identical. We will show that when $\Lambda$ is a convex container domain of macroscopic proportions, then $\eta_m^\Lambda(r) < \eta_M^\Lambda(r)$ for a subset of pairs $(\alpha, \gamma) \in \Theta_{\Lambda}^{\text{sh}}([|V|])$. This will be achieved by showing that for the favorable subset of $(\alpha, \gamma) \in \Theta_{\Lambda}^{\text{sh}}([|V|])$ the pressure functional $\mathcal{P}_{\Lambda,\gamma}^\Lambda[\eta]$ evaluated with $\eta_m^\Lambda(r)$ is bounded above by a bound which is surpassed by the evaluation of $\mathcal{P}_{\Lambda,\gamma}^\Lambda[\eta]$ with $\eta_M^\Lambda$. This implies that the locally $\mathcal{P}$ stable pointwise minimal solution is not a global maximizer, so another solution of (8) exists which is, yet it does not establish that this solution is a hard-sphere fluid solution. This in turn is guaranteed by imposing the “no non-fluid solutions condition” (35) of Proposition 3.3 on $(\alpha, \gamma) \in \Theta_{\Lambda}^{\text{sh}}([|V|])$, which leaves us with a bounded but non-empty set of favorable $(\alpha, \gamma)$ values for sufficiently large $\Lambda$. This set is then extended by continuity to the multiplicity set $\Theta_{\Lambda}^{\text{sh}}$ introduced in Theorem 6.1.

In the second part of the proof we establish the existence of the phase transition in $\Theta_{\Lambda}^{\text{sh}}$. Having already established, in part one, that the locally $\mathcal{P}$ stable pointwise minimal solution is not a global maximizer of $\mathcal{P}_{\Lambda,\gamma}^\Lambda(\eta)$ when “$\alpha$ and $\gamma$ are big enough,”
we recall our uniqueness results to establish that the pointwise minimal solution is in
fact the unique global maximizer of \( P_{\alpha, \gamma}^\Lambda (\eta) \) when \( \alpha \) and \( \gamma \) are small enough.” The
rest of the proof consists in using continuity arguments to show that for favorable
\((\alpha, \gamma)\) the pointwise minimal solution is a global maximizer of \( P_{\alpha, \gamma}^\Lambda (\eta) \) but not the
only one.

This ends the outline of our strategy of proof.

So our first task is to estimate \( P_{\alpha, \gamma}^\Lambda [\eta^m_\Lambda] \) from above. Since each solution \( \bar{\eta}_{vdw} \) of (6) is a constant solution \( \bar{r} \mapsto \bar{\eta}_{vdw} \) of (7), when restricted to \( \Lambda \), this constant solution
is strictly supersolution for (8) with the same \((\alpha, \gamma)\), and so the small solution of (8) is necessarily bounded above by the small solution of (6), i.e. \( \eta^m_\Lambda (\bar{r}) \leq \bar{\eta}_{vdw}; \) see Proposition 3.4. Incidentally, we also know that \( \bar{\eta}_{vdw} \leq \bar{\eta}_s \) uniformly for all small
solutions of (6) when \((\alpha, \gamma) \in \Theta_{\text{obs}}(\|V\|_s)\). Also, \(- (V \ast 1)_\Lambda (\bar{r}) \leq \|V\|_s \forall \bar{r} \in \Lambda \). These
pieces of information allow us to find the following upper estimate to \( P_{\alpha, \gamma}^\Lambda [\eta^m_\Lambda] \),

\[
P_{\alpha, \gamma}^\Lambda [\eta^m_\Lambda] = \int_\Lambda \varphi_\ast (\gamma - (\alpha V \ast \eta^m_\Lambda)_\Lambda (\bar{r})) d^3 r + \frac{1}{2} \int_\Lambda \alpha V (|\bar{r} - \bar{r}|) \eta^m_\Lambda (\bar{r}) \eta^m_\Lambda (\bar{r}) d^3 r d^3 \tilde{r}
\]

\[
\leq \int_\Lambda \varphi_\ast (\gamma + \alpha \|V\|_1 \bar{\eta}_{vdw}) |\Lambda| + \frac{1}{2} \int_\Lambda \alpha V (|\bar{r} - \bar{r}|) \eta^m_\Lambda (\bar{r}) \eta^m_\Lambda (\bar{r}) d^3 r d^3 \tilde{r}.
\]

\[
= \left( \Pi_{\alpha, \gamma} (\bar{\eta}_{vdw}^m) + \frac{1}{2} \alpha \|V\|_1 \bar{\eta}_{vdw}^{m, 2} \right) |\Lambda| + \frac{1}{2} \alpha \int_\Lambda \eta^m_\Lambda (\bar{r}) (V \ast \eta^m_\Lambda)_\Lambda (\bar{r}) d^3 r,
\]

and so

\[
|\Lambda|^{-1} P_{\alpha, \gamma}^\Lambda [\eta^m_\Lambda] \leq \Pi_{\alpha, \gamma} (\bar{\eta}_{vdw}^m) + \frac{1}{2} \alpha \left( \|V\|_1 \bar{\eta}_{vdw}^{m, 2} + \langle \eta^m_\Lambda (V \ast \eta^m_\Lambda)_\Lambda \rangle \right),
\]

where \( \langle \cdot \rangle_\Lambda \) denotes average over \( \Lambda \) w.r.t. normalized Lebesgue measure. We will
next show that

\[
\|V\|_1 \bar{\eta}_{vdw}^{m, 2} + \langle \eta^m_\Lambda (V \ast \eta^m_\Lambda)_\Lambda \rangle = O(\varnothing(\Lambda)^{-2/3}).
\]

(83)

We abbreviate dist(\( \bar{r}, \partial \Lambda \)) \( \equiv s(\bar{r}), \) and \( \|V(\cdot)\|_{L^1(\partial s(\bar{r}))} \equiv \|V\|_{s(\bar{r})}. \) We note the
obvious pointwise estimate

\[
- (V \ast 1)_\Lambda (\bar{r}) \geq \|V\|_{s(\bar{r})}.
\]

(84)

Now we add zero, in the form of \( \|V\|_1 - \|V\|_1, \) to r.h.s. (84), then average the so
rewritten (84) over \( \Lambda \) w.r.t. normalized Lebesgue measure, multiply by the constant function \( \bar{\eta}_{vdw}^{m, 2} \), and get

\[
- \langle \bar{\eta}_{vdw}^m (V \ast \bar{\eta}_{vdw}^m)_\Lambda \rangle_\Lambda \geq \|V\|_1 \bar{\eta}_{vdw}^{m, 2} - \left( \|V\|_1 - \|V\|_{s(\bar{r})} \right)_\Lambda \bar{\eta}_{vdw}^{m, 2}.
\]

(85)
The average at r.h.s.\textsuperscript{(85)} is estimated as follows. The integrand $\|V\|_1 - \|V\|_{s(r)}$ depends on $r$ only through $s(r) = \text{dist}(r, \partial \Lambda)$, and when extended to all $s > 0$, it is decreasing fast to zero (at least like $Cs^{-3}$) for $s$ large (in molecular units); just asymptotically expand (A.4) and (A.5) for large $R$. Hence, and since $\Lambda$ is convex,

$$\int_\Lambda (\|V\|_1 - \|V\|_{s(r)}) d^3r \leq C(V)|\partial \Lambda|$$

where

$$C(V) = \int_0^\infty (\|V\|_1 - \|V(| \cdot |)\|_{L^1(\mathbb{R})}) dR$$

is independent of $\Lambda$. With (86), (87) inserted into (85), we obtain the estimate

$$\|V\|_1 \tilde{m}_\text{vdW} \leq - \langle \tilde{m}_\text{vdW} (V * \tilde{m}_\text{vdW}) \rangle_\Lambda + C(V)\tilde{m}_\text{vdW}^2|\partial \Lambda|/|\Lambda|$$

with $|\partial \Lambda|/|\Lambda| = O(\varnothing(\Lambda)^{-1})$, by hypothesis. So for the l.h.s.\textsuperscript{(83)} we arrive at

$$\|V\|_1 \tilde{m}_\text{vdW} + \langle \tilde{m}_\text{vdW}^2 \rangle_\Lambda \leq - \langle \tilde{m}_\text{vdW} (V * \tilde{m}_\text{vdW}) \rangle_\Lambda - \langle \tilde{m}_\text{vdW}^2 \rangle_\Lambda - \langle \tilde{m}_\text{vdW} \rangle_\Lambda + O[\varnothing(\Lambda)^{-1}] =$$

$$- \langle \tilde{m}_\text{vdW} - \tilde{m}_\text{vdW} \rangle_\Lambda + O[\varnothing(\Lambda)^{-1}].$$

The last displayed integral in (89) we estimate thusly,

$$- \langle \langle \tilde{m}_\text{vdW} - \tilde{m}_\text{vdW} \rangle_\Lambda \rangle_\Lambda \leq$$

$$-2 \langle \langle \tilde{m}_\text{vdW} - \tilde{m}_\text{vdW} \rangle_\Lambda \rangle_\Lambda \leq$$

$$-2 \langle \langle \tilde{m}_\text{vdW} - \tilde{m}_\text{vdW} \rangle_\Lambda \rangle_\Lambda =$$

$$2 \|V\|_1 \tilde{m}_\text{vdW} \langle \langle \tilde{m}_\text{vdW} \rangle_\Lambda \rangle_\Lambda =$$

$$2 \|V\|_1 \tilde{m}_\text{vdW} \langle \langle \tilde{m}_\text{vdW} \rangle_\Lambda \rangle_\Lambda.$$

To estimate $\langle \tilde{m}_\text{vdW} \rangle_\Lambda$, we recall that for $(\alpha, \gamma) \in \Theta^\perp_{\text{vdW}|} (\|V\|_1)$ the small hard-sphere fluid solution $\tilde{m}_\text{vdW} < \tilde{m}_\text{vdW} \leq \tilde{m}_\text{vdW}$, and that for such pairs $(\alpha, \gamma)$ the map $\eta \mapsto \tilde{m}_\text{vdW}^{\alpha \gamma} - \tilde{m}_\text{vdW}$ is convex when restricted to $C^0_b(\Lambda) \cap \tilde{m}_\text{vdW}$. Jensen’s inequality then gives

$$\langle \tilde{m}_\text{vdW} \rangle_\Lambda \geq \tilde{m}_\text{vdW} - \langle \langle \tilde{m}_\text{vdW} \rangle_\Lambda \rangle_\Lambda.$$
We now notice that
\[ \langle (V \ast \eta^m_{\Lambda}) \rangle_{\Lambda} = \langle \eta^m_{\Lambda}(V \ast 1) \rangle_{\Lambda} \]  
and recall our pointwise estimate (84) and that \( \|V\|_1 - \|V\|_{s(V)} \) is decreasing to zero at least like \( Cs^{-3} \) for \( s \) large in molecular units. So if \( \delta \Lambda \subset \Lambda \) is a corridor of thickness \( O[\varnothing(\Lambda)^{1/3}] \) next to the boundary \( \partial \Lambda \), then upon splitting \( \Lambda = \delta \Lambda \cup (\Lambda \setminus \delta \Lambda) \) we get
\[ \langle \eta^m_{\Lambda} \rangle_{\Lambda} \geq \varphi'_{\delta}(\gamma^\delta + \alpha \tau^\delta \langle \eta^m_{\Lambda} \rangle_{\Lambda}), \]  
where
\[ \gamma^\delta = \gamma - O[\varnothing(\Lambda)^{-2/3}] \]
and
\[ \tau^\delta = \|V\|_1 - O[\varnothing(\Lambda)^{-1}]. \]
So \( \langle \eta^m_{\Lambda} \rangle_{\Lambda} \) is a supersolution for the algebraic fixed point problem
\[ \overline{\eta} = \varphi'_{\delta}(\gamma^\delta + \alpha \tau^\delta \overline{\eta}), \]
and this yields the lower bound
\[ \langle \eta^m_{\Lambda} \rangle_{\Lambda} \geq \overline{\eta}^\delta \]
where \( \overline{\eta}^\delta \) is the smallest solution of (93). We also know that \( \langle \eta^m_{\Lambda} \rangle_{\Lambda} < \overline{\eta}^m_{\text{vdW}} \leq \overline{\eta}_{\delta} \), so by the concavity of \( \overline{\eta} \mapsto g_2(\overline{\eta}) \) for \( \overline{\eta} < \overline{\eta}_{\delta} \), we easily find the explicit lower bound
\[ \overline{\eta}^\delta > \overline{\eta}^\delta, \]
where \( \overline{\eta}^\delta \) solves the linear algebraic equation
\[ g_2(\overline{\eta}^m_{\text{vdW}}) + g'_2(\overline{\eta}^m_{\text{vdW}})(\eta - \overline{\eta}^m_{\text{vdW}}) = \gamma - O[\varnothing(\Lambda)^{-2/3}] + \alpha(\|V\|_1 - O[\varnothing(\Lambda)^{-1}]\overline{\eta}). \]
which gives
\[ \overline{\eta}^\delta = \overline{\eta}^m_{\text{vdW}} - O[\varnothing(\Lambda)^{-2/3}]. \]  
Hence,
\[ \overline{\eta}^m_{\text{vdW}} - \langle \eta^m_{\Lambda} \rangle_{\Lambda} \leq O[\varnothing(\Lambda)^{-2/3}]. \]
All in all, this proves (83), i.e. we have shown that
\[ |\Lambda|^{-1} \mathcal{P}_{\alpha,\gamma}^\Lambda [\eta^m_{\Lambda}] \leq \Pi_{\alpha,\gamma} (\overline{\eta}^m_{\text{vdW}}) + O[\varnothing(\Lambda)^{-2/3}]. \]
We next recall that the maximum of $\mathcal{P}_{\alpha,\gamma}[\eta]$ is estimated below (in particular) by

$$\max_\eta \mathcal{P}_{\alpha,\gamma}[\eta] \geq \mathcal{P}_{\alpha,\gamma}[\mathcal{T}_{\text{vaw}}^M].$$

We estimate $\mathcal{P}_{\alpha,\gamma}[\mathcal{T}_{\text{vaw}}^M]$ from below by using that our $\alpha V = A_w V_w + A_y V_y$ is of molecular effective range, and that $\Lambda$ is convex and of macroscopic proportions, so that our earlier $\delta$-corridor estimate tells us that we can find $\vartheta = 1 - O[\varnothing(\Lambda)^{-1}] \in (0, 1)$ and $\varsigma = 1 - O[\varnothing(\Lambda)^{-2/3}] \in (0, 1)$ so that $-(V * 1)_\Lambda(r) \geq \vartheta \|V\|_1 \forall r \in \varsigma \Lambda$. Using also that $-(V * 1)_\Lambda(r) \leq \|V\|_1 \forall r \in \Lambda$, we find

$$\mathcal{P}_{\alpha,\gamma}[\mathcal{T}_{\text{vaw}}^M] = \int_\Lambda \varphi_*(\gamma - (\alpha V * \mathcal{T}_{\text{vaw}}^M)(r)) d^3 r + \frac{1}{2} \varphi_{\mathcal{T}_{\text{vaw}}^M}^2 \int_\Lambda \alpha V(|r - \bar{r}|) d^3 r$$

$$\geq \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) \varsigma \Lambda - 2\alpha \varphi_{\mathcal{T}_{\text{vaw}}^M}^2 \|V\|_1 \|1 \Lambda\|

= \left( \varsigma \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) - (1 - \varsigma) \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) - \varsigma \left( \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) - \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) \right) \right),$$

(105)

and by the mean value theorem we have the further identity

$$\varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) - \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) = (1 - \vartheta) \varphi_*(\mathcal{T}) \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}$$

