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Nonuniform van der Waals Theory

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The liquid–vapor interface of a confined fluid at the condensation phase transition is studied in a combined hydrostatic/mean-field limit of classical statistical mechanics. Rigorous and numerical results are presented. The limit accounts for strongly repulsive short-range forces in terms of local thermodynamics. Weak attractive longer-range ones, like gravitational or van der Waals forces, contribute a self-consistent mean potential. Although the limit is fluctuation-free, the interface is not a sharp Gibbs interface, but its structure is resolved over the range of the attractive potential. For a fluid of hard balls with $\sim -r^{-6}$ interactions the traditional condensation phase transition with critical point is exhibited in the grand ensemble: A vapor state coexists with a liquid state. Both states are quasiuniform well inside the container, but wall-induced inhomogeneities show up close to the boundary of the container. The condensation phase transition of the grand ensemble bridges a region of negative total compressibility in the canonical ensemble which contains canonically stable proper liquid–vapor interface solutions. Embedded in this region is a new, strictly canonical phase transition between a quasiuniform vapor state and a small droplet with extended vapor atmosphere. This canonical transition, in turn, bridges a region of negative total specific heat in the microcanonical ensemble. That region contains subcooled vapor states as well as superheated very small droplets which are microcanonically stable.

KEY WORDS: Liquid–vapor interface; continuum limit; van der Waals theory; rigorous results; numerical results.

1. INTRODUCTION

The three-dimensional liquid–vapor interface poses one of the outstanding problems in the statistical mechanics of the classical phase transition; see ref. 1 for a review of the field. A satisfactory theory should be based on a

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microscopic Hamiltonian and deduce observable structures using tools of statistical mechanics. However, in an infinitely extended field-free 3D system, we expect an interface to be definable only on time scales which are (i) sufficiently long to justify the assumption of thermodynamic equilibrium locally and (ii) sufficiently short as compared to the time scale of typical large-scale fluctuations.[1,2] The standard Gibbs formalism in the thermodynamic bulk limit[3] represents time averages over sufficiently long times that an ergodic system has visited essentially all distinct typical macroconfigurations, so that any local interface structure will be averaged out. Even if one conceives of a mathematical device that allows one to discriminate between the two time scales just alluded to, in general the resulting snapshot interface may be a topological monster and far from easy to analyze.

Instead of inquiring into the time scales, we will here concentrate on a different approach, which is a variation on the mean-field theme basic to the work of van der Waals[4] and successors. The basic idea is to assume that the short-range repulsive part of the intermolecular potential V creates particle correlations on a much shorter length scale than the longer-range but weak attractive part of V. Under favorable conditions very many particles live on the correlation scale imposed by the attractive part of V. If this is the case, one expects that macroscopically locally there appears a fluid with an equation of state to which only the repulsive part of the pair interactions contributes. The attractive tail interactions manifest themselves in the form of a mean-field force, generated by the local fluid density. Van der Waals (who had not realized the underlying mean-field assumption in his theory; see the editorial in ref. 4) at first restricted the fluid to be uniform in space and found his celebrated equation of state which produced the unstable negative compressibility loop. J. Thomson had speculated about its existence. Being an artifact in a bulk theory, this was later improved on thermodynamically by Maxwell's[5] equal-area construction, yielding a not unreasonable theory of the bulk thermodynamic functions, and by Ornstein,[6] who obtained all this and also the phase fractions at a condensation phase transition. The asymptotic character of the van der Waals–Maxwell–Ornstein theory was established in the rigorous works of Kac[7] and Kac *et al.*[8] for one-dimensional systems, and of Lebowitz and Penrose[9] for arbitrary-dimensional systems; see ref. 10 for a review. The spatial distribution of the liquid and vapor phases was addressed by Percus[11] and by van Kampen,[12] who focused on the concept of a self-consistent nonuniform mean-field approximation to the problem. They derived a nonlinear equation for the approximate one-particle density in all space and showed it has planar interface solutions.[1,11,12]

These nonuniform extensions of the vdWMO theory, as far as we know, have not been subject to rigorous treatment and the status of the approximations involved not clarified. In particular, some ambiguities have shown up in the discussion of interface fluctuations.[1,13,14] In the present work we rigorously construct a hydrostatic/mean-field limit for nonuniform systems in which the continuum equation of refs. 11 and 12 is restricted to a bounded domain $\Lambda \subset \mathbb{R}^3$ and becomes an exact equations for the one-particle density. This gives us sufficient control of the problem to construct three-dimensional nonplanar interface solutions and discuss their stability. The limit plays the role of a "law or large numbers." We hope to address a "central limit theorem" in a subsequent work. This should clarify the above-mentioned ambiguities at the level of the equilibrium interface fluctuations.