(106)

for some $\mathcal{T}$ inbetween the two arguments at the l.h.s. of (106). The monotonic increase of $\varphi_*$ now gives

$$\varphi_*(\mathcal{T}) < \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}).$$

(107)

The r.h.s. of (107) is independent of $\Lambda$ and depends on $(\alpha, \gamma)$ as displayed plus implicitly through $\varphi_{\mathcal{T}_{\text{vaw}}^M}$. Since $1 - \vartheta = O[\varnothing(\Lambda)^{-1}]$ and $1 - \varsigma = O[\varnothing(\Lambda)^{-2/3}]$, we conclude that

$$\varsigma \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) \geq \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) - O[\varnothing(\Lambda)^{-2/3}],$$

(108)

and so

$$|\Lambda|^{-1} \max_\eta \mathcal{P}_{\alpha,\gamma}[\eta] \geq \varphi_*(\gamma + \alpha \|V\|_1 \varphi_{\mathcal{T}_{\text{vaw}}^M}) - \frac{1}{2} \alpha \varphi_{\mathcal{T}_{\text{vaw}}^M}^2 \|V\|_1 - O[\varnothing(\Lambda)^{-2/3}]$$

$$= \Pi_{\alpha,\gamma}(\varphi_{\mathcal{T}_{\text{vaw}}^M}) - O[\varnothing(\Lambda)^{-2/3}],$$

(109)
Combining (102) with (109) now yields the desired estimate

\[ |\Lambda|^{-1} \left( \max_{\eta} \mathcal{P}_{\alpha,\gamma}[\eta] - \mathcal{P}_{\alpha,\gamma}[\eta^m] / \eta_{\Lambda} \right) \geq \Pi_{\alpha,\gamma}(\eta_{vdW}^m) - \Pi_{\alpha,\gamma}(\eta_{vdW}^m) - O[\varnothing(\Lambda)^{-2/3}] . \]  

(110)

But for \((\alpha, \gamma)\) in the triplicity set \(\Theta^{vl}_{\delta}([V]_1)\), the \(\Lambda\)-independent function

\[ \varpi(\alpha, \gamma) := \Pi_{\alpha,\gamma}(\eta_{vdW}^m) - \Pi_{\alpha,\gamma}(\eta_{vdW}^m) \]  

(111)

vanishes only on the van der Waals gas & liquid coexistence curve \(\alpha \mapsto \gamma = \gamma_{vdW}^{vl}(\alpha)\), thereby dividing \(\Theta^{vl}_{\delta}([V]_1)\) into two disjoint subsets, in one of which \(\varpi(\alpha, \gamma) < 0\), and \(\varpi(\alpha, \gamma) > 0\) in the other. Since \(\varpi(\alpha, \gamma)\) is independent of \(\Lambda\), while \(O[\varnothing(\Lambda)^{-2/3}] \downarrow 0\) as \(\varnothing(\Lambda) \to \infty\), it follows that for each pair \((\alpha, \gamma)\) for which \(\varpi(\alpha, \gamma) > 0\), we have

\[ |\Lambda|^{-1} \left( \max_{\eta} \mathcal{P}_{\alpha,\gamma}[\eta] - \mathcal{P}_{\alpha,\gamma}[\eta^m] / \eta_{\Lambda} \right) \geq \varpi(\alpha, \gamma) - O[\varnothing(\Lambda)^{-2/3}] > 0 \]  

(112)

eventually, for large enough \(\Lambda\). So for this subset of \(\Theta^{vl}_{\delta}([V]_1)\), a locally \(\mathcal{P}\) stable small hard-sphere fluid solution \(\eta^*_\Lambda(r) < \eta_t\) exists, but it is not globally \(\mathcal{P}\) stable.

Our result (112) for the \(\varpi(\alpha, \gamma) > 0\) subset of \(\Theta^{vl}_{\delta}([V]_1)\) in sufficiently large \(\Lambda\) does not establish that the global maximizer is a hard-sphere fluid solution, or even that any other hard-sphere fluid solution of (8) exists for the “parameters” \((\alpha, \gamma)\) and \(\Lambda\) under consideration. Yet, since (112) holds for any particular \((\alpha, \gamma)\) in the \(\varpi(\alpha, \gamma) > 0\) subset of \(\Theta^{vl}_{\delta}([V]_1)\) \textit{whenever} \(\Lambda\) is sufficiently large, we can impose the additional condition (35) (with \([V]_1\) in place of \(\Phi_{\delta}\)) on \((\alpha, \gamma)\), so that no solution to the extended (8) exists which somewhere in \(\Lambda\) is not a (hard-sphere) fluid; see Proposition 3.3. Notice that (35) is a sufficient but certainly not a necessary condition, yet to improve on it we would need to have better control over the solid branch of \(\gamma \mapsto \varphi_{\delta}(\gamma)\). In absence of such better control we consider

\[ (\alpha, \gamma) \in \Theta^{vl}_{\delta}([V]_1) \cap \{ \varpi(\alpha, \gamma) > 0 \land \gamma + \alpha [V]_1 \eta^*_\ell \leq \gamma_{vl}\} . \]  

(113)

This set, which is defined entirely in terms of the algebraic van der Waals theory with spatially uniform density functions, is non-empty, as can be verified by evaluating this van der Waals model. We conclude that when \((\alpha, \gamma)\) satisfies (113) and is fixed, then for large enough \(\Lambda\) a locally \(\mathcal{P}\) stable pointwise minimal hard-sphere fluid solution \(\eta^*_\Lambda(r) < \eta_t\) of (8) exists, but the global \(\mathcal{P}_{\alpha,\gamma}\) maximizer is given by another,
pointwise larger hard-sphere fluid solution of (8) which is locally $\mathcal{P}$ stable, or locally $\mathcal{P}$ indifferent in exceptional cases.

The existence of a third, unstable (under iterations and in $\mathcal{P}$ sense) solution sandwiched between the locally $\mathcal{P}$ stable minimal solution and the globally $\mathcal{P}$ stable solution of (8) now follows via the mountain pass lemma thanks to the strong $C^0_b(\Lambda)$ differentiability of the functional $\mathcal{P}_{\alpha,\gamma}[\eta]$. By continuity we can extend the so constructed multiplicity sub-region of hard-sphere fluid solutions of (8) to a larger set $\Theta_{\alpha,\gamma}$, which is the open set of pairs $(\alpha, \gamma)$ for which at least three ordered hard-sphere fluid solutions of (8) exist, (at least) two of which are locally $\mathcal{P}$ stable (or, exceptionally, locally $\mathcal{P}$ indifferent), and no non-fluid solution.

This completes the part of our proof of Theorem 6.1 which establishes multiplicity of hard-sphere fluid solutions of (8) in a certain domain in $(\alpha, \gamma)$ space. We next prove that somewhere in this multiplicity region of hard-sphere fluid solutions a first-order phase transition occurs between a small and a large(r) hard-sphere fluid solution.

We already know from part one of our current proof that for any $(\alpha, \gamma)$ satisfying (113), whenever $\Lambda$ is large enough, then the global $\mathcal{P}_{\alpha,\gamma}$ maximizer is given by a hard-sphere fluid solution of (8) which is pointwise larger than the locally $\mathcal{P}$ stable pointwise minimal hard-sphere fluid solution $\eta^m_{\alpha}(r)$ of (8), which exists also, satisfies $\eta^m_{\alpha}(r) < \pi_{\alpha}$, but which is not a global $\mathcal{P}_{\alpha,\gamma}$ maximizer in this $(\alpha, \gamma)$ region. Moreover, if we pick any $(\alpha, \gamma)_0$ satisfying (113) and pick a large enough $\Lambda$ so that the globally $\mathcal{P}$ stable solution of (8) is pointwise larger than $\eta^m_{\alpha}(r)$ for the chosen $(\alpha, \gamma)_0$ and $\Lambda$, then by the continuity of the map $(\alpha, \gamma) \mapsto P_{\alpha,\gamma}[\eta^m_{\alpha}]$ restricted to $\eta^m_{\alpha} < \pi_{\alpha}$, for $\Lambda$ as chosen and now fixed, there exists a whole finite-measure $(\alpha, \gamma)$ neighborhood of $(\alpha, \gamma)_0$ in r.h.s. (113) for which the globally $\mathcal{P}$ stable hard-sphere fluid solution of (8) is pointwise larger than $\eta^m_{\alpha}(r)$, which in turn is not globally stable. Let this subset of r.h.s. (113) be denoted by $^6\Theta_{\alpha,\gamma}$.

It is a fortiori contained in the multiple hard-sphere fluid region $\Theta_{\alpha,\gamma}$.

On the other hand, recall that according to Corollary 4.5 the hard-sphere fluid solution $\eta_{\alpha}$ of (8) is unique if both of the following are true, $\psi^0_{cs}(\gamma)\alpha\Phi_{\alpha} > 1$ (with $\psi^0_{cs}(\gamma) \approx 0.047$) and $\gamma < \gamma_{\alpha}(\alpha)$ (with $\gamma_{\alpha}(\alpha)$ given in Definition 4.4). A unique hard-sphere fluid solution is necessarily the pointwise minimal solution, $\eta_{\alpha} \equiv \eta^m_{\alpha}$, and the conditions of Corollary 4.5 guarantee that $\eta_{\alpha} \in C^0_{b,+] \cap \mathcal{B}_{\alpha,\gamma}$, so the solution

---

$^6$ The map $(\alpha, \gamma) \mapsto \mathcal{P}_{\alpha,\gamma}[\eta^m_{\alpha}]$ is generally not continuous without the size restriction on $\eta^m_{\alpha}$. For instance, think of the $S$-shape sections of the solution diagram of the space-uniform van der Waals problem (8).
is “small” in the sense that $\eta^m_\alpha < \overline{\eta}_1$. If we supplement the conditions of Corollary 4.5 with the condition $\gamma + \alpha \| V \|_1 \overline{\eta}^c_{fcc} \leq \gamma_b$, then no solution to the extended $(\Sigma)$ exists which is somewhere in $\Lambda$ not fluid, and then the unique hard-sphere fluid solution automatically is the unique maximizer of $\mathcal{P}_{\alpha, \gamma}^\Lambda$ for any compliant $(\alpha, \gamma)$ point.

Now note that the condition on $\alpha$ in Corollary 4.5 is fulfilled for all $(\alpha, \gamma) \in \Theta^\Lambda$, and so is the no-non-fluid condition $\gamma + \alpha \| V \|_1 \overline{\eta}^c_{fcc} \leq \gamma_b$. Hence we conclude from the discussion in the previous two paragraphs that along any constant-$\alpha$ ray which begins in $\Theta^*_\alpha$, and continues to arbitrarily negative $\gamma$ values there occurs a discontinuity in the map $\gamma \mapsto \{ \eta_{\Lambda}^{GC}(r) \}$ from $\gamma$ to the set of global maximizers of $\mathcal{P}_{\alpha, \gamma}^\Lambda$ which are all fluid. Indeed, along any such ray the constant-$\alpha$ map $\gamma \mapsto \eta^m_\alpha(r)$ furnishes the unique global $\mathcal{P}_{\alpha, \gamma}^\Lambda$ maximizer when $\gamma$ is negative enough, i.e. $\eta^m_\alpha(r) \equiv \eta_{\Lambda}^{GC}(r)$ for $\gamma$ negative enough. Moreover, this map $\gamma \mapsto \eta^m_\alpha(r)$ extends continuously differentiably into the region $\Theta^\Lambda$, for which a hard-sphere fluid solution $\eta_{\Lambda}^{GC}(r) > \eta^m_\alpha(r)$ of $(\Sigma)$ is the global maximizer of $\mathcal{P}_{\alpha, \gamma}^\Lambda$, while $\eta^m_\alpha(r)$ is not. Furthermore, by the local $\mathcal{P}$ stability of the pointwise minimal solutions a branch of pointwise non-minimal global maximizers cannot bifurcate off of this continuously differentiable branch of pointwise minimal small solution. Hence, some discontinuous change in the set of global maximizers must happen along each such ray, as claimed. We next clarify the nature of the discontinuity.

For fixed suitable $\Lambda$ and $\alpha$ as just described, we now define $\gamma^m_{sl}(\alpha)$ to be the supremum of $\gamma$ values for which $\eta_{\Lambda}^{GC}(r) \equiv \eta^m_\alpha(r) < \overline{\eta}_1$ is the unique global maximizer of $\mathcal{P}_{\alpha, \gamma}^\Lambda$ for all $\gamma < \gamma^m_{sl}(\alpha)$; clearly, $\gamma^m_\alpha(\alpha) \leq \gamma^m_{sl}(\alpha) < \hat{\gamma}^m_{sl}(\alpha \| V \|_1)$. We also define $\gamma^m_{gsl}(\alpha)$ to be the infimum of $\gamma$ values for which $\eta^m_\alpha(r) < \overline{\eta}_1$ is not a global maximizer of $\mathcal{P}_{\alpha, \gamma}^\Lambda$ for all $\gamma \in (\gamma^m_{sl}(\alpha), \hat{\gamma}^m_{sl}(\alpha) + \epsilon)$ for some $\epsilon > 0$; clearly, $\gamma^m_{gsl}(\alpha) \leq \gamma^m_{sl}(\alpha) < \hat{\gamma}^m_{sl}(\alpha \| V \|_1)$. We next show that $\gamma^m_{gsl}(\alpha) = \gamma^m_{sl}(\alpha)$.

Indeed, suppose $\gamma^m_{gsl}(\alpha) \neq \gamma^m_{sl}(\alpha)$. Then $\gamma^m_{gsl}(\alpha) < \gamma^m_{sl}(\alpha)$, and now it follows from the definitions of $\gamma^m_{sl}(\alpha)$ and $\gamma^m_{gsl}(\alpha)$ that $\eta^m_\alpha(r) < \overline{\eta}_1$ is a global maximizer of $\mathcal{P}_{\alpha, \gamma}^\Lambda$ for all $\gamma < \gamma^m_{gsl}(\alpha) < \gamma < \gamma^m_{sl}(\alpha)$, though not the unique one. But then, not only are the values of $\mathcal{P}_{\alpha, \gamma}^\Lambda[\eta]$ the same for its pointwise minimal maximizer $\eta^m_\alpha$ and for its other maximizer(s) $\eta^m_{\alpha'}$, also the $\gamma$-derivatives of $\mathcal{P}_{\alpha, \gamma}^\Lambda[\eta]$ must be the same for $\eta^m_\alpha$ and for $\eta^m_{\alpha'}$. By the implicit function theorem, the derivative of $\gamma \mapsto \mathcal{P}_{\alpha, \gamma}^\Lambda[\eta]$ exists along any constant-$\alpha$ section of a solution branch of $(\Sigma)$, except at the bifurcation points where it might or might not exist, but in any event either the left or right derivative w.r.t. $\gamma$ exists, then. Now, since any currently contemplated $(\alpha, \gamma)$ is not a bifurcation point for the pointwise minimal solution, the partial $\gamma$ derivative of $\mathcal{P}_{\alpha, \gamma}^\Lambda[\eta]_\alpha$ exists.
at \((\alpha, \gamma)\). Any other maximizer of \(P_{\alpha,\gamma}^\Lambda[\eta]\) belongs to a different solution branch, and we may assume that in general it is not at a bifurcation point either, so the partial \(\gamma\) derivative of \(P_{\alpha,\gamma}^\Lambda[\eta]\) generally exists at the contemplated \((\alpha, \gamma)\), too. Now, with the help of (8) one can easily show that, away from bifurcation points,

\[
\partial_\gamma P_{\alpha,\gamma}^\Lambda[\eta_\Lambda] = \int_\Lambda \psi_\Lambda'(\gamma - (\alpha V * \eta_\Lambda)(\mathbf{r}))d^3\mathbf{r};
\]  

(114)

note that in terms of the functional for the total number of particles (13) we can re-express this derivative as \(\partial_\gamma P_{\alpha,\gamma}^\Lambda[\eta_\Lambda] = \mathcal{N}^\Lambda[\eta_\Lambda]\). So we conclude that the two maximizers \(\eta^{\ast}_\Lambda\) and \(\eta^m_\Lambda\) of \(P_{\alpha,\gamma}^\Lambda[\eta]\) also have the same \(\mathcal{N}\), i.e. \(\mathcal{N}^\Lambda[\eta^{\ast}_\Lambda] = \mathcal{N}^\Lambda[\eta^m_\Lambda]\), which is impossible because \(\eta^m_\Lambda\) is the pointwise minimal solution for the given \((\alpha, \gamma)\). This proves that \(\gamma^\Lambda_\ast(\alpha) = \gamma^\Lambda_\ast(\alpha)\). Incidentally, the proof also shows that \(\eta_\Lambda(\mathbf{r}) < \overline{\eta}\) is not a global maximizer of \(P_{\alpha,\gamma}^\Lambda\) for all \(\gamma > \gamma^\Lambda_\ast(\alpha)\).

Now, by the continuity of the maps \((\alpha, \gamma) \mapsto P_\Lambda(\alpha, \gamma)\) and \((\alpha, \gamma) \mapsto P_{\alpha,\gamma}^\Lambda[\eta^m_\Lambda]\) at \((\alpha, \gamma^\Lambda_\ast(\alpha))\) it follows that \(\alpha \mapsto \gamma^\Lambda_\ast(\alpha)\) is continuous in its (restricted) domain of definition.\(^7\) Moreover by the continuity of the maps \((\alpha, \gamma) \mapsto P_\Lambda(\alpha, \gamma)\) and \((\alpha, \gamma) \mapsto P_{\alpha,\gamma}^\Lambda[\eta^m_\Lambda]\) at \((\alpha, \gamma^\Lambda_\ast(\alpha))\), we also conclude that the pointwise minimal solution \(\eta^m_\Lambda\) is certainly a global maximizer of \(P_{\alpha,\gamma}^\Lambda\) also at \((\alpha, \gamma^\Lambda_\ast(\alpha))\), and then denoted \(\eta^\Lambda_{GC}\). However, the definition of \(\gamma^\Lambda_\ast(\alpha)\) leaves it open whether or not \(\eta^m_\Lambda\) is the unique maximizer also at \((\alpha, \gamma^\Lambda_\ast(\alpha))\), in which case the “sup” in the definition of \(\gamma^\Lambda_\ast(\alpha)\) could be replaced by “max.” We next show that at \((\alpha, \gamma^\Lambda_\ast(\alpha))\) the global maximizers of \(P_{\alpha,\gamma}^\Lambda\) is not unique.

Let \((\alpha, \gamma)\) be a point on a ray emanating from \(r_{\ast}(\Lambda)\) which is to the right of but near the curve \(\gamma = \gamma^\Lambda_\ast(\alpha)\). Then, by the just proven fact that \(\gamma^\Lambda_\ast(\alpha) = \gamma^\Lambda_\ast(\alpha)\), and by their definitions, it follows that some hard-sphere fluid solution \(\eta_\Lambda(\mathbf{r}) > \eta^m_\Lambda(\mathbf{r})\) of (8) is a global \(P_{\alpha,\gamma}^\Lambda\) maximizer for each \(\gamma > \gamma^\Lambda_\ast(\alpha)\) in a right \(\epsilon\)-neighborhood of \(\gamma^\Lambda_\ast(\alpha)\). For each such \(\gamma > \gamma^\Lambda_\ast(\alpha)\) pick such a maximizer \(\eta_\Lambda(\mathbf{r})(> \eta^m_\Lambda(\mathbf{r}))\) and consider the map \(\gamma \mapsto \eta_\Lambda(\mathbf{r})\). Notice that the set \(\{\gamma > \gamma^\Lambda_\ast(\alpha)\}\) is open. Since \(\gamma \mapsto \psi_\Lambda'(\gamma)\) is monotonic increasing, each solution \(\eta_\Lambda\) of (8) is a supersolution for (8) with \(\gamma \mapsto \gamma^\Lambda_\ast(\alpha)\). This implies that the branch \(\gamma \mapsto \eta_\Lambda(\mathbf{r})\) of the globally stable hard-sphere fluid maximizers of \(P_{\alpha,\gamma}^\Lambda\) which are bigger than \(\eta^m_\Lambda(\mathbf{r})\), is pointwise monotonic increasing in \(\gamma\). We conclude that the following limit exists pointwise and strongly in \(C^0_\Phi(\Lambda) \cap \overline{B_{\eta^m_\Lambda}}\),

\[
\lim_{\gamma \downarrow \gamma^\Lambda_\ast(\alpha)} \eta_\Lambda =: \eta^\Lambda_{GC},
\]  

(115)

\(^7\)Once again, the restriction \(\eta^m_\Lambda(\mathbf{r}) < \overline{\eta}\) is vital; without it, the domain of definition of \(\alpha \mapsto \gamma^\Lambda_\ast(\alpha)\) can be extended to all \(\alpha \in \mathbb{R}_+\) but then this map is not continuous.
The strong $C^0$ continuity of $\eta \mapsto \varphi'_\alpha(\gamma - (\alpha V \ast \eta)_\Lambda)$ implies that $\eta_{\Lambda, \ell}^{GC}$ also solves (8). By the continuity of $\gamma \mapsto P_\Lambda(\alpha, \gamma)$ it follows that $\eta_{\Lambda, \ell}^{GC}$ is also a global maximizer of $P_{a, \gamma}^\Lambda$. This proves that at $(\alpha, \gamma_{\Lambda}(\alpha))$ the global maximizers of $P_{a, \gamma}^\Lambda$ is not unique, interpreted as a first order phase transition in the sense of mathematical coexistence of two distinct global maximizers of $P_{a, \gamma}^\Lambda$, not to be confused with the physical coexistence of two locally pure phases, separated by an interface, described by a single solution.

It remains to prove that the phase transition is of first order also in the sense of Ehrenfest. In Ref. [33] we showed that for fixed $\Lambda$, the map $(\alpha, \gamma) \mapsto P_{a, \gamma}^\Lambda$, defined in (10), is the limit of a family of functions which are convex in $\alpha$ and $\gamma$, and so itself (bi-)convex in $(\alpha, \gamma)$, thus continuous and almost everywhere differentiable in both variables. We now show that at $(\alpha, \gamma_{\Lambda}(\alpha))$ generally there is a kink in both, $\alpha \mapsto P_{a, \gamma}^\Lambda(\alpha)$ and $\gamma \mapsto P_{a, \gamma}^\Lambda(\alpha)$; we ignore the exceptional case $\gamma_{\Lambda}(\alpha) = c$. In that case by the bi-convexity of $(\alpha, \gamma) \mapsto P_{a, \gamma}^\Lambda$ both partial derivatives jump up when crossing the grand canonical phase transition curve from smaller to larger $\alpha$ or $\gamma$ values.

By repeating almost verbatim the arguments used to prove that $\gamma_{\Lambda}(\alpha) = \gamma_{\Lambda}^a(\alpha)$, one proves that the $\gamma$-derivative of $P_{a, \gamma}^\Lambda(\alpha, \gamma)$ jumps at $\gamma_{\Lambda}^a(\alpha)$. Now, since we ignore when $\gamma_{\Lambda}(\alpha) = constant$, locally there exists $\gamma \mapsto \alpha_{\Lambda}^a(\gamma)$, the inverse function of $\gamma_{\Lambda}(\alpha)$, and arguing almost verbatim again, but now using also that $V < 0$, for $\gamma$ suitably fixed we find that

$$\lim_{\alpha \downarrow \alpha_{\Lambda}^a(\gamma)} \eta_{\Lambda, \ell}^\Lambda = \eta_{\Lambda, \ell}^{GC};$$

too. Moreover, away from bifurcation points of a solution branch $(\alpha, \gamma) \mapsto \eta_\Lambda$ of (8),

$$\partial_\alpha P_{a, \gamma}^\Lambda[\eta_\Lambda] = -\frac{1}{2} \int_{\Lambda} \int_{\Lambda} V(|r - \tilde{r}|) \eta_\Lambda(r) \eta_\Lambda(\tilde{r}) d^3 r d^3 \tilde{r}. \quad (117)$$

Incidentally, we can also re-express this derivative in terms of the functionals for the total number of particles (13) and total energy (14) of a density function $\eta$, viz.

$$\alpha \partial_\alpha P_{a, \gamma}^\Lambda[\eta_\Lambda] = \frac{3}{2} N_{\Lambda}[\eta_\Lambda] - E_{\alpha}^\Lambda[\eta_\Lambda],$$

but we will not use this rewriting. Now, since $(\alpha, \gamma_{\Lambda}(\alpha))$ is not a bifurcation point for the pointwise minimal solution, also the partial $\alpha$-derivative of $P_{a, \gamma}^\Lambda[\eta_\Lambda]$ exists at $(\alpha, \gamma_{\Lambda}(\alpha))$. Since at $(\alpha, \gamma_{\Lambda}(\alpha))$ a pointwise larger global maximizer of $P_{a, \gamma}^\Lambda[\eta]$ exists, too, which belongs to a solution branch which continues to carry the global maximizers for some right neighborhood of $(\alpha, \gamma_{\Lambda}(\alpha))$, it now follows from (117) together with $V < 0$ that also the $\alpha$-derivative of $P_{a, \gamma}^\Lambda(\alpha, \gamma)$ jumps. The transition is therefore of first order in the sense of Ehrenfest. □
The maximizer $\eta_{L_g}^{\text{GC}}$ is of pointwise minimal type $\eta_{L_g}^{\alpha}(r)$ and called the gas solution. The pointwise larger maximizer $\eta_{L_g}^{\text{GC}}$ we call the liquid solution (33), although our proof does not establish that $\eta_{L_g}^{\text{GC}}$ is quasi-uniform up to a boundary layer; numerically this is the case, though.

Theorem 6.1 and its proof do not establish that $\eta_{L_g}^{\text{GC}}$ is the pointwise largest hard-sphere fluid solution $\eta_{L_g}^{M}$; more generally it does not establish that $\eta_{L_g}^{M}$ is the global maximizer of $P_{\alpha,\gamma}[\eta]$ for $(\alpha, \gamma)$ satisfying (113) and $\Lambda$ sufficiently large. The proof only shows that under these conditions the global maximizer of $P_{\alpha,\gamma}[\eta]$ is a hard-sphere fluid solution which is larger than the pointwise minimal solution $\eta_{L_g}^{\alpha}$. While this necessarily implies that $\eta_{L_g}^{M}(r) > \eta_{L_g}^{\alpha}(r) \forall r \in \Lambda$ it does not even imply that $P_{\alpha,\gamma}[\eta_{L_g}^{M}] > P_{\alpha,\gamma}[\eta_{L_g}^{\alpha}]$. This result in turn holds in strict form and in more generality, as we show next.

**Proposition 6.2:** If $(\alpha, \gamma)$ lies in the $\omega(\alpha, \gamma) > 0$ subset of $\Theta_{\alpha,\gamma}^{\text{dis}}(\|V\|_{1})$ and $\Lambda$ is sufficiently large so that (112) holds, then $P_{\alpha,\gamma}[\eta_{L_g}^{M}] > P_{\alpha,\gamma}[\eta_{L_g}^{\alpha}]$. Thus $\eta_{L_g}^{M}(r) > \eta_{L_g}^{\alpha}(r) \forall r \in \Lambda$, and an unstable third hard-sphere fluid solution is sandwiched inbetween.

**Proof:** Pick any $(\alpha, \gamma)$ in the $\omega(\alpha, \gamma) > 0$ subset of $\Theta_{\alpha,\gamma}^{\text{dis}}(\|V\|_{1})$, and suppose $\Lambda$ is big enough so that (112) holds. Consider the iteration $\eta^{(n+1)} = \varphi'_{\alpha,\gamma}(\gamma - (\alpha V * \eta^{(n)}))_{\Lambda}$, starting from $\eta^{(0)} \equiv \eta_{L_g}^{M} < \eta_{L_g}^{\alpha}$. By Proposition 3.1 and 3.2 it iterates downward to the pointwise maximal solution $\eta_{L_g}^{M}$ in the truncated cone $C_{b,\text{vdW}}(\Lambda) \cap \overline{B}_{\text{vdW}}$. As remarked after Proposition 3.1, *a priori* the minimal and maximal solutions may coincide, but having proved (112), this cannot happen because the functional $P_{\alpha,\gamma}[\eta]$ increases along any monotone converging iteration sequence. Indeed, setting $\hat{\eta}^{(n)} \equiv \eta^{(n+1)} - \eta^{(n)}$ for the difference of any two subsequent iterates, and $[\eta]^{(n)} \equiv \eta^{(n+1)} + \eta^{(n)}/2$ for their arithmetical mean, if $\hat{\eta}^{(n)}(r) \neq 0 \forall r \in \Lambda$, then by the mean value theorem (applied to the $\varphi$ integral) and a binomial identity (applied to the $V$ double integral) we have

$$P_{\alpha,\gamma}[\eta^{(n+1)}] - P_{\alpha,\gamma}[\eta^{(n)}] = \int_{\Lambda} (\varphi'_{\alpha,\gamma}(\gamma^{(n)}(r)) - [\eta]^{(n)}(r))( - \alpha V * \eta^{(n)})_{\Lambda}(r) d^3r > 0,$$  \hspace{1cm} (118)

where $\gamma^{(n)}(r) = \gamma - (\alpha V * [\eta]^{(n)})_{\Lambda}(r)$ and $[\eta]^{(n)}(r)$ is a (bounded) continuous function which takes values between the smaller and the larger one of the two iterates $\eta^{(n)}(r)$ and $\eta^{(n+1)}(r)$; the inequality in (118) holds because $-V > 0$ and, for monotonic iterations, $\varphi'_{\alpha,\gamma}(\gamma^{(n)}(r)) - [\eta]^{(n)}(r)$ has the same overall sign as $\hat{\eta}^{(n)}(r)$. So, $P_{\alpha,\gamma}[\eta^{M}] > P_{\alpha,\gamma}[\eta^{\alpha}]$, which implies that $\eta_{L_g}^{M} \neq \eta_{L_g}^{\alpha}$, and therefore $\eta_{L_g}^{M}(r) > \eta_{L_g}^{\alpha}(r) \forall r \in \Lambda$. Thus we have established the existence of at least two distinct hard-sphere
fluid solutions in the $\varpi(\alpha, \gamma) > 0$ subset of $\Theta^\text{sk}((\|V\|_1)_1)$ when $\Lambda$ is big enough so that (112) holds.

Moreover, in this case, as limits of respective monotone iterations associated with the Gâteaux derivative of $P^\Lambda_{\alpha, \gamma}$ both the pointwise minimal solution $\eta^\alpha_\Lambda(r)$ and the pointwise maximal solution $\eta^\beta_\Lambda(r)$ are locally $\mathcal{P}$ stable, or at most $\mathcal{P}$ indifferent in exceptional cases. Save such exceptional cases the existence of a third, unstable (under iterations and in $\mathcal{P}$ sense) solution sandwiched between $\eta^\alpha_\Lambda(r)$ and $\eta^\beta_\Lambda(r)$ now follows, via the mountain pass lemma, from the local $\mathcal{P}$ stability of these two solutions and the strong $C^0_\text{b}(\Lambda)$ differentiability of the functional $P^\Lambda_{\alpha, \gamma}[\eta]$. 