Although for the sake of generality we will include it in the construction of the limit, an external gravitational field will *not be needed* to enforce a stable interface. Therefore our results should be of interest for so-called microgravity experiments. Stable interfaces exist when the total amount of matter in the container is fixed such that there is not enough material to fill the container completely with the liquid state, and too much material to fill it entirely with vapor. Without an ordering external field the interface structure then is determined by the competition between the mean field forces due to V_A and the "stiff" local thermodynamic pressure gradients of the reference fluid, due to V_R. It is also weakly influenced by the shape of the container Λ. Physically, the presence of the container in some sense "freezes in" one particular kind of interface geometry among the multitude of possibilities which would only be locally realized as transient phenomena in a fluctuating thermodynamic (bulk) limit system. Mathematically it provides the compactification of the function space so that the continuum/mean-field equation does have nonplanar finite interface solutions in 3D.

With Kac[7] we write

$$V(x, y) = V_R(x-y) + V_A(x-y) \tag{1.1}$$

for the pair potential, with $x, y \in \mathbb{R}^3$. Here V_R is a repulsive core and V_A an attractive tail part. We treat the two parts differently when the number of particles $N \to \infty$. In particular, to resolve the finite thickness of an interface, we keep the range of V_A fixed, unlike Kac, and pass over to a finite-volume cousin of the Kac–Uhlenbeck–Hemmer–Lebowitz–Penrose limit, in which infinitely many particles live on the range of V_A. This requires multiplying V_A by a scaling factor which goes to zero with $N \to \infty$, in such a way that the contribution to the energy per particle due to V_A is basically fixed along the limit sequence. Simultaneously V_R has to be scaled to zero in such a way that the contribution to the energy per particle due to V_R

is basically fixed along the limit sequence, too. This procedure results in what is properly termed a combined hydrostatic/mean-field limit. We stress that it is different from a pure mean-field limit insofar as correlations due to V_R contribute to the local thermodynamics. To prove existence of this limit for the thermodynamic and the correlation functions requires a number of modifications of the Lebowitz–Penrose technique, besides rescaling into a finite volume, because the one-particle density is now nonuniform. Our limit is conceptually related to other limits of nonuniform mean-field type, for which the local density structure is that of an ideal gas. These have been studied for classical systems with bounded[15–17] and logarithmically singular interactions,[18,19] and for quantum systems with Coulomb and Newton interactions and various statistics.[20–22] Our approach, though yet classical, goes beyond these limits insofar as our system is locally not the ideal gas, but a fluid of particles with a nonintegrable repulsive core interaction.

We take

$$V_R(x-y)=\sum_{k=4}^{K}\sigma_R^{(k)}\,|x-y|^{-k} \tag{1.2}$$

with $K\geqslant 4$, and coupling constants $\sigma_R^{(k)}\geqslant 0$ (strict inequality holds for $k=K$). The form (1.2) covers many cases of interest and is chosen for convenience, but we could be more general and merely require V_R to be positive, diverging at the origin, and tempered at infinity, i.e., $V(|x|)\leqslant C\,|x|^{-3-\varepsilon}$ for $|x|$ large.[23] We shall make explicit use of (1.2) in Sections 3 and 4 to obtain easy estimates, but with only minor additional effort, these can be generalized. The typical case for V_A which we have in mind is, e.g.,

$$V_A(x-y)=-\sigma_A(|x-y|^2+r_0^2)^{-K'/2} \tag{1.3}$$

Here, r_0 is a small "typical interaction radius" and $\sigma_A>0$ is a coupling constant. For a model of particles with short-range interactions, we have $K>K'>3$. Of primary interest is the case $K=12$, $\sigma_R^{(k)}=0$ for $k<K$, and $K'=6$. This is a slight modification of the Lennard-Jones potential. By setting $K'=1$ and $K\geqslant 4$, we obtain a model of a gravitating system of particles with repulsive cores; taking $K\to\infty$ gives hard spheres with attractive interactions. More generally, we take for V_A a nonpositive, weak attractive interaction, such that $-V_A(x-y)$ is the kernel of a positive-definite bilinear form on some appropriate function space. Moreover, V_A is required to be continuous and bounded from below by $V_A(0)$. This covers many physically important interactions, but is quite restrictive from a mathematical point of view. We need the restrictions because we want to apply Laplace's method in function space.