Remark: Note that the assumptions in Proposition 6.2 do not imply that the global maximizer of $P^\Lambda_{\alpha, \gamma}$ is a hard-sphere fluid solution; for this we need to assume more, e.g. (113) as in the proof of Theorem 6.1. For the proof of Proposition 6.2 we therefore could not assume that $\eta^\alpha_\Lambda \neq \eta^\beta_\Lambda$, but instead had to (and did) prove it anew. 

Remark: Variants of Theorem 6.1 and Proposition 6.2 and their proofs hold with $\Theta^\text{sk}((\|V\|_1)_1)$ replaced by $\Theta^\text{sk}(\Phi_\Lambda)$ and $\mathcal{P}_{\alpha, \gamma}^\Lambda$ by $\mathcal{P}_{\alpha, \gamma}^{\alpha, \gamma}$, as well as $\mathcal{P}_{\alpha, \gamma}^\Lambda$ by $\mathcal{P}_{\alpha, \gamma}^{\alpha, \gamma}$. In that case the $L^1(\mathbb{R}^3)$ integrability of $V$ is not required so that we can even add $A_\Lambda V_N$ to $\alpha V$. If $V = V_N$, then (8) can have many more than three hard-sphere fluid solutions for the same $(\alpha, \gamma)$, cf. Ref. [51, 32], even though the algebraic fixed point problem (26) has at most three solutions, still. This shows that naïve inferences from the algebraic fixed point problem (26) onto the integral equation (8) are not to be drawn. 

Remark: Neither the proof of Theorem 6.1 nor the one of Proposition 6.2 imply that the pointwise maximal hard-sphere fluid solution of (8) is the global maximizer of $P^\Lambda_{\alpha, \gamma}$ when the pointwise minimal solution is not. If one could show, possibly by the index theorems of Ref. [4, 40], that in the no non-fluid solutions regime at most two locally stable hard-sphere fluid solutions exist, but otherwise arbitrarily many unstable hard-sphere fluid solutions, then the pointwise maximal solution is the global maximizer whenever the pointwise minimal solution is not, and vice versa. 

In the $(\alpha, \gamma)$ region where the pointwise minimal solutions of (8) are not globally $\mathcal{P}$ stable, by their local $\mathcal{P}$ stability they are $\mathcal{P}$ metastable. Such metastability regions usually terminate at a spinodal line, the location of which in $(\alpha, \gamma)$ space can be estimated. Namely, on the one hand we already know that a metastable $\eta^m_\Lambda < \eta_l$
exists for each \((\alpha, \gamma) \in \Theta^{\#}(\Phi_{\mathbb{R}^3}) \cap \{\varpi(\alpha, \gamma) > 0\}\) whenever \(\Lambda\) is sufficiently large. On the other hand, by our nonexistence result of any solution which would take only hard-sphere fluid values, we also know that neither \(\alpha\) nor \(\gamma\) can be arbitrarily big. Yet, for bounded \(\Lambda\) we can get a more subtle result, valid even if \(A_N V_N\) is added to \(\alpha V\).

**Proposition 6.3:** Let \(\alpha V = A_w V_w + A_V V_V + A_N V_N\), with \(A_w, A_V, \) and \(A_N\) non-negative, and let \(v_\Lambda > 0\) be the spectral radius of \(-\langle V * \cdot \rangle_\Lambda\) for \(\Lambda \subset \mathbb{R}^3\) bounded. Assume that

\[
\alpha v_\Lambda \geq \min_{\eta \in (0, 1)} g'_2(\eta) = g'_2(\eta) \approx 21.20.
\]

Let \(\overline{\eta}_\Lambda = \eta_\Lambda(\alpha v_\Lambda)\) denote the smallest solution to the equation

\[
\alpha v_\Lambda = g'_2(\eta),
\]

and set

\[
\hat{\gamma}(\alpha v_\Lambda) = g'_2(\overline{\eta}_\Lambda) - \alpha v_\Lambda \overline{\eta}_\Lambda.
\]

Let \(\eta(r) \leq \overline{\eta} \equiv g^{-1}_2(\gamma_1) \approx 0.130\) be a small fluid solution of (8). Then \(\gamma < \hat{\gamma}(\alpha v_\Lambda)\).

**Proof:** For any container \(\Lambda \subset \mathbb{R}^3\) with finite Lebesgue measure \(|\Lambda|\), each kernel \(\alpha V = A_w V_w + A_V V_V + A_N V_N\), with \(A_w, A_V, \) and \(A_N\) non-negative, is a Hilbert–Schmidt kernel (i.e. \(V \in L^2(\Lambda \times \Lambda)\)), and so the positive definite operator \(-\langle V * \cdot \rangle_\Lambda\) is a compact operator on \(L^2(\Lambda)\). By the Krein-Rutman theorem, the spectral radius \(v_\Lambda > 0\) of \(-\langle V * \cdot \rangle_\Lambda\) is the largest eigenvalue of \(-\langle V * \cdot \rangle_\Lambda\), its eigenspace non-degenerate, and the corresponding eigenfunction nonvanishing everywhere.

Now let \(\eta_\Lambda^m(r) \leq \overline{\eta}_\Lambda\) once again be the pointwise smallest solution of (8). Since r.h.s. (8) is acting as a strictly convex function on the truncated cone \(C_{b_+, \infty} \cap \overline{B}_{\overline{\eta}}\), we can apply Fujita’s strategy\[\text{[18]}\] as generalized by Amann.\[\text{[5]}\] Let \(\eta(r)\) be the eigenfunction of \(-\langle V * \cdot \rangle_\Lambda\) for \(v_\Lambda\), normalized as probability density function so that it integrates to 1. Let \(\langle \cdot \rangle\) be the averaging functional w.r.t. \(\xi\). Taking now the average of (8) with \(\langle \cdot \rangle\) and using Jensen’s inequality, we find

\[
\langle \eta_\Lambda^m \rangle > \phi'_2(\gamma + \alpha v_\Lambda \langle \eta_\Lambda^m \rangle),
\]

which cannot be satisfied if \(\gamma \geq \hat{\gamma}(\alpha v_\Lambda)\).

Proposition 6.3 implies the existence of a \(\gamma_\Lambda^*(\alpha) < \hat{\gamma}(\alpha v_\Lambda)\) such that

\[
\eta_\Lambda^m := \lim_{\gamma \uparrow \gamma_\Lambda^*(\alpha)} \eta_\Lambda^m|_{\alpha}.
\]
which exists and solves (8), satisfies the following alternative: either \( \| \eta^m_\Lambda \|_C^0(\Lambda) = \tau_i \), and then the constant-\( \alpha \) section of \((\alpha, \gamma) \mapsto \eta^m_\Lambda \) may continuously extend to \( \gamma > \gamma^*_\Lambda(\alpha) \), only then with \( \eta^m_\Lambda(\gamma) \not\leq \tau \) for some \( \gamma \in \Lambda \); or \( \| \eta^m_\Lambda \|_C^0(\Lambda) < \tau_i \), and then the constant-\( \alpha \) section of \((\alpha, \gamma) \mapsto \eta^m_\Lambda \) is discontinuous, i.e. left and right limits of the map \( \gamma \mapsto \eta^m_\Lambda|_\alpha \) at \( \gamma^*_\Lambda(\alpha) \) disagree. When the second alternative holds, the metastability region for the pointwise minimal gas-type solutions terminates at the curve \( \alpha \mapsto \gamma^*_\Lambda(\alpha) \), which in this case is the spinodal curve for supersaturated vapor.

The computation of the function \( \gamma^*_\Lambda(\alpha) \) seems generally possible only implicitly, through studying the family of pointwise minimal solutions \( \eta^m_\Lambda(\cdot) \). However, its upper bound \( \hat{\gamma}(\alpha v_\Lambda) \) can be easily computed when the spectral radius \( v_\Lambda \) is known. The latter can be computed to any desired degree of precision by monotone iteration.

**Lemma 6.4:** The spectral radius \( v_\Lambda \) of the positive operator \(-(V \ast \cdot)_\Lambda \) is given by

\[
\ln v_\Lambda = \lim_{n \to \infty} \frac{1}{n} \ln \| \xi^{(n)} \|_{L^2(\Lambda)}
\]  

(124)

where \( \xi^{(n+1)} = -(V \ast \xi^{(n)})_\Lambda \) with \( \xi^{(0)} \equiv 1 \). Moreover, it is bounded by

\[
- \langle (V \ast 1)_\Lambda \rangle \leq v_\Lambda < \| V(\cdot \cdot) \|_{L^1(\Lambda)}.
\]

(125)

**Proof of Lemma 6.4:** The identity (124) is just the formula for the largest Lyapunov exponent (= \( \ln v_\Lambda \)) of our linear iteration, viewed as a dynamical system. The lower bound in (125) is obtained from the Ritz type variational principle for \( v_\Lambda \) with the help of the trial function \( \xi(\cdot) \equiv |\Lambda|^{-1/2} \), the upper bound by applying the sharp Young inequality\(^{36}\) to this variational principle.

**Remark:** Since the evaluation of (124) or (125) in Lemma 6.4 may only be feasible numerically for general \( \Lambda \), the following weaker estimates are of interest, too:

\[
\| V(\cdot \cdot) \|_{L^1(\Lambda)} \leq \| V \ast 1 \|_{C^0(\Lambda)} \leq \| V \ast 1 \|_{C^0(B_R)} \leq \| V \|_1,
\]

(126)

with \( |B_R| = |\Lambda| \). The first upper bound (= \( \Phi_\Lambda \)) is elementary. The second upper bound (= \( \| V(\cdot \cdot) \|_{L^1(B_R)} \)) follows from a simple radial rearrangement inequality; this bound is explicitly evaluated in Appendix A. The third upper bound is again elementary but nontrivial only if \( A_N = 0 \). In that case, when \( \Lambda \not\supset \mathbb{R}^3 \) in the sense of Fisher\(^{17}\), then both the lower bound and upper bound in (125) converge.
to \( \|V\|_1 = (A_0 \pi^2/4 \kappa^3 + A_4 \pi/\kappa^2)/\alpha \), which therefore is the \( \Lambda \nearrow \mathbb{R}^3 \) limit of the spectral radius.

We end this subsection with the observation that in the (at least) triclinity region of hard-sphere fluid solutions of (8) where the pointwise smallest solutions \( \eta^m_\Lambda(\mathbf{r}) \) are globally \( \mathcal{P} \) stable, the locally \( \mathcal{P} \) stable pointwise maximal solutions \( \eta^M_\Lambda(\mathbf{r}) \) are \( \mathcal{P} \) metastable. Clearly, the extent of this region has a lower \( \gamma \) bound because of Corollary 4.5, and a lower \( \alpha \) bound because of Corollary 4.3. Moreover, since we imposed the sufficient condition (35) for all solutions to be fluid, we also have an upper bound on \( \alpha \) given by \( \alpha \|V\|_1 < 28.9 \) (approximately); indeed, if this bound is violated by \( \alpha \), then for no choice of \( \gamma \) satisfying (35) (with \( \|V\|_1 \) in place of \( \Phi_\Lambda \)) is \( (\alpha, \gamma) \in \Theta^{\text{loc}}_\Lambda(\|V\|_1) \). Recall that this bound can be improved when better control over the solid branch of \( \gamma \mapsto \mathfrak{p}_\bullet(\gamma) \) becomes available. The accurate determination of the boundary of this metastability region is generally feasible only indirectly through numerical solution of the problem. Numerical solution\(^{33}\) reveals that in this metastability region the fluid assumes the shape of a giant liquid drop barely separated from the container walls by a thin layer of vapor. This metastability boundary is a spinodal curve which represents the smallest giant liquid drop which can be contained in \( \Lambda \) given \( (\alpha, \gamma) \).

7 \( \mathcal{F} \) STABILITY AND THE VAPOR ↔ DROP PHASE TRANSITION

In this section we discuss the thermodynamic stability of our non-uniform hard-sphere fluid solutions in bounded containers for the thermodynamic contact condition “heat reservoir,” i.e. what we called \( \mathcal{F} \) stability.

Substituting the Carnahan–Starling approximation \( p_\bullet(\eta) = (g_1^{-1} \circ g_2)(\eta) \) into the entropy functional (15), one can carry out the \( \eta \) integration to obtain

\[
\mathcal{S}_\bullet^\Lambda[\eta] = \frac{11}{2} \mathcal{N}_\Lambda[\eta] - \int_{\Lambda} \eta(\mathbf{r}) \left[ \ln \eta(\mathbf{r}) + \frac{3}{(1 - \eta(\mathbf{r}))^2} \right] d^3r,
\]  

so for a hard-sphere fluid we have, within the Carnahan–Starling approximation,

\[
\mathcal{F}_\alpha^\Lambda[\eta] = \mathcal{E}_\alpha^\Lambda[\eta] - \mathcal{S}_\bullet^\Lambda[\eta].
\]  

In the following, when we speak of a hard-sphere fluid density function \( \eta(\mathbf{r}) \) as being globally or locally \( \mathcal{F} \) stable, we mean a global or local minimizer of (128) under the
constraint
\[ N^\Lambda[\eta] = N. \] (129)

**Proposition 7.1:** Any hard-sphere fluid density function \( \eta(r) \) which is locally or globally \( F \)-stable under the constraint (129) is a solution \( \eta^\Lambda(r) \) of (8) for the same \( \alpha \) but with \( \gamma \) determined by the constraint (129). Any globally (locally) \( P \)-stable solution of (8) is also globally (locally) \( F \)-stable.

**Proof of Proposition 7.1:** Since the free energy functional (128) is strongly \( C_0^b(\Lambda) \) differentiable and coercive, its local and global minimizers satisfy the Euler–Lagrange equation for (128) under the constraint (129). When this constraint is taken into account in the usual manner with the help of a Lagrange multiplier \( \gamma \), viz. the “null functional” \( N^\Lambda[\eta] - N \) is multiplied by \( \gamma \) and then subtracted from \( F^\Lambda_\alpha[\eta] \) and \( \eta \) then varied unconditionally, a straightforward calculation gives the Euler–Lagrange equation
\[- \gamma + (\alpha V \ast \eta)^\Lambda + g_2(\eta) = 0, \] (130)
which is precisely our (8) with the Carnahan–Starling approximation for the hard-sphere fluid equation of state. So the local and global minimizers of (128) under the constraint (129) are among the solutions of (8), with \( \gamma \) determined by (129).