To keep the paper of reasonable size, the limit will be rigorously constructed only in the grand canonical ensemble. For the microcanonical and the (petit) canonical ensembles we confine ourselves to a nonrigorous presentation. Numerical evaluations will be given for the grand and the petit canonical ensembles. We stress that in our finite-volume limit the ensembles are generally *not* thermodynamically equivalent.[16] Although the interactions are short range, the finite-volume corrections to the bulk limit fall into two categories: (1) boundary layer effects at the container wall; (2) interface effects inside the container. The effects of category 1 are simple and as expected. However, category 2 contains some highly nontrivial effects. They include a new structural phase transition in the petit canonical ensemble. It is embedded in a region of negative total compressibility which is bridged in the grand canonical ensemble by the (classical) condensation phase transition. The reader should not find him or herself balking at the negative total compressibility. This is not defined just as the integral over the local compressibility, which is positive. The total compressibility is the difference of two positive terms and compares states of different amount of matter and/or volume. Transitions between such states are impossible in the petit and the microensembles, which explains why a structure with negative total compressibility can be (conditionally) stable. We point out that our negative compressibility loops have a very different origin than the famous van der Waals loop.

We approach the limit in three steps. The first is simple and consists in rescaling the bulk limit for a uniform system into a finite domain, given in Section 2. The particles have repulsive pair interactions (1.2). This defines the local thermodynamics of what is commonly termed the reference system. In Section 3 we construct a limit of the grand potential which yields the reference system in a nonuniform external field. In Section 4 we establish the continuum limit for a nonuniform system with all interactions present. The limiting grand potential is given by the global minimum of a grand potential functional on the space of one-particle densities. It will be shown that those solutions of the nonlinear Euler–Lagrange equation which globally minimize this functional are limiting one-particle densities of the grand ensemble. In Section 5 we present the corresponding formulas for the petit and the microcanonical ensembles, without proof.

We then go over to applications. Section 6 deals with a system of hard balls with attractive interactions (1.3) which is confined by a spherical container. We discuss first the relevant details of the local thermodynamics which is provided for by the hard-balls system without attractive interactions. We then address the complete system of hard balls with attractive interactions and prove uniqueness of the solutions of the hydrostatic/mean-field equation at high temperature. We then present numerical results which for sufficiently low temperature show a condensation phase transition in the grand ensemble, and, further, metastability regions with spinodal points. This is the finite-volume analog of the bulk condensation phase transition with a critical point. We also present calculations for the petit canonical ensemble, which reveal a new structure: an explosion/implosion phase transition between a quasiuniform vapor state and a small droplet with extended vapor atmosphere. This transition is not seen in the grand ensemble. Our canonical results imply an additional region with negative specific heat in the microcanonical ensemble. We believe that our results should be observable in microgravity experiments.

Connection with the original van der Waals–Maxwell–Ornstein theory of condensation is made in Section 7, where a secondary, singular limit $V_{\mathrm{A}}(x-y) \rightharpoonup A\delta(x-y)$, with $A<0$, gives the classical theory plus Maxwell construction. Some open problems are listed in Section 8.

2. THE LOCAL REFERENCE SYSTEM

We collect here a number of results for systems of particles with pair interactions (1.2). They readily follow by rescaling the standard thermodynamic limit sequence[23–25] into a finite volume $|\Lambda|$. In the following, $v \geqslant 1$ is the "voluminosity" parameter, in the sense that an equivalent system of the standard thermodynamic limit sequence would have volume $v\,|\Lambda|$.

We discuss first the thermodynamic functions. In the microcanonical ensemble, a physical system with $N_\Lambda \gg 1$ particles in a bounded open domain $\Lambda \subset \mathbb{R}^3$ has total energy E_Λ. Its Hamiltonian is

$$H_{\mathrm{R}}^{(N_\Lambda)}(X, P) = \sum_{i=1}^{N_\Lambda} \frac{p_i^2}{2m} + U_{\mathrm{R}}^{(N_\Lambda)}(X) \tag{2.1}$$

with $(X, P) \equiv (x_1, ..., x_N; p_1, ..., p_N)$, $x_i \in \Lambda$, $p_i \in \mathbb{R}^3$, and

$$U_{\mathrm{R}}^{(N_\Lambda)}(X) = \sum_{1 \leqslant i < j \leqslant N_\Lambda} V_{\mathrm{R}}(x_i - x_j) \tag{2.2}$$