As for the global \( F \)-stability, we note that the maximum \( P^\Lambda_\alpha(\alpha, \gamma) \) of the pressure functional \( P^\Lambda_\alpha,\gamma[\eta] \) is also given by the Legendre–Fenchel transform (15) (sending \( N \to \gamma \))
\[ P^\Lambda_\alpha(\alpha, \gamma) = \sup_N \left\{ \gamma N - F^\Lambda_\alpha(\alpha, N) \right\}, \] (131)
which, upon recalling the definition of \( F^\Lambda_\alpha(\alpha, N) \), can be rephrased as the variational principle
\[ P^\Lambda_\alpha(\alpha, \gamma) = \sup_\eta \left\{ \gamma N^\Lambda[\eta] - F^\Lambda_\alpha[\eta] \right\}. \] (132)

Since \( P^\Lambda_\alpha(\alpha, \gamma) \) is given by the variational principle (10), which defines the globally \( P \)-stable solutions \( \eta^{GC}_\Lambda \) of (8), it follows that each \( \eta^{GC}_\Lambda \) also saturates the variational principle (132) — for suppose to the contrary that \( \gamma N^\Lambda[\eta^{GC}_\Lambda] - F^\Lambda_\alpha[\eta^{GC}_\Lambda] < P^\Lambda_\alpha(\alpha, \gamma) \), then \( \gamma N^\Lambda[\eta^{GC}_\Lambda] - F^\Lambda_\alpha[\eta^{GC}_\Lambda] < P^\Lambda_{\alpha,\gamma}[\eta^{GC}_\Lambda] \), which we show to be impossible. Indeed, after some straightforward manipulations of (16), given by the difference of (14) and (15), using only (8) in its reverse form (130), and recalling (9), one finds that
\[ \gamma N^\Lambda[\eta_\Lambda] - F^\Lambda_\alpha[\eta_\Lambda] = P^\Lambda_{\alpha,\gamma}[\eta_\Lambda] \] (133)
for any solution $\eta_\Lambda$ of (8), not just those which are globally $\mathcal{P}$ stable. So each globally $\mathcal{P}$ stable $\eta^{GC}_\Lambda$ also saturates the variational principle (131). But then each $\eta^{GC}_\Lambda$ also saturates the variational principle for global $\mathcal{F}$ stability, with $N = \mathcal{N}_\Lambda[\eta^{GC}_\Lambda]$.

A variation on the theme of this global stability proof gives the local $\mathcal{F}$ stability of locally $\mathcal{P}$ stable solutions $\eta_\Lambda$. The proof again uses the identity (133), valid for any solution $\eta_\Lambda$ of (8), but replaces $P_\Lambda(\alpha, \gamma)$ in (131) by $P_{\alpha, \gamma}[\eta_\Lambda]$ and the variation in the global Legendre–Fenchel transform (131) by a restriction to a neighborhood of $\eta_\Lambda$.

**Remark:** Incidentally, (131) guarantees that $P_\Lambda(\alpha, \gamma)$ is convex in $\gamma$. 

**Remark:** The infimum of $\mathcal{F}_\Lambda[\eta]$ under the constraint $N = \mathcal{N}_\Lambda[\eta]$ is generally not given by the Legendre–Fenchel transform of $P_{\alpha, \gamma}[\eta]$ (sending $\gamma \to N$). Put differently, $P_{\alpha, \gamma}[\eta]$ and $\mathcal{F}_\Lambda[\eta]$ are generally not convex duals of each other. As a spin-off of this, the reversal of the stability conclusion in Proposition 7.1 is not allowed; i.e., not all globally (locally) $\mathcal{F}$ stable solutions of (8) are also globally (locally) $\mathcal{P}$ stable. 

**Remark:** When $V \in L^1(\mathbb{R}^3)$ we can take the infinite volume limit. The Legendre–Fenchel type variational principle (132) then becomes the thermodynamic variational principle

$$\pi_{\star}(\alpha, \gamma) = \sup_{\eta \in C_b^0(\mathbb{R}^3)} \left\{ \gamma \langle \eta \rangle_{\mathbb{R}^3} - f_\alpha[\eta] \right\},$$

where, for each $\eta \in C_b^0(\mathbb{R}^3)$,

$$\langle \eta \rangle_{\mathbb{R}^3} := \lim_{\Lambda \uparrow \mathbb{R}^3} |\Lambda|^{-1} \mathcal{N}_\Lambda[\eta],$$

$$f_\alpha[\eta] := \lim_{\Lambda \uparrow \mathbb{R}^3} |\Lambda|^{-1} \mathcal{F}_\alpha[\eta].$$

For spatially uniform density functions $\eta(\mathbf{r}) \equiv \bar{\eta}$, the functional (136) for the free-energy density : temperature ratio of $\eta$ takes the simple van der Waals form

$$f_\alpha[\bar{\eta}] = \bar{\eta} g_4(\bar{\eta}) - g_1(\bar{\eta}) - \frac{1}{2} \alpha \|V\|_1 \bar{\eta}^2,$$

here with the local hard-sphere thermodynamics treated in the Carnahan–Starling approximation. Note that the infimum of (136) under the constraint $\langle \eta \rangle_{\mathbb{R}^3} = \bar{\eta}$, denoted

$$f_{\star}(\alpha, \bar{\eta}) := \inf_{\eta \in C_b^0(\mathbb{R}^3)} \left\{ f_\alpha[\eta] \mid \langle \eta \rangle_{\mathbb{R}^3} = \bar{\eta} \right\},$$

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is generally not achieved by a constant function \( r \mapsto \eta \), but by a piecewise constant \( \eta_{\text{PC}}(r) \not\in C_0^1(\mathbb{R}^3) \) (PC for “petit canonical” coming in handy), and satisfies the van der Waals–Maxwell formula

\[
f_\star(\alpha, \eta) = CH\{f_\alpha[\eta]\}, \tag{139}
\]

where \( CH\{\cdot\} \) denotes the convex hull. This formula for the thermodynamic free energy density : temperature ratio can be rigorously obtained by taking a van der Waals (Kac) limit with infinitely far ranging, infinitely weak pair interactions after the thermodynamic (infinite volume) limit \([17, 18, 49]\) has been taken, see Ref. \([27]\) for one-dimensional, Ref. \([35]\) for three-dimensional systems, both with Kac interactions, and see Refs. \([19, 20]\) for larger classes of interactions. Formula (139) means that in the thermodynamic limit the van der Waals free energy density : temperature ratio is itself a Legendre transform, namely the Legendre transform w.r.t. \( \gamma \) of the convex function \( \gamma \mapsto \pi(\alpha, \gamma) \). This example of equivalence of ensembles at the level of the thermodynamic functions free energy and pressure is generally false for the finite volume functionals, as noted in the previous remark. For certain types of \( V \) non-equivalence of ensembles in van der Waals-type theory occurs even in a coupled limit of infinite volume and infinitely far ranging, infinitely weak pair interactions.\([19]\)

\[\square\]

In our numerical investigations\([33]\) of the canonical non-uniform van der Waals theory for \( V = V_w \) and \( \Lambda \) a ball of radius \( 50\kappa^{-1} \) we found \( \mathcal{F} \) stable liquid drops surrounded by a vapor atmosphere when \( \alpha \| V \|_1 \approx 31.2 \). Note that for this \( \alpha \| V \|_1 \) value the sufficient no-non-fluid solutions condition \( \gamma + \alpha \| V \|_1 \gamma_{\text{fs}} \leq \gamma_{\text{fs}} \) is violated for the relevant \( \gamma \) values used to compute hard-sphere fluid solutions, yet solid solutions can nevertheless be ruled out with our more refined knowledge of the solid branch. We remark that the droplet solutions that we found were all situated in the \((\alpha, N)\)-region where \( F_\Lambda(\alpha, N) \) displays the “wrong” convexity which is “jumped over” by the grand canonical phase transition.

Interestingly enough, our numerical studies\([33, 32, 51]\) revealed that the change from quasi-uniform vapor state to droplet state in the canonical ensemble is not gradual but involves another first-order phase transition which is embedded in the \((\alpha, N)\)-region “jumped” by the grand canonical phase transition; see also Refs. \([32, 51]\). While a complete analytical proof of all the interesting details revealed by our numerical studies seems futile, our next theorem does assert the existence of a petit canonical first-order transition between a quasi-uniform vaporous and a strongly non-
uniform free energy minimizer with same \((\alpha, N)\). It generalizes our proof\[20\] from regularized Newtonian interactions and simpler equation of state of the perfect gas to the hard-sphere equation of state and interactions which include the shorter range van der Waals and Yukawa interactions. To state our theorem, we recall that for \((\alpha, \gamma) = (\alpha, \gamma_{\ell}^{\Lambda}(\alpha))\) the functional \(P_{\alpha,\gamma}^{\Lambda}[\eta]\) has two global maximizers in the hard-sphere fluid regime, the gas solution \(\eta^{GC}_{\Lambda,\gamma}(r)\) of the pointwise minimal type \(\eta^{m}_{\Lambda}(r)\) and the liquid solution \(\eta^{GC}_{\Lambda,\gamma}(r) > \eta^{GC}_{\Lambda,\gamma}(r)\).

**Theorem 7.2:** Let \(\Lambda\) be a convex container of macroscopic proportions, i.e. \(\cap(\Lambda) \gg 1\) and \(\cap(\Lambda)/|\Lambda|^{1/3} = O(1)\), such that a ball domain \(B\) of volume \(|B| = |\Lambda|/8\) is a strict subset of \(\Lambda\). Let \(V \in L^{1}(\mathbb{R}^{3})\) and let \(\alpha \|V\|_{1} \in (31-\epsilon, 31+\epsilon)\). Then \(\alpha\) is in the domain of the map \(\alpha \mapsto \gamma = \gamma_{\ell}^{\Lambda}(\alpha)\), the grand canonical gas vs. liquid phase transition curve, and there exists an \(N_{\Lambda,\gamma}^{m}(\alpha) \in [N_{\Lambda,\gamma}^{GC}(\eta^{GC}_{\Lambda,\gamma}), N_{\Lambda,\gamma}^{GC}]\) for which two distinct solutions of \(8\) minimize \(F_{\Lambda}[\eta]\) globally under the constraint \(N_{\Lambda}[\eta] = N_{\Lambda,\gamma}^{m}(\alpha)\). The transition between the global \(F\) minimizers is of first order in the sense of Ehrenfest, i.e. the partial derivatives of \((\alpha, N) \mapsto F_{\Lambda}(\alpha, N)\) jump at the canonical phase transition curve \(\alpha \mapsto N_{\Lambda,\gamma}^{m}(\alpha)\), provided the radial symmetric decreasing rearrangements of the two \(F\) minimizers intersect at a single level value.

**Remark:** One of the two global \(F\) minimizers is of the pointwise minimal (given \(\alpha, \gamma\)) type \(\eta^{m}_{\Lambda}(r)\) and represents the supersaturated vapor phase. Our proof will suggest that the other one is very likely of droplet type, having a high density (liquid) core surrounded by a low density (vapor) atmosphere, but our proof does not conclusively establish the existence of such a solution type for \(8\). Numerically\[33\] such solutions do exist, and they do intersect the equal-\(N\) vapor solution at a single level value. □

**Remark:** The global \(F\) minimizer representing a supersaturated vapor phase is \(P\) metastable. The global \(F\) minimizer representing a liquid drop surrounded by a vapor atmosphere is \(P\) unstable. □

**Remark:** A compromise between taking the infinite volume limit \(\Lambda \to \mathbb{R}^{3}\) (in the sense of, e.g., Fisher) and to work in a strictly finite domain is to work in \(\mathbb{R}^{3}\) but with the restriction that all densities are periodic w.r.t. to the 3-torus \(T^{3} = \mathbb{R}^{3}/\mathbb{Z}^{3}\). The canonical non-uniform van der Waals theory in \(T^{3}\) was studied most recently in Ref.\[10\]. For strictly finite-range pair interactions and the equation of state of the lattice gas model, they proved the existence of minimizers of the so-called Gates-Lebowitz-Penrose free-energy functional which, when restricted to a single fundamental cell, look like a liquid drop surrounded by a vapor atmosphere in a finite container \(\Lambda\). □
Proof of Theorem 7.2: For our proof we apply the strategy of Ref. [29] where a canonical phase transition of the type as stated in Theorem 7.2 is proved for $V$ given by a class of regularizations of $V_\alpha$ and $\varphi$ given by the perfect gas law — except for the Ehrenfest part concerning the $\alpha$ derivative of $F_\alpha(\alpha, N)$, for which we follow Ref. [30]. We note though that the more rapid decay of $V_\alpha(r)$ and $V_\gamma(r)$ with $r$ and the more complicated local thermodynamics require much more delicate estimates in the current proof. In particular, the condition of Proposition 3.3 for the absence of not-all-fluid solutions is too restrictive now, so that our full knowledge of the solid branch $\varphi_\bullet(\gamma)$ will be brought in. With that we now begin our proof.

First, by evaluating the algebraic van der Waals problem for our hard-sphere fluid one easily verifies that when $\alpha \|V\|_1 \approx 31$ and $\Lambda$ is large, then $\alpha$ is in the domain of $\gamma_\alpha^\Lambda(\alpha)$, the grand canonical gas vs. liquid phase transition curve described in Theorem 6.1. Just draw a family of straight parallel lines with slope $\approx \gamma$ the second figure and note that the whole fluid triplicity $\gamma$-interval for this $\alpha$ value can be covered without intersecting the solid branch. Note that the condition of Proposition 3.3 for the absence of not-all-fluid solutions is violated, though.

Moreover, since the two $\mathcal{P}$ maximizers along the grand canonical phase transition curve are pointwise ordered, $\eta^\text{GC}_\alpha(r) < \eta^\text{GC}_{\alpha,r}(r) \forall r \in \Lambda$, we conclude that $\mathcal{N}_\Lambda[\eta^\text{GC}_\alpha] < \mathcal{N}_\Lambda[\eta^\text{GC}_{\alpha,r}]$ so that the half-open $N$-interval stated in Theorem 7.2 is not empty.

We next recall Proposition 7.1, according to which any globally $\mathcal{P}$ stable solution of (8) is also globally $\mathcal{F}$ stable. So in particular $\eta^\text{GC}_{\alpha,r} \equiv \eta^\text{GC}_\alpha$ is a global minimizer of $\mathcal{F}_\alpha[\eta]$ under the constraint $N = N^\Lambda[\eta^\text{GC}_\alpha]$. This global $\mathcal{F}$ minimizer $\eta^\text{GC}_\alpha \equiv \eta^\text{GC}_{\alpha,r}$ is of the pointwise minimal (given $\alpha, \gamma$) type $\eta^\text{m}_\alpha(r)$ and situated on a fixed $\alpha$-section of the solution branch $(\alpha, N) \mapsto \eta^\text{m}_\alpha(r)$ of quasi-uniform small solutions ($< \eta_\alpha^m$), given in terms of the invertible parameter representation $\gamma \mapsto \eta^\text{m}_\alpha(r)$ and $\gamma \mapsto N = N^\Lambda[\eta^\text{m}_\alpha]$ for each $\alpha$. This representation is well-defined because for fixed $\alpha$ the map $\gamma \mapsto \eta^\text{m}_\alpha(r)$ is pointwise increasing and (by the implicit function theorem) continuous (even continuously differentiable) in the half-open $\gamma$ interval $(-\infty, \hat{\gamma}_\bullet(\alpha \|V\|_1)]$ containing $\gamma^\Lambda_\alpha(\alpha)$, where $\hat{\gamma}_\bullet(\alpha \|V\|_1)$ is the right limit (7.4) of the van der Waals triplicity region $\Theta^\text{ala}_{\bullet}(\|V\|_1)$ of the hard-shell fluid (recall our Propositions 3.1 and 3.4). This $\gamma$ interval maps into the $N$ interval $(0, \hat{N}(\alpha)]$, where $\hat{N}(\alpha) := N^\Lambda[\hat{\eta}^\alpha_\Lambda]$ and $\hat{\eta}^\alpha_\Lambda$ is the pointwise minimal solution of (8) for $\gamma = \hat{\gamma}_\bullet(\alpha \|V\|_1)$. Note that $\mathcal{N}_\Lambda[\eta^\text{GC}_{\alpha,r}] < \hat{N}(\alpha)$, by Theorem 6.1. Moreover, since by Theorem 6.1 for each $\alpha$ in the domain of $\gamma^\Lambda_\alpha$, the map $\gamma \mapsto \eta^\text{m}_\alpha(r)$ furnishes the unique globally $\mathcal{P}$ stable solution $\eta^\text{GC}_\alpha(r)$ for each $\gamma < \gamma^\Lambda_\alpha(\alpha)$, by Proposition 7.1 for each admissible $\alpha$ as stated in Theorem
7.2 the map $N \mapsto \eta^\alpha_n(r)$ then furnishes a globally $\mathcal{F}$ stable solution $\eta^\text{sc}_\alpha(r)$ for each $N \in (0, \mathcal{N}^\alpha[\eta_{\alpha,g}^\text{sc}])$, with $\eta^\text{sc}_\alpha(r) \equiv \eta_{\alpha,g}^\text{sc}(r)$ at $N = \mathcal{N}^\alpha[\eta_{\alpha,g}^\text{sc}]$.