The asymptotic (in v) macroscopic equilibrium properties are captured by the entropy scaling limit

$$S_{\mathrm{R}}(N_\Lambda, E_\Lambda) = \lim_{v \to \infty} S_{\mathrm{R}}(N_\Lambda, E_\Lambda; \Lambda; v) \tag{2.3}$$

where

$$k_{\mathrm{B}}^{-1} S_{\mathrm{R}}(N_\Lambda, E_\Lambda; \Lambda; v) = \frac{N_\Lambda}{N} \ln \left\{ \frac{v^N}{N!\, h^{3N}}\, \Phi_{\mathrm{R}}(N_\Lambda,\ E_\Lambda; \Lambda; v) \right\} \tag{2.4}$$

and

$$\Phi_{\mathrm{R}}(N_\Lambda, E_\Lambda; \Lambda; v)$$
$$= \mathrm{vol}\{(X, P) \in \Lambda^N \times \mathbb{R}^{3N} : H_{\mathrm{R}}^{(N)}((N/N_\Lambda)^{1/3} X, P) \leqslant (N/N_\Lambda) E_\Lambda\} \tag{2.5}$$

with

$$N = [\![vN_\Lambda]\!] \tag{2.6}$$

the integer part of vN_Λ.

Proposition 2.1. The function $S_{\mathrm{R}}(N_\Lambda, E_\Lambda)$ exists and is increasing and concave w.r.t. $E_\Lambda \in \mathbb{R}^+$, $E_\Lambda > E_\Lambda^{(0)} > 0$, where $E_\Lambda^{(0)}$ is the ground-state energy. It is concave w.r.t. $N_\Lambda \in \mathbb{N}$. Its density $S_{\mathrm{R}}/|\Lambda|$ is independent of volume $|\Lambda|$ and shape of Λ.

For given Λ, N_Λ, and reciprocal temperature $k_{\mathrm{B}}\beta$, the asymptotic macroscopic equilibrium properties are given by the free energy scaling limit

$$F_{\mathrm{R}}(N_\Lambda, \beta) = \lim_{v \to \infty} F_{\mathrm{R}}(N_\Lambda, \beta; \Lambda; v) \tag{2.7}$$

where

$$\beta F_{\mathrm{R}}(N_\Lambda, \beta; \Lambda; v) = -\frac{N_\Lambda}{N} \ln \left\{ \frac{v^N}{N!} Q_{\mathrm{R}}(N_\Lambda, \beta; \Lambda; v) \right\} \tag{2.8}$$

and

$$Q_{\mathrm{R}}(N_\Lambda, \beta; \Lambda; v) = \int_{\Lambda^N} \exp\{-\beta U_{\mathrm{R}}^{(N)}[(N/N_\Lambda)^{1/3} X]\}\, m(d^{3N}x) \tag{2.9}$$

with

$$m(d^{3N}x) = \lambda^{-3N}\, d^{3N}x \tag{2.10}$$

and λ is the thermal deBroglie wavelength. Again, N is given by (2.6).

Proposition 2.2. The function $\beta F_{\mathrm{R}}(N_\Lambda, \beta)$ exists and is concave and decreasing in $\beta \in \mathbb{R}^+$ and convex in $N_\Lambda \in \mathbb{N}$. It is related to $S_{\mathrm{R}}(N_\Lambda, E_\Lambda)$ through

$$\beta F_{\mathrm{R}}(N_\Lambda, \beta) = \inf_{E_\Lambda \geqslant E_\Lambda^{(0)}} \{\beta E_\Lambda - k_{\mathrm{B}}^{-1} S_{\mathrm{R}}(N_\Lambda, E_\Lambda)\} \tag{2.11}$$

Its density $F_{\mathrm{R}}/|\Lambda|$ is independent of volume $|\Lambda|$ and shape of Λ.

For given Λ, $k_B\beta$, and chemical potential $\mu \in \mathbb{R}$, the asymptotic macroscopic properties are given by the scaling limit for the grand potential

$$\Omega_R(\mu, \beta) = \lim_{v \to \infty} \Omega_R(\mu, \beta; \Lambda; v) \tag{2.12}$$

where, with $\mathbb{N}_0 = \mathbb{N} \cup \{0\}$,

$$\beta\Omega_R(\mu, \beta; \Lambda; v) = -\frac{1}{v} \ln \sum_{N \in \mathbb{N}_0} \frac{e^{\beta\mu N}}{N!} v^N \mathcal{Q}_R^{(N)}(\beta; \Lambda; v) \tag{2.13}$$

and

$$\mathcal{Q}_R^{(N)}(\beta; \Lambda; v) = \int_{\Lambda^N} \exp\{-\beta U_R^{(N)}(v^{1/3}X)\}\, m(d^{3N}x) \tag{2.14}$$

Proposition 2.3. The function $-\beta\Omega_R(\mu, \beta)$ exists and is positive and convex both in β and μ, and increasing in μ. It is related to $\beta F_R(N_\Lambda, \beta)$ through

$$\beta\Omega_R(\mu, \beta) = \inf_{N_\Lambda \geq 1} \{\beta F_R(N_\Lambda, \beta) - \beta\mu N_\Lambda\} \tag{2.15}$$

Its intensive partner $-\Omega_R/|\Lambda|$ is identical with the thermodynamic pressure and independent of volume $|\Lambda|$ and shape of Λ.