Furthermore, by the monotonicity of $\gamma \mapsto N = \mathcal{N}^\alpha[\eta^\alpha_n]$ and the pointwise minimality of $\eta^\alpha_n$ (for given $\alpha, \gamma$), and by its uniqueness as solution of (8) for $\gamma < \gamma_n(\alpha)$ (see Corollary 4.5), the fixed-$\alpha$ section of the branch of locally stable gas solutions $N \mapsto \eta^\alpha_n(r)$ furnishes the unique globally $\mathcal{F}$ stable solution for each $N < \mathcal{N}^\alpha[\eta^\alpha_n]$, where $\eta^\alpha_n$ is $\eta^\alpha_n(r)$ for $(\alpha, \gamma) = (\alpha, \gamma_n(\alpha))$. Now let $\mathcal{N}^\text{st}_\alpha(\alpha)$ be the supremum over $N \in (0, \hat{N}(\alpha))$ for which $N \mapsto \eta^\alpha_n(r)(< \overline{n})$ furnishes the unique globally $\mathcal{F}$ stable solution for each $N < \mathcal{N}^\text{st}_\alpha(\alpha)$. Clearly, $\mathcal{N}^\text{st}_\alpha(\alpha) \geq \mathcal{N}^\alpha[\eta^\alpha_n]$. We also define $\mathcal{N}^\text{st}_\alpha(\alpha)$ as the infimum over $N \in (0, \hat{N}(\alpha))$ for which $N \mapsto \eta^\alpha_n(r)(< \overline{n})$ is not globally $\mathcal{F}$ stable for each $N \in (\mathcal{N}^\text{st}_\alpha(\alpha), \mathcal{N}^\text{st}_\alpha(\alpha) + \epsilon)$ for some $\epsilon > 0$. Clearly, $\mathcal{N}^\text{st}_\alpha(\alpha) \geq \mathcal{N}^\text{st}_\alpha(\alpha)$. We show:

(a) $\mathcal{N}^\text{st}_\alpha(\alpha) = \mathcal{N}^\text{st}_\alpha(\alpha)$;
(b) $\mathcal{N}^\alpha[\eta_{\alpha,g}^\text{sc}] \leq \mathcal{N}^\text{st}_\alpha(\alpha) < \hat{N}(\alpha)$;
(c) at $\mathcal{N}^\text{st}_\alpha(\alpha)$ the global $\mathcal{F}$ minimizer is not unique.

To prove claim (a) suppose that $\mathcal{N}^\text{st}_\alpha(\alpha) > \mathcal{N}^\text{st}_\alpha(\alpha)$. Then from the definitions of $\mathcal{N}^\text{st}_\alpha(\alpha)$ and $\mathcal{N}^\text{st}_\alpha(\alpha)$ it follows that $N \mapsto \eta^\alpha_n(r)(< \overline{n})$ is globally $\mathcal{F}$ stable for all $N \in (\mathcal{N}^\text{st}_\alpha(\alpha), \mathcal{N}^\text{st}_\alpha(\alpha))$, but at least one other global $\mathcal{F}$ minimizer exists for each such $N$ (given $\alpha$). It suffices to assume that exactly one other global $\mathcal{F}$ minimizer $\eta^{\text{sc}}_\alpha$ exists for each such $N$ (given $\alpha$). But then these two minimizers of $\mathcal{F}^\alpha[\eta]$ not only have the same $\mathcal{F}^\alpha$ value for each such $N$, also the derivative of $N \mapsto \mathcal{F}^\alpha[\eta]$ is the same for both minimizers. Now it follows right away from (133) that along a constant-$\alpha$ section of a solution branch of (8) we have

$$\partial_N \mathcal{F}^\alpha[\eta] = \Gamma[\eta],$$

(140)

where $\Gamma[\eta_\alpha]$ is the $\gamma$-value for which $\eta_\alpha$ solves (8). So both hypothetical global $\mathcal{F}$ minimizers solve (8) for the same $(\alpha, \gamma) = (\alpha, \Gamma[\eta^\alpha_n])$, but since $\eta^\alpha_n$ is the pointwise minimal solution at $(\alpha, \gamma) = (\alpha, \Gamma[\eta^\alpha_n])$, it follows that $\mathcal{N}^\alpha[\eta^{\text{sc}}_\alpha] > \mathcal{N}^\alpha[\eta^\alpha_n]$, which contradicts the hypothesis that both density functions are global minimizers of $\mathcal{F}^\alpha[\eta]$ for the same $(\alpha, N)$. This proves that $\mathcal{N}^\text{st}_\alpha(\alpha) = \mathcal{N}^\text{st}_\alpha(\alpha)$; incidentally, the same type of argument also proves that $N \mapsto \eta^\alpha_n(r)(< \overline{n})$ is not globally $\mathcal{F}$ stable for $N > \mathcal{N}^\text{st}_\alpha(\alpha)$.

As for (b), to prove the first inequality we recall that by Proposition 7.1 and Theorem 6.1 we know that $\eta^\alpha_n$ is a global minimizer of $\mathcal{F}^\alpha$ for all $N \in (0, \mathcal{N}^\alpha[\eta_{\alpha,g}^\text{sc}])$. Now suppose that beside $\eta^\alpha_n$ there exists a second global minimizer of $\mathcal{F}^\alpha$ for some
\( N_* \) satisfying \( \mathcal{N}_\alpha^\Lambda[\eta_*^\Lambda] \leq N_* < \mathcal{N}_\alpha^\Lambda[\eta_{c\text{av}}^\Lambda] \). But then, by the proof of point (a), it follows that \( N \mapsto \eta_*^m(r)(< \tilde{\eta}_0) \) is not globally \( \mathcal{F} \) stable for each \( N > N_* \), which is a contradiction. This proves the first inequality in (b).

To prove the second inequality in (b) we show that for \( N = \tilde{N}(\alpha) \) a droplet type density function has lower free energy than the vapor type solution \( \hat{\eta}_\alpha^m \) which defines \( \tilde{N}(\alpha) \), and by continuity this will be so also for some left neighborhood of \( \tilde{N}(\alpha) \).

Since for each \( N \) we will only compare densities which all integrate to the given \( N \), we can ignore the \( \mathcal{N}_\alpha^\Lambda \) functionals in \( \mathcal{F}_\alpha^\Lambda \) and compare

\[
\mathcal{A}_\alpha^\Lambda[\eta] = \frac{1}{2} \int_{\Lambda} \int_{\Lambda} \alpha V(|r - \tilde{r}|) \eta(r) \eta(\tilde{r}) \, d^3r \, d^3\tilde{r} + \int_{\Lambda} \eta(r) \left[ \ln \eta(r) + \frac{3 - 2\eta(r)}{(1 - \eta(r))^2} \right] \, d^3r
\]

evaluated with \( \eta_*^m \) versus its evaluation with some droplet like density of the same \( N \).

First, let \( N = \tilde{N}(\alpha) \). Recalling the upper bound on the gas solutions \( \eta_*^m(r) \leq \tilde{\eta}_{c\text{av}}^m \) where the spatially uniform van der Waals solution is for the same \( \gamma \) as \( \eta_*^m \), we have in particular \( \hat{\eta}_\Lambda^m(r) \leq \tilde{\eta}_{c\text{av}}^m \). We apply this bound to the interaction integral, plus use the estimate \( \langle (V \star 1) \rangle_{\Lambda} > -\|V\|_1 \). We also apply Jensen’s inequality w.r.t. uniform spatial average to the (negative of the) entropy integral, noting the convexity of the map \( x \mapsto x \ln x + x(3-2x)/(1-x)^2 \), and use that \( \langle \eta_*^m \rangle_{\Lambda} = N/|\Lambda| \) for all \( N \in (0, \tilde{N}(\alpha)] \). This yields the lower bound on \( \mathcal{A}_\alpha^\Lambda[\hat{\eta}_\alpha^m] \) given by

\[
|\Lambda|^{-1} \mathcal{A}_\alpha^\Lambda[\hat{\eta}_\alpha^m] \geq -\frac{1}{2} \alpha \|V\|_1 \hat{\eta}_{c\text{av}}^m + \frac{N}{|\Lambda|} \left[ \ln \frac{N}{|\Lambda|} + \frac{3 - 2N/|\Lambda|}{(1 - N/|\Lambda|)^2} \right],
\]

where we wrote \( \tilde{N} \) for \( \tilde{N}(\alpha) \). Also \( \hat{\eta}_{c\text{av}}^m \) is a function of \( \alpha \), and by (101) and \( \langle \hat{\eta}_\alpha^m \rangle_{\Lambda} = \tilde{N}/|\Lambda| \) we have that

\[
\hat{\eta}_{c\text{av}}^m = \frac{\tilde{N}}{|\Lambda|} \left( 1 + O[\varnothing(\Lambda)^{-2/3}] \right),
\]

so that up to a correction of \( O[\varnothing(\Lambda)^{-2/3}] \), we can substitute \( \tilde{N}/|\Lambda| \) for \( \hat{\eta}_{c\text{av}}^m \), or the other way round. On the other hand, by inserting into \( \mathcal{A}_\alpha^\Lambda[\eta] \) a trial density of the type “liquid drop with vapor atmosphere” which integrates to \( \tilde{N} \), we get an upper bound on the minimum of the reduced free energy functional for \( \tilde{N} \), given \( \alpha \). It suffices to choose a spherically symmetric trial density without atmosphere,

\[
\hat{\eta}_\alpha(r) = \frac{\tilde{N}}{|\Omega|} \chi_B(r),
\]

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where $B \subset \Lambda$ is a ball whose volume is determined by setting $\hat{N}/|B| = \hat{\eta}^M_{\text{vdW}}$, the pointwise largest van der Waals solution at $\hat{\gamma}(\alpha \| V \|_1)$. This yields the upper bound

$$|\Lambda|^{-1} \inf_{\eta} \mathcal{A}_{\alpha}^i[\eta] \leq |\Lambda|^{-1} \mathcal{A}_{\alpha}^i[\hat{\eta}_M]$$

$$= \frac{1}{\pi} \alpha \langle (V \ast 1)_{B} \rangle_{B} \frac{\hat{N}}{|B|} \frac{\hat{N}}{|\Lambda|} + \hat{N} \left( \ln \frac{\hat{N}}{|B|} + \frac{3-2\hat{N}/|B|}{(1-\hat{N}/|B|)} \right). \quad (145)$$

Subtracting (142) from (145) and using (see Appendix A.) that

$$\langle (V \ast 1)_{B} \rangle_{B} = - \| V \|_1 (1 - O[1/\Theta(B)]), \quad (146)$$

and anticipating that $|\Lambda|/|B| = O[1]$ so that we can neglect the $O[1/\Theta(B)]$ correction, we find that the upper bound (145) on the infimum of $\mathcal{A}$ is lower than the lower bound (142) on the free energy of the gas solution at $N = \hat{N}$ when

$$\alpha \| V \|_1 > 2 \frac{\ln \frac{|\Lambda|}{|B|} + \frac{3-2\hat{N}/|B|}{(1-\hat{N}/|B|)}}{\frac{\hat{N}}{|B|} - \frac{\hat{N}}{|\Lambda|}}$$

$$= \frac{3-2\hat{N}/|B|}{(1-\hat{N}/|B|)}, \quad (147)$$

up to a correction of $O[\Theta(\Lambda)^{-2/3}]$. The criterion (147) can be re-expressed as

$$\alpha \| V \|_1 > 2 \frac{\ln \hat{\eta}^M_{\text{vdW}} + \frac{3-2\hat{\eta}^M_{\text{vdW}}}{(1-\hat{\eta}^M_{\text{vdW}})}}{\hat{\eta}^M_{\text{vdW}} - \hat{\eta}^M_{\text{vdW}}}$$

$$= \frac{3-2\hat{\eta}^m_{\text{vdW}}}{(1-\hat{\eta}^m_{\text{vdW}})}, \quad (148)$$

up to a correction of $O[\Theta(\Lambda)^{-2/3}]$. Now, for $\alpha \| V \|_1 = 31$ as stipulated in Theorem 7.2, the ratio $\hat{\eta}^M_{\text{vdW}} : \hat{\eta}^m_{\text{vdW}} \approx 9$, with $\hat{\eta}^M_{\text{vdW}} \approx 0.41$ and $\hat{\eta}^m_{\text{vdW}} \approx 0.045$. These values yield r.h.s. (148) $\approx 28.75 < 31$, and also $|\Lambda|/|B| \approx 9 > 8$ so that $B$ fits into $\Lambda$, satisfying the hypothesis of Theorem 7.2. This proves that the droplet-type density function has a lower free-energy : temperature ratio than the quasi-uniform vaporous solution of the same $\hat{N} = \hat{N}(\alpha)$ for $\alpha \| V \|_1 = 31$. By continuity the regime where droplet type densities have lower free-energy : temperature ratio than the quasi-uniform solutions extends to an open neighborhood of the chosen $\alpha$ for the corresponding $\hat{N}(\alpha)$.

Second, by continuity again, the same conclusion also extends to some open left neighborhood of $\hat{N}(\alpha)$ for each such $\alpha$ in the neighborhood of the chosen $\alpha \| V \|_1 = 31$. This completes the proof of claim (b).

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Continuity and closedness arguments for the solution curves prove claim (c) in a similar fashion of reasoning as used in the proof of Theorem 6.1. Here we also use Proposition 7.1, according to which the solution \( \eta^m \) is also locally \( \mathcal{F} \) stable for each \( \alpha \) and \( N \) in the domain of the map \( N \mapsto \eta^m \) because the pointwise minimal (given \( (\alpha, \gamma) \)) solutions \( \eta^m \) are locally \( \mathcal{P} \) stable (we ignore the exceptional cases when \( \eta^m \) is locally \( \mathcal{P} \) indifferent). By its local \( \mathcal{F} \) stability, no bifurcation off of this gas branch occurs for \( N < \hat{N}(\alpha) \), in particular not for \( N = N^\Lambda[\eta^\Lambda_G] \) (\( < \hat{N}(\alpha) \)).

Henceforth we will write \( \eta^m \equiv \eta^\Lambda_{\Lambda,v} \) for the quasi-uniform, vaporous \( \mathcal{F} \) minimizer, and \( \eta \equiv \eta^\Lambda_{\Lambda,d} \) for the non-quasi-uniform minimizer of (presumed) droplet type; we say “presumed” for, strictly speaking we haven’t shown that it is a droplet, although our above proof and the numerical evidence\[33\] suggests it is. We remark that even though in our proof we worked with a trial droplet without atmosphere, any droplet type minimizer of \( \mathcal{F}^\Lambda_{\alpha}[\eta] \) must solve (8) and therefore must have a low-density atmosphere, as r.h.s.\[8\] is bounded away from 0.

Finally, we show that the canonical vapor versus droplet transition is of first order in the sense of Ehrenfest, for which we need the hypothesiz ed, yet empirically suggested, level intersection property.