Proof. We define $\Lambda(t)$ to be a scaled domain, obtained from $\Lambda \equiv \Lambda(1)$ by a uniform dilation, with $|\Lambda(t)| = t\,|\Lambda|$, where $|\Lambda|$ denotes the volume of Λ. Then $\Lambda(t) \nearrow \mathbb{R}^3$ as $t \to \infty$ in the sense of Fisher. We know the following limits exist:

Let $t = N/N_\Lambda$ with $N = [\![vN_\Lambda]\!]$. Then

$$s_R = \lim_{v \to \infty} \frac{k_B}{|\Lambda(t)|} \ln\left[\frac{1}{N!\,h^{3N}} \operatorname{vol}\{(X, P) \in \Lambda^N(t) \times \mathbb{R}^{3N}: H_R^{(N)}(X, P) \leq tE_\Lambda\}\right] \tag{2.16}$$

$$f_R = \lim_{v \to \infty} -\frac{k_B T}{|\Lambda(t)|} \ln \frac{1}{N!} \int_{\Lambda^N(t)} \exp\{-\beta U_R^{(N)}(X)\}\, m(d^{3N}x) \tag{2.17}$$

and (N is a dummy now)

$$p_R(\mu, \beta) = \lim_{v \to \infty} \frac{k_B T}{|\Lambda(v)|} \ln \sum_{N \in \mathbb{N}_0} \frac{e^{\beta\mu N}}{N!} \int_{\Lambda^N(v)} \exp\{-\beta U_R^{(N)}(X)\}\, m(d^{3N}x) \tag{2.18}$$

are the standard bulk thermodynamic limit definitions of the entropy density in the microcanonical, the free energy density in the canonical, and the pressure in the grand canonical ensemble, respectively. Since U_R is positive and weakly tempered for $K > 3$, these limits exist and have all the thermodynamic convexity properties.[3,23,24] The limit functions are related by the standard thermodynamic Legendre transformations; see, for instance, ref. 3. The trivial rescaling of these limits into $\Lambda(1) = \Lambda$ results in our finite-volume formulas. Q.E.D.

The limit of the grand potential enjoys a variational principle which is shared only by certain thermodynamic limit systems. It is potentially useful for certain estimates relating a finite system to the asymptotic limit.

Proposition 2.4. For given Λ, β, μ,

$$\Omega_R(\mu, \beta) = \sup_v \Omega_R(\mu, \beta; \Lambda; v) \tag{2.19}$$

Proof. Fröhlich and Park[26] noticed that for systems with strictly positive interactions, $-\Omega$ is subadditive in the volume along the standard thermodynamic limit sequence. Well-known facts about subadditive functions, e.g., ref. 27, imply the analog of (2.19) for any sequence of standard cubes, hence for any sequence in the sense of van Hove by approximation with standard cubes. All limits are identical by the previous theorem. Thus (2.19) holds by rescaling. Q.E.D.

This concludes the collection of the thermodynamic functions. By rescaling and by the spatial uniformity of the one-particle density in the infinite volume limit, the one-particle density of our reference system (2.1) is uniform. It will be seen to become nonuniform as soon as we introduce the other interactions.

3. REFERENCE SYSTEM IN AN EXTERNAL FIELD

We upgrade our description and consider the reference system in a nonuniform, external potential field $\phi(x)$ of class $C^0(\Lambda)$. For instance, $\phi(x) = -x \cdot \mathbf{e}_z$ represents a homogeneous gravitational force field. The resulting limit functions exist, but they no longer follow merely by a rescaling from known results of the standard thermodynamic limit. We discuss only the grand canonical ensemble.

The grand potential at parameter v is now given by

$$\beta\Omega_{R,\phi}(\mu, \beta; \Lambda; v) = -\frac{1}{v} \ln \sum_{N \in \mathbb{N}_0} \frac{e^{\beta\mu N}}{N!} v^N \mathcal{Q}_{R,\phi}^{(N)}(\beta; \Lambda; v) \tag{3.1}$$

with

$$\mathscr{Q}_{\mathrm{R},\phi}^{(N)}(\beta; \Lambda; v) = \int_{\Lambda^N} \exp\{-\beta U_{\mathrm{R}}^{(N)}(v^{1/3}X) - \beta\Phi(X)\}\, m(d^{3N}x) \tag{3.2}$$

$$\Phi(X) = \sum_{i=1}^{N} \phi(x_i) \tag{3.3}$$

Theorem 3.1. The scaling limit

$$\Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda) = \lim_{v \to \infty} \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda; v) \tag{3.4}$$

exists and is given by

$$\Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda) = -\int_{\Lambda} p_{\mathrm{R}}[\mu - \phi(x), \beta]\, d^3x \tag{3.5}$$

The grand pressure $p_{\mathrm{R},\phi} = -|\Lambda|^{-1}\, \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda)$ is positive; it is increasing and convex in μ, and $\beta p_{\mathrm{R},\phi}$ is convex in β. In general it does depend on the shape of Λ.

Remark 1. This theorem states that the grand pressure $p_{\mathrm{R},\phi}$ is the uniform spatial average over Λ of pressures p_{R} with local chemical potential $\mu_{\mathrm{loc}}(x) = \mu - \phi(x)$. By the convexity of $\mu_{\mathrm{loc}} \mapsto p_{\mathrm{R}}(\mu_{\mathrm{loc}}, \beta)$, Jensen's inequality applied to (3.5) yields the useful estimate

$$p_{\mathrm{R},\phi}(\mu, \beta; \Lambda) \geqslant p_{\mathrm{R}}(\mu - \bar{\phi}, \beta) \tag{3.6}$$

Here, $\bar{\phi} = |\Lambda|^{-1} \int_{\Lambda} \phi(x)\, d^3x$.

Remark 2. Since ϕ is continuous, it takes its maximum ϕ^* and minimum ϕ_* on the closure $\bar{\Lambda}$ of Λ. Thus

$$\Omega_{\mathrm{R}}(\mu - \phi^*, \beta; \Lambda; v) \geqslant \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda; v) \geqslant \Omega_{\mathrm{R}}(\mu - \phi_*, \beta; \Lambda; v) \tag{3.7}$$

for all v. Taking limits, we obtain

$$\limsup_{v \to \infty} \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda; v) \leqslant \Omega_{\mathrm{R}}(\mu - \phi^*, \beta) \tag{3.8}$$

and

$$\liminf_{v \to \infty} \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda; v) \geqslant \Omega_{\mathrm{R}}(\mu - \phi_*, \beta) \tag{3.9}$$

whence the existence of limit points of (3.4). The bounds (3.8), (3.9) hint at the structure (3.5).

Proof of Theorem 3.1. We notice that given any continuous ϕ, then for any small $\varepsilon > 0$, we can find a Lipschitz constant $L(\varepsilon)$, and $L(\varepsilon)$-Lipschitz-continuous upper and lower approximations to ϕ which differ from ϕ by less than ε in the uniform norm. Since $p_{\mathrm{R}}(\mu)$ is continuous, the right-hand side of (3.5) can be approximated arbitrarily closely from above and below by replacing a continuous ϕ with, respectively, an appropriate upper and lower Lipschitz-continuous approximation to ϕ. Hence it suffices to prove (3.5) for all Lipschitz-continuous ϕ.

Thus, let ϕ satisfy

$$|\phi(x) - \phi(y)| \leqslant L_\phi \, |x - y| \tag{3.10}$$

with some Lipschitz constant $L_\phi > 0$. Let $\mathscr{P}(\varepsilon)$ be a partition of $\mathbb{R}^3$ into cubes of side length ε, such that after at most a rotation, a translation, and a dilation their centers coincide with $\mathbb{Z}^3$. Let $\Lambda(\varepsilon)$ be the subset of $\mathscr{P}(\varepsilon)$ which consists of those cubes whose intersection with Λ is nonvoid. In $\Lambda(\varepsilon)$ there are $|M|$ (ε) cubes Λ_k, $k \in M \equiv \{1, 2, ..., |M|\}$. Let $x^{(k)}$ be the center of Λ_k.