First, in our proof of point (a) above we showed that the constant-\( \alpha \) derivatives of \( N \mapsto \mathcal{F}^\Lambda_{\alpha}[\eta] \) at \( N = N_{vd}(\alpha) \) cannot be the same for the quasi-uniform minimizer \( \eta^\Lambda_{\Lambda,v} \) and for the non-quasi-uniform minimizer \( \eta^\Lambda_{\Lambda,d} \). So our proof of point (a) above already proves that the constant-\( \alpha \) derivative of \( N \mapsto \mathcal{F}^\Lambda_{\alpha}(\alpha, N) \) is discontinuous at \( N = N_{vd}(\alpha) \). In fact, the constant-\( \alpha \) derivative of \( N \mapsto \mathcal{F}^\Lambda_{\alpha}(\alpha, N) \) jumps down when \( N \) increases. This follows from (140) and the monotonicity properties of the pointwise minimal solution branch of (8). For suppose that \( \Gamma[\eta^\Lambda_{\Lambda,d}] \geq \Gamma[\eta^\Lambda_{\Lambda,v}] \). Then, since \( \eta^\Lambda_{\Lambda,d} \neq \eta^m \), which denotes the pointwise minimal solution at \( (\alpha, \Gamma[\eta^\Lambda_{\Lambda,d}]) \), we have \( \mathcal{N}^\Lambda[\eta^\Lambda_{\Lambda,d}] > \mathcal{N}^\Lambda[\eta^m] \geq \mathcal{N}^\Lambda[\eta^\Lambda_{\Lambda,v}] \), which contradicts the fact that \( \mathcal{N}^\Lambda[\eta^\Lambda_{\Lambda,d}] = \mathcal{N}^\Lambda[\eta^\Lambda_{\Lambda,v}] \). Note that for this part of our proof of the Ehrenfest property we did not need to invoke that the two global \( \mathcal{F} \) minimizers intersect only at a single level value.

Next, to prove that the constant-\( N \) map \( \alpha \mapsto \mathcal{F}^\Lambda_{\alpha}[\eta] \) has a kink at \( \alpha_{vd}(N) \), where \( N \mapsto \alpha = \alpha_{vd}(N) \) is the local inverse function to the curve \( \alpha \mapsto N = N_{vd}(\alpha) \), and which exists locally unless the latter is constant, we adapt, and improve on, the strategy of Ref.\[30\]. First, being \( \mathcal{F} \) minimizers, the free-energy : temperature ratio is the same for the quasi-uniform minimizer \( \eta^\Lambda_{\Lambda,v} \) and for the non-quasi-uniform minimizer \( \eta^\Lambda_{\Lambda,d} \), i.e. \( \mathcal{F}^\Lambda_{\alpha}[\eta^\Lambda_{\Lambda,v}] = \mathcal{F}^\Lambda_{\alpha}[\eta^\Lambda_{\Lambda,d}] \). Recalling the identity \[133\] we see that this
implies the equality
\begin{equation}
N(\Gamma[\eta_{\Lambda,d}^\text{PC}] - \Gamma[\eta_{\Lambda,v}^\text{PC}]) = \mathcal{P}_{\alpha,\Gamma[\eta_{\Lambda,d}^\text{PC}]}[\eta_{\Lambda,d}^\text{PC}] - \mathcal{P}_{\alpha,\Gamma[\eta_{\Lambda,v}^\text{PC}]}[\eta_{\Lambda,v}^\text{PC}],
\end{equation}
(149)
where \(\Gamma[\eta_{\Lambda}]\) is the \(\gamma\)-value for which \(\eta_{\Lambda}\) is a solution of (8). Now suppose that, for given \(N\), the derivative of \(\alpha \mapsto \mathcal{F}_\alpha[\eta_{\Lambda}^\text{PC}]\) at \(\alpha = \alpha_{vd}(N)\) is the same for both minimizers. By the implicit function theorem these derivatives exist along the constant-\(N\) sections of the solution branches of (8); at \(\alpha = \alpha_{vd}(N)\) the derivative for \(\eta_{\Lambda,d}^\text{PC}\) may have to be read as right-derivative, though generically it will be a derivative. Using the variational principle for \(F_\Lambda(\alpha, N)\) and the definition of \(F_\Lambda[\eta]\) we obtain
\begin{equation}
\partial_\alpha \mathcal{F}_\alpha[\eta_{\Lambda}] = \frac{1}{2} \int_{\Lambda} \int V(|\mathbf{r} - \mathbf{\tilde{r}}|) \eta_{\Lambda}(\mathbf{r}) \eta_{\Lambda}(\mathbf{\tilde{r}}) d^3\mathbf{r} d^3\tilde{r}.
\end{equation}
(150)
Incidentally, for our \(V < 0\) (150) shows that \(\alpha \mapsto F_\Lambda(\alpha, N)\) is monotonic decreasing, but we won’t need that. By (150) we conclude that the hypothesized equality \(\partial_\alpha \mathcal{F}_\alpha[\eta_{\Lambda,d}^\text{PC}] = \partial_\alpha \mathcal{F}_\alpha[\eta_{\Lambda,v}^\text{PC}]\) for the two \(\mathcal{F}_\alpha\) minimizers at the same \((\alpha, N)\) implies that their potential energy : temperature ratios are the same, too. Inspection of the definition (9) of the pressure : temperature ratio functional of a density function \(\eta\) now reveals
\begin{equation}
\mathcal{P}_{\alpha,\gamma}[\eta_{\Lambda,d}^\text{PC}] - \mathcal{P}_{\alpha,\gamma}[\eta_{\Lambda,v}^\text{PC}] = \int_{\Lambda} \left[ p_{\bullet}(\eta_{\Lambda,d}^\text{PC}(\mathbf{r})) - p_{\bullet}(\eta_{\Lambda,v}^\text{PC}(\mathbf{r})) \right] d^3\mathbf{r},
\end{equation}
(151)
where \(p_{\bullet}(\eta) = g_{\eta}(\eta)\). By inserting (151) into (149) we obtain the equality
\begin{equation}
N(\Gamma[\eta_{\Lambda,d}^\text{PC}] - \Gamma[\eta_{\Lambda,v}^\text{PC}]) = \int_{\Lambda} \left[ p_{\bullet}(\eta_{\Lambda,d}^\text{PC}(\mathbf{r})) - p_{\bullet}(\eta_{\Lambda,v}^\text{PC}(\mathbf{r})) \right] d^3\mathbf{r}.
\end{equation}
(152)
Recall that at the end of the first part of the Ehrenfest proof, i.e. of the discontinuity of the constant-\(\alpha\) derivative of \(N \mapsto \mathcal{F}_\alpha[\eta_{\Lambda}^\text{PC}]\), we showed that the l.h.s. (152) < 0.

We now complete our proof that the constant-\(N\) derivative of \(\alpha \mapsto \mathcal{F}_\alpha[\eta_{\Lambda}^\text{PC}]\) is discontinuous at the canonical phase transition curve provided the radial symmetric

\footnote{This formula may cause some temporary consternation, for a thermodynamic free-energy : temperature ratio should satisfy the “thermodynamic relation” \(\partial_\alpha \mathcal{F}_\alpha[\eta_{\Lambda}] = \mathcal{E}_\alpha[\eta_{\Lambda}]\) along the globally \(\mathcal{F}\) stable solution branch of (8), with \(\mathcal{E}_\alpha[\eta_{\Lambda}]\) given in (13). This puzzle is resolved by noticing that in our strictly classical setup we have omitted even the minimal amount of quantum mechanics normally injected into classical statistical mechanics with the help of the de Broglie wavelength, as per “normalization” of the entropy and chemical potential; see our Appendix C.}
decreasing rearrangements of the two \( F \) minimizers intersect at only a single density value \( x \) by showing that r.h.s.\((152)\) \(\geq 0\) under this provision.

For any density function \( \eta(r) \in C^0_b(\Lambda) \), let \( ^*\eta(|r|) \) denote its radially symmetric decreasing equimeasurable rearrangement supported in the ball \( B \) of volume \( |B| = |\Lambda| \). Then, using that

\[
\int_{\Lambda} f(\eta(r)) d^3r = \int_{B} f(\eta(|r|)) d^3r
\]

for any continuous function \( f : \mathbb{R} \to \mathbb{R} \), and using the mean-value theorem (with \( \eta(|r|) \) sandwiched between the two \( F \) minimizers uniquely determined), and invoking the hypothesized level intersection property of the two minimizers, we find

\[
\int_{\Lambda} \left[ p_{*}(\eta_{\Lambda,d}^{PC}(r)) - p_{*}(\eta_{\Lambda,v}^{PC}(r)) \right] d^3r = \int_{B} \left[ p_{*}(\eta_{\Lambda,d}^{PC}(|r|)) - p_{*}(\eta_{\Lambda,v}^{PC}(|r|)) \right] d^3r
\]

\[
= \int_{B} p'_{*}(|r|) \left[ \eta_{\Lambda,d}^{PC}(|r|) - \eta_{\Lambda,v}^{PC}(|r|) \right] d^3r
\]

\[
\geq p'_{*}(x) \int_{B} \left[ \eta_{\Lambda,d}^{PC}(|r|) - \eta_{\Lambda,v}^{PC}(|r|) \right] d^3r
\]

\[
= 0,
\]

(154)

where the inequality is readily proved by estimating the penultimate integral separately on the positive and negative parts of its integrand. This already concludes the second part of the proof of the Ehrenfest property, but we supplement the result by showing that the constant-\( N \) derivative of \( \alpha \mapsto F_{\alpha}(\alpha, N) \) jumps down when \( \alpha \) increases.

Indeed, since for \( \alpha < \alpha_{vd}(N) \) the vaporous solution is the unique global \( F \) minimizer, suppose now that at \( \alpha = \alpha_{vd}(N) \) we have \( \partial_{\alpha} F_{\alpha}[\eta_{\Lambda,v}^{PC}] < \partial_{\alpha} F_{\alpha}[\eta_{\Lambda,d}^{PC}] \). But then by straightforward adaptation of our proof of the discontinuity of \( \partial_{\alpha} F_{\alpha}(\alpha, N) \) we now conclude that

\[
0 > N(\Gamma[\eta_{\Lambda,d}^{PC}] - \Gamma[\eta_{\Lambda,v}^{PC}]) = \mathcal{P}_\alpha^{\Lambda}[\eta_{\Lambda,d}^{PC}] - \mathcal{P}_\alpha^{\Lambda}[\eta_{\Lambda,v}^{PC}] > 0,
\]

(155)

and so the derivative \( \partial_{\alpha} F_{\alpha}(\alpha, N) \) must jump down at \( \alpha = \alpha_{vd}(N) \).

The proof of Theorem 7.2 is complete.

We end section VII with some comments regarding the proof of Theorem 7.2.
Remark: Since our proof of the Ehrenfest property relies on the provision of the level intersection property of the two global $\mathcal{F}$ minimizers, it seems prudent to have a backup strategy just in case the provision turns out not to hold for non-spherical containers; also for spherical containers it hasn’t been proven yet, although in that case there is numerical evidence in its favor. The following argument does not rely on the provision of Theorem 7.2, and could be completed with some sharper estimates.

Namely, we use that $\eta_{\Lambda,v}^{pc} < \overline{\eta}_t$ is the pointwise minimal solution for $(\alpha, \gamma) = (\alpha, \Gamma[\eta_{\Lambda,v}^{pc}])$, so that for the same $(\alpha, \gamma)$ we have the bound $\eta_{\Lambda,v}^{pc} \leq \overline{\eta}_{vaw}^{m}(< \overline{\eta}_t)$. Moreover, $\eta_{\Lambda,v}^{pc}$ is quasi-uniform in the sense that it is nearly constant except for a small boundary layer near $\partial \Lambda$, viz. (recalling (101))

$$\overline{\eta}_{vaw}^{m} - \langle \eta_{\Lambda,v}^{m} \rangle_{\Lambda} \leq O[\varnothing(\Lambda)^{-2/3}],$$

(156)

where $\langle \eta_{\Lambda,v}^{pc} \rangle_{\Lambda} = N/|\Lambda|$ is the uniform mean over $\Lambda$. Furthermore, since both $\mathcal{F}$ minimizers have equal “mass” $N$, we have the identity

$$\langle \eta_{\Lambda,v}^{pc} \rangle_{\Lambda} = \langle \eta_{\Lambda,d}^{pc} \rangle_{\Lambda}.\quad (157)$$

Since $x \mapsto p_{\bullet}(x)$ is a positive, increasing, convex function, dividing l.h.s. (154) by $|\Lambda|$ and applying Jensen’s inequality combined with these identities and estimates yields

$$\langle p_{\bullet}(\eta_{\Lambda,d}^{pc}(r)) \rangle_{\Lambda} - \langle p_{\bullet}(\eta_{\Lambda,v}^{pc}(r)) \rangle_{\Lambda} \geq p_{\bullet}(\langle \eta_{\Lambda,d}^{pc} \rangle_{\Lambda}) - p_{\bullet}(\overline{\eta}_{vaw}^{m})$$

$$= p_{\bullet}(\langle \eta_{\Lambda,v}^{pc} \rangle_{\Lambda}) - p_{\bullet}(\overline{\eta}_{vaw}^{m})$$

$$\geq -O[\varnothing(\Lambda)^{-2/3}],\quad (158)$$

where the small error, due to the boundary layer effects, goes to zero as $\Lambda$ goes to $\mathbb{R}^3$, but is not identically zero.

Thus, to complete this proof one would need to show that the difference $\Gamma[\eta_{\Lambda,d}^{pc}] - \Gamma[\eta_{\Lambda,v}^{pc}] < 0$ stays away from zero; alternatively, the proof would be completed if one could control the error term in Jensen’s inequality to the effect that $\langle p_{\bullet}(\eta_{\Lambda,d}^{pc}(r)) \rangle_{\Lambda} - p_{\bullet}(\langle \eta_{\Lambda,d}^{pc}(r) \rangle_{\Lambda}) \geq C > 0$ independently of sufficiently large $\Lambda$.

Remark: In the limit of vanishing hard-sphere volume the local thermodynamics goes over into that of the perfect gas. In this case the hard-sphere pressure : temperature ratio as function of $\overline{\eta}$ is simply the identity map, and then r.h.s. (152) is
identically zero, and the proof of the discontinuity of the constant-$N$ derivative of $\alpha \mapsto F_\alpha^\Lambda[\eta^\text{pc}_\Lambda]$ is complete, then. This in fact is the proof of Ref.\cite{30}.

Remark: We note that the jumping down of the constant-$N$ derivative of $\alpha \mapsto F_\alpha(\alpha, N)$ at $\alpha = \alpha_{vd}(N)$ also implies (for our $V < 0$) that $E_\alpha^\Lambda[\eta^\text{pc}_\Lambda] > E_\alpha^\Lambda[\eta^\text{pc}_{\Lambda,d}]$, which is seen by noting (150) and recalling the definition (14) of the energy, keeping in mind the constancy of $\mathcal{N}^\Lambda[\eta^\text{pc}]$ at $\alpha = \alpha_{vd}(N)$. With the jumping down of the energy : temperature ratio at $\alpha = \alpha_{vd}(N)$, the constancy of $F_\alpha^\Lambda[\eta^\text{pc}_\Lambda]$ at $\alpha = \alpha_{vd}(N)$ then in turn implies that $S_\alpha^\Lambda[\eta^\text{pc}_{\Lambda,v}] > S_\alpha^\Lambda[\eta^\text{pc}_{\Lambda,d}]$, i.e. the entropy jumps down also.

Remark: Our proof of the canonical phase transition reveals two metastability regions in its $(\alpha, N)$ neighborhood in which locally $F$ stable solutions of (8) exist. Also these metastability regions should terminate at their spinodal lines. We have to leave the determination of their location in $(\alpha, N)$ space for some future work.