By Lipschitz continuity of $\phi(x)$ and the positivity of U_R, we estimate

$$\sum_{N \in \mathbb{N}_0} \frac{e^{\beta\mu N}}{N!} v^N \mathscr{Q}_{\mathrm{R},\phi}^{(N)}(\Lambda; v) \leqslant \prod_{k \in M} \sum_{N_k \in \mathbb{N}_0} \frac{e^{\beta\mu^{(k)}(\varepsilon) N_k}}{N_k!} v^{N_k} \mathscr{Q}_{\mathrm{R}}^{(N_k)}(\Lambda_k; v) \tag{3.11}$$

$$\mu^{(k)}(\varepsilon) = \mu - \phi(x^{(k)}) + 2L_\phi \varepsilon \tag{3.12}$$

Taking the lim inf of $-v^{-1} \ln(3.11)$ gives

$$\liminf_{v \to \infty} \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda; v) \geqslant -\sum_{k \in M} |\Lambda_k| \; p_{\mathrm{R}}[\mu^{(k)}(\varepsilon), \beta] \tag{3.13}$$

for all ε. We now let $\varepsilon \downarrow 0$, and from the Riemann sum definition of a Riemann integral obtain

$$\liminf_{v \to \infty} \Omega_{\mathrm{R},\phi}(\mu, \beta; \Lambda; v) \geqslant -\int_\Lambda p_{\mathrm{R}}[\mu - \phi(x), \beta] \, d^3x \tag{3.14}$$

Next, to obtain an estimate in the opposite direction, we inscribe in each cube of $\Lambda(\varepsilon)$ a smaller cocentered, parallel cube of side length $\delta\varepsilon$, with $\delta < 1$. We delete from this array of smaller cubes all those which are not entirely contained in Λ. The resulting array consists of $|\dot{M}|$ (δ, ε) cubes $\dot{\Lambda}_k$, $k \in \dot{M} \equiv \{1, 2, ..., |\dot{M}|\}$. The complement $\Lambda - \{\dot{\Lambda}_k\}$ is called "the corridors."

We now use Lipschitz continuity of $\phi(x)$, a typical corridor estimate[23] for U_{R}, and then Jensen's inequality to obtain

$$\begin{aligned}
&\sum_{N\in\mathbb{N}_0} \frac{\exp(\beta\mu N)}{N!} v^N \mathcal{Q}^{(N)}_{\mathrm{R},\phi}(\beta; \dot{\Lambda}_k; v) \\
&\quad\geqslant \sum_{N_1\in\mathbb{N}_0} \cdots \sum_{N_{|\dot{M}|}\in\mathbb{N}_0} \prod_{k\in\dot{M}} \frac{\exp[\beta\mu^{(k)}(-\delta\varepsilon)N_k]}{N_k!} v^{N_k}\mathcal{Q}^{(N_k)}_{\mathrm{R}}(\beta; \dot{\Lambda}_k; v) \\
&\quad\quad\times \exp\left[-J(v)\sum_{k'\in\dot{M}\setminus\{k\}} N_k N_{k'}\right] \\
&\quad\geqslant \exp\left[-J(v)\sum_{l\in\dot{M}}\sum_{l'\in\dot{M}\setminus\{l\}} \langle N_l N_{l'}\rangle_\varepsilon\right] \prod_{k\in\dot{M}} \sum_{N_k\in\mathbb{N}_0} \frac{\exp[\beta\mu^{(k)}(-\delta\varepsilon)N_k]}{N_k!} \\
&\quad\quad\times v^{N_k}\mathcal{Q}^{(N_k)}_{\mathrm{R}}(\beta; \dot{\Lambda}_k; v)
\end{aligned} \tag{3.15}$$

where

$$J(v) = \tfrac{1}{2}\sum_{n=4}^{K} \beta\sigma^{(n)}_{\mathrm{R}} v^{-n/3}(2[1-\delta]\,\varepsilon)^{-n} \tag{3.16}$$

The average here is, with $l \neq l'$,

$$\langle N_l N_{l'}\rangle_\varepsilon = \frac{\prod_{k\in\dot{M}}\sum_{N_k\in\mathbb{N}_0} N_l N_{l'}\tau^{(k)}}{\prod_{k\in\dot{M}}\sum_{N=0}^{\infty}\tau^{(k)}} = \langle N_l\rangle_\varepsilon\,\langle N_{l'}\rangle_\varepsilon \tag{3.17}$$

with

$$\tau^{(k)} = \exp[\beta\mu^{(k)}(-\delta\varepsilon)N_k]\; N_k!^{-1} v^{N_k}\mathcal{Q}^{(N)}_{\mathrm{R}}(\beta; \dot{\Lambda}_k; v) \tag{3.18}$$

From (3.17) we readily obtain

$$v^{-1}\langle N_k\rangle = -\partial_\mu \Omega_{\mathrm{R}}[\mu^{(k)}(-\delta\varepsilon), \beta; \dot{\Lambda}_k; v] \tag{3.19}$$

Since $-\Omega_{\mathrm{R}}(v)$ is increasing and convex in $\mu^{(k)}$, its limit function for $v\to\infty$, i.e., $|\dot{\Lambda}_k|\; p_{\mathrm{R}}[\mu^{(k)}(-\delta\varepsilon), \beta]$ has the same properties. By standard facts about convex functions (e.g., ref. 27), the right derivative of a convex function always exists and is not less than its left derivative, which exists, too. This implies the estimate

$$\limsup_{v\to\infty} v^{-1}\langle N_k\rangle \leqslant |\dot{\Lambda}_k|\;\partial^+_\mu p_{\mathrm{R}} \tag{3.20}$$

Clearly, $J(v) = O(v^{-4/3})$ for $v \to \infty$. This and (3.20) imply that lim sup of $-v^{-1}\ln(3.15)$ gives

$$\limsup_{v \to \infty} \Omega_{R,\phi}(\mu, \beta; \Lambda; v) \leqslant -\sum_{k \in \dot{M}} |\dot{\Lambda}_k|\, p_R[\mu^{(k)}(-\delta\varepsilon), \beta] \tag{3.21}$$

for all ε and $\delta < 1$. We now choose $\delta = 1 - \varepsilon$ and take the limit $\varepsilon \downarrow 0$, noting again the Riemann sum, and obtain

$$\limsup_{v \to \infty} \Omega_{R,\phi}(\mu, \beta; \Lambda; v) \leqslant -\int_\Lambda p_R[\mu - \phi(x), \beta]\, d^3x \tag{3.22}$$

The bounds (3.14) and (3.22) prove (3.5) for all Lipschitz-continuous ϕ, and by the argument given at the beginning of proof, also for any continuous ϕ. Q.E.D.

We can now go further and readily obtain the local one-particle density of the system in all cases in which for all $x \in \Lambda$, $\mu - \phi(x)$ belongs to the set of t for which $t \mapsto p_R(t, \beta)$ is differentiable. By convexity, p_R is differentiable except at most at denumerably many points. In case of differentiability we thus obtain, by taking the functional derivative[28]

$$\rho(x) = -\frac{\delta}{\delta\phi}\frac{1}{|\Lambda|}\int_\Lambda p_R[\mu - \phi(x), \beta]\, d^3x \tag{3.23}$$

which results in

$$\rho(x) = \partial_\mu p_R[\mu - \phi(x), \beta] \tag{3.24}$$

It is readily checked, noting the μ convexity of p_R, that $\rho(x)$ given in (3.23) coincides with the limit $v \to \infty$ of the corresponding finite-v definitions of $\rho(x; v)$.

If for an x_0, $\mu - \phi(x_0)$ takes a value for which p_R is not differentiable, and if $\phi(x_0)$ is not a maximum or minimum of ϕ, then by the implicit function theorem there exists a piecewise continuous surface which devides Λ into disjoint subsets. For instance, at μ_{SF}, the solid–fluid transition, $\mu - \phi(x_0) = \mu_{SF}$ defines the interface between open sets Λ_F and Λ_S, which are the interiors of the supports of fluid and solid, respectively. We may then obtain the particle density in each of the supports by the appropriate restriction of (3.24) to that set. The different densities form a sharp Gibbs interface. Clearly, at those Gibbs interfaces the sequence of finite-v expressions for the density *does not* converge. In the present work we are not investigating such reference system interfaces.

4. THE HYDROSTATIC/MEAN-FIELD LIMIT

The case of particles with both core and tail interactions, subject to an external continuous potential field $\phi(x)$, can be reduced essentially to the one of the previous section by using functional Laplace transform techniques for the weak attractive tail part. This is outlined in refs. 1, 13, and 14. We state first our main results and then present their proofs. Let us also stipulate the notation $\Omega(\mu, \beta; \Lambda; v)$ for $\Omega_{\mathrm{R,A},\phi}(\mu, \beta; \Lambda; v)$, etc., when all interactions are present.

The grand potential at finite voluminosity, $\Omega(\mu, \beta; \Lambda; v)$, is given by

$$\beta\Omega(\mu, \beta; \Lambda; v) = -\frac{1}{v} \ln \sum_{N \in \mathbb{N}_0} \frac{e^{\beta\mu N}}{N!} v^N \mathcal{Q}^{(N)}(\beta; \Lambda