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APPENDIX

A. THE INTERACTION INTEGRALS IN SPHERICAL GEOMETRY

In spherical geometry we are in the position to obtain several explicit results.

Lemma A.1: Let $\Lambda = B_R$ be a ball of radius $R$ centered at the origin. Then

\begin{align}
-(V_w * 1)_{B_R}(r) &= \frac{\pi}{4\kappa^3} \left[ \arctan(\kappa(R + r)) + \arctan(\kappa(R - r)) + \frac{2\kappa R(\kappa^2R^2 - r^2) - 1}{(\kappa^2(R^2 + r^2) + 1)^2 - 4\kappa^4 R^2 r^2} \right], \\
-(V_y * 1)_{B_R}(r) &= \frac{4\pi}{\kappa^2} \left[ 1 - (1 + \kappa R)e^{-\kappa R} \sinh(\kappa r)/\kappa r \right], \\
-(V_n * 1)_{B_R}(r) &= 2\pi \left( R^2 - \frac{1}{3}r^2 \right).
\end{align}

(159)

Setting $r = 0$ in (A.1), (A.2), and (A.3) produces

\begin{align}
\| (V_w * 1)_{B_R} \|_{C^0_b} &= \| V_w(\cdot) \|_{L^1(B_R)} = \frac{\pi}{2\kappa^3} \left[ \arctan(\kappa R) + \kappa R \frac{\kappa^2 R^2 - 1}{(\kappa^2 R^2 + 1)^2} \right], \\
\| (V_y * 1)_{B_R} \|_{C^0_b} &= \| V_y(\cdot) \|_{L^1(B_R)} = \frac{4\pi}{\kappa^2} \left[ 1 - (1 + \kappa R)e^{-\kappa R} \right], \\
\| (V_n * 1)_{B_R} \|_{C^0_b} &= \| V_n(\cdot) \|_{L^1(B_R)} = 2\pi R^2.
\end{align}

(160)

Integrating (A.1), (A.2), and (A.3) over $B_R$ yields

\begin{align}
\| (V_w * 1)_{B_R} \|_{L^1(B_R)} &= \frac{\pi^2}{6\kappa^6} \left[ 4\kappa^2 R^3 \arctan(2\kappa R) - 4\kappa^2 R^2 + \ln \left( 1 + 4\kappa^2 R^2 \right) \right], \\
\| (V_y * 1)_{B_R} \|_{L^1(B_R)} &= \frac{16\pi^2}{3\kappa^3} R^3 \left[ 1 - (1 + \kappa R) \frac{3}{2} \left( 1 + e^{-2\kappa R} \right) \kappa^2 R^2 - e^{-2\kappa R} \kappa^3 R^3 \right], \\
\| (V_n * 1)_{B_R} \|_{L^1(B_R)} &= \frac{8\pi^2}{45} R^5.
\end{align}

(161)

B. ASSOCIATED PARTIAL DIFFERENTIAL EQUATIONS

For Yukawa and Newton kernels the integral equation (8) for the density $\eta(\mathbf{r})$ in $\Lambda \subset \mathbb{R}^3$ is equivalent to a semilinear elliptic PDE of second order together
with consistent boundary condition for the corresponding chemical self potential per particle, \(-V \ast \eta\). Thus, setting \(-V \ast \eta \equiv \psi\), we find from (8) that \(\psi\) solves

\[ -\Delta \psi(r) = 4\pi \phi'(r) (\gamma + \alpha \psi(r)) - \kappa^2 \psi(r) . \] (B.1)

In the formal Newtonian limit \(\kappa \to 0\) we have \(V_{\gamma} \to V_N\), and (B.1) reduces to

\[ -\Delta \psi(r) = 4\pi \phi'(r) (\gamma + \alpha \psi(r)) . \] (B.2)

In the low density limit, (B.1) reduces to

\[ -\Delta \psi(r) = 4\pi \zeta e^{\alpha \psi(r)} - \kappa^2 \psi(r) , \] (B.3)

and (B.2) to

\[ -\Delta \psi(r) = 4\pi \zeta e^{\alpha \psi(r)} , \] (B.4)

with \(\zeta = e^{\gamma}\) the fugacity. In each case, (5) evaluated at \(\partial \Lambda\) provides a nonlinear and nonlocal boundary condition for \(\psi\), which makes it quite difficult to study these PDEs in general domains.

**Remark:** If in (8) one replaces \(\phi'(\gamma)\) by the strictly convex function \(\exp(\gamma)\), then the alternative stated after Proposition 6.3 ceases to exist and the map \(\gamma \mapsto \eta^\Lambda_{\alpha} \in C^0_b(\Lambda)\) actually terminates at \(\gamma^\Lambda_{\alpha}\); see Refs. [18, 5].

For spherically symmetric solutions, i.e. \(\psi(r) = \phi(r)\) in a ball of radius \(R\), satisfying the regularity condition \(\phi'(0) = 0\), the PDEs (B.1), (B.2), (B.3), and (B.4) simplify to ODEs with nonlinear and nonlocal boundary conditions that read, for (B.1):

\[ \phi(R) = 4\pi \frac{e^{-\kappa R}}{\kappa R} \int_0^R r \sinh(\kappa r) \phi'(r) (\gamma + \alpha \phi(r)) dr , \] (B.5)

for (B.2):

\[ \phi(R) = 4\pi \frac{1}{R} \int_0^R r^2 \phi'(r) (\gamma + \alpha \phi(r)) dr , \] (B.6)

for (B.3):

\[ \phi(R) = 4\pi \zeta \frac{e^{-\kappa R}}{\kappa R} \int_0^R r \sinh(\kappa r) e^{\alpha \phi(r)} dr , \] (B.7)

for (B.4):

\[ \phi(R) = 4\pi \zeta \frac{1}{R} \int_0^R r^2 e^{\alpha \phi(r)} dr , \] (B.8)
For spherical symmetry, (B.2) has nice scaling properties which facilitate its discussion and aid in its numerical integration on a machine; see Refs. [51, 32]. Its low density limit (B.4) becomes the homologously invariant isothermal gaseous ball equation, which has been extensively studied by Emden, Chandrasekhar, and others. Such scaling properties are not shared by (B.1), or (B.3), for which numerical studies of radial solutions apparently have not yet been carried out.

The spherical version of (8), with $V = V_w$ in (5), does not seem to reduce to an ODE, and numerical integration of the integral equation (8) with $V = V_w$ are correspondingly more involved, see Ref. [33].

The special case $\Lambda = \mathbb{R}^3$, with $\eta(r)$ solving (7), is of interest in itself, as explained in the introduction. Since equations (B.1), (B.2), (B.3), and (B.4) do not depend on $\Lambda$, the same PDEs cover the case $\Lambda = \mathbb{R}^3$. However, instead of taking the formal limits $\Lambda \to \mathbb{R}^3$ for their self-consistent boundary conditions, the situation is more subtle. We illustrate this with the spherically symmetric situation, with finite $R$ boundary conditions (B.5), (B.6), (B.7), and (B.8). In fact we need to drop (B.6) and (B.8), for their limits are infinite because the respective equations (B.2) and (B.4) do not possess solutions with their right-hand side in $L^1(\mathbb{R}^3)$. For (B.1) under spherical symmetry, we may or may not include the limit $R \to \infty$ of (B.5), which is easily shown to be zero because $\psi'(r)$ is bounded; similarly, for bounded radially symmetric solutions of (B.3) the limit $R \to \infty$ of (B.7) vanishes. Yet if we do include the condition that $\psi(r) \to 0$ as $|r| \to \infty$, then we throw out all the constant solutions $r \mapsto \psi_{vdW}(r) \equiv -\eta_{vdW} \|V_Y\|_1$. This shows that the spatially constant van der Waals densities $r \mapsto \eta_{vdW}$ are more subtle limits of the finite volume non-uniform van der Waals densities, namely in the sense of supnorm convergence of the members of any sequence of nested compact subsets of $\mathbb{R}^3$, which sequence converges to $\mathbb{R}^3$; of course, convergence is also weak, i.e. pointwise.

In the wide interface approximation, for our short ranged $V_w \in L^1(\mathbb{R}^3)$ and $V_Y \in L^1(\mathbb{R}^3)$ the convolution $V * \eta$ given by (5) for $\Lambda = \mathbb{R}^3$ can be expanded to second order, and the fixed point equation (7) reduces to a PDE for $\eta$ (not $\psi$), viz.

$$-\alpha M_2(V) \Delta \eta(r) + \alpha \|V\|, \eta(r) = \psi_{\lambda}^{-1}(\eta(r)) - \gamma, \quad (B.9) \quad (170)$$

where

$$M_2(V) = \frac{1}{6} \int_{\mathbb{R}^3} |x|^2 V(|x|) d^3r \quad (B.10) \quad (171)$$

is the “second moment” of $V$. Notice that (B.9) is the Euler–Lagrange equation for a so-called Cahn–Hilliard functional, studied recently in Ref. [9].
Our numerical studies of \( (8) \) for \( \Lambda = B_R \) with \( R = 50 \) and \( \varkappa = 1 \) revealed that near the critical point one finds solutions with inhomogeneity scale \( R \). This leads us to the following (mildly vague) conjecture:

**Conjecture:** For \( (\alpha, \gamma) \) in some droplet neighborhood of the (weakly \( \Lambda \)-dependent) critical point, the wide interface approximation becomes asymptotically exact, in the sense that one finds droplet solutions \( \eta_{\Lambda, d} \) of \( (8) \) which converge in a suitable but reasonable sense to solutions of \( (B.9) \) in some "universal" limit as \( \Lambda \to \mathbb{R}^3 \).

**C. REVERSAL TO THE DIMENSIONAL QUANTITIES OF PHYSICS**

As conventional in chemical physics we have used dimensionless units in which the "density" \( \overline{\rho} \) is actually the volume fraction occupied by all the microscopic balls. Thus, if \( N \) balls, having volume \( |b| \) each, are inside a container \( \Lambda \) of volume \( |\Lambda| \), then \( \overline{\rho} = N |b| / |\Lambda| \). Also, we have absorbed several "constants of nature" in our quantities, and moreover ignored the usual heuristic injection of quantum mechanics as per the thermal de Broglie wavelength. To make contact with physics one needs to reconver our dimensionless into dimensional variables. It suffices to do the conversion for the model with the van der Waals interaction potential; the conversion for the model with Yukawa or Newton interactions is done entirely analogously.

Thus, \( |b| \) is dimensional (a volume), and we have to make the following replacements "dimensionless" → "dimensional" quantities: \( \mathbf{r} \to \mathbf{r} / |b|^{1/3} \) for the position vectors, and therefore all lengths — in particular, \( \varkappa \to |b|^{1/3} \varkappa \); next, \( \alpha \to \beta \alpha \) for the coupling constant : temperature ratio; \( \gamma \to \beta \mu - \ln (\lambda_{ab}^3 / |b|) \) for the chemical potential per particle : temperature ratio; \( \eta \to |b| \rho \) for the particle density. We now have \( \beta = (k_B T)^{-1} \), with \( T \) the temperature in degree Kelvin, and \( \lambda_{ab} \) is the thermal de Broglie wavelength. In the same vein, we need to replace \( \ln \eta (\mathbf{r}) \to \ln (\rho (\mathbf{r}) / \overline{\rho}_{ab}) \) in the entropy functional, where \( \overline{\rho}_{ab} = (2\pi m k_B T)^{3/2} / h^3 \) is the thermal "de Broglie density."

For applications to, say, fluids made of the noble elements, the physical ordering is \( |b| < 4\pi \varkappa^{-3}/3 \) and \( \varkappa \sigma (\Lambda) \gg 1 \). Numerically, \( |b| \approx 1 \Lambda^3 \), and \( \varkappa^{-1} \approx 2 \Lambda \) seem reasonable, while \( \sigma (\Lambda) \approx 10 - 10^2 \text{cm} \) seems a reasonable range of laboratory container sizes. Also, the dimensional van der Waals coupling constant \( \alpha \) has physical dimension of energy, numerically in the range of "typical molecular binding energies" of the natural gases, although of course there is no quantum mechanical formation of \( \text{Ne}_2 \), \( \text{Ar}_2 \), etc. molecules in nature. The attraction between Ne, Ar, etc. atoms is manifested most dramatically through the condensation / evaporation phase transition exhibited by these chemical elements of matter.
D. ERRATA FOR REFS. [29] and [33]

All corrections to our previous papers Refs. [29] and [33] are easy to make. Those in the categories typo and slip of pen are just listed without comment, those which deserve a commentary are commented on in footnotes. Expressions to be replaced are surrounded by quotation marks.

D.a. Errata for Ref. [29]

p.223: above (2.66), replace “it has been shown (1)” by “it has been argued (1)”.

p.238: in (4.7a), replace “|U” by “|U”.

p.248: replace “Then also s(\(\rho_1\)) = s(\(\rho_2\)). That implies that there exists an incompressible mapping \(\rho_1 \mapsto \rho_2\). (Note that entropy is conserved for incompressible mappings.) As has been shown in ref. 10 (see also refs. 8 and 21), any given \(\rho_0\) can be mapped incompressibly to a unique spherical minimizer \(\rho_M\) of \(e(\rho)\) with \(s(\rho_0) = s(\rho_M)\). By construction both \(\rho_1\) and \(\rho_2\) minimize \(e(\rho)\) under conservation of entropy; hence, \(\rho_1 \equiv \rho_2\), in contradiction to the assumption that the densities are not identical.”

by [10]

“Since also \(\tilde{f}(\rho_1) = \tilde{f}(\rho_2)\) (where \(\tilde{f}(\rho)\) is given in (3.28), here with \(\psi \equiv 0\)), we then conclude that \(\int_{\Lambda} \exp(-\beta_{1t}U \ast \rho_1) d^3r = \int_{\Lambda} \exp(-\beta_{1t}U \ast \rho_2) d^3r\) as well. Hence, \(\eta(\beta_{1t}; \rho_1) = \eta(\beta_{1t}; \rho_2) \equiv \eta_{tr}\) (see p. 238 for the definition of \(\eta(\beta; \rho)\)). But then, since \(\rho_1 = \bar{\rho}_{1tr}\), so that \(-\beta_{1t}U \ast \rho_1 = -\beta_{1t}U \ast \bar{\rho}_{1tr} = \Psi_{\eta_{tr}}\) is the unique pointwise minimal solution of (4.6) for this value of \(\eta = \eta_{tr}\), it follows that \(\int_{\Lambda} \exp(-\beta_{1t}U \ast \rho_1) d^3r < \int_{\Lambda} \exp(-\beta_{1t}U \ast \rho_2) d^3r\), which is a contradiction.”

[9] In fact, there is a small mistake in ref. 1 of Ref. [29] to the effect that the factor \((N - 1)\) in (2.66) (quoted from ref. 1) is incorrect. The correct factor is \(N\); see Ref. [31].

[10] The critical sentence is: “That implies that there exists an incompressible mapping \(\rho_1 \mapsto \rho_2\).” While true for some types of phase transitions associated with symmetry breaking, it is not clear that such incompressible mappings exist in the context of the theorem. M.K. is grateful to Elliott Lieb for kindly pointing this out.

[11] Notice that the correction given here not only avoids the pitfall of the original proof, it also eliminates the requirement of the original proof that \(\Lambda\) be spherical. This nonspherical argument, taken from Ref. [30], is a special case of the argument in our proof of Theorem 7.2; see the penultimate remark in section VII.
D.b. **Errata for Ref.[33]**

p.1353: replace “The Hilbert space” by “The space”
p.1364: in (6.19), replace “$O[r_0/R]$” by “$O[(r_0/R)^3]$”
p.1376: in Ref.33, replace “Phnys.” by “Phys.”

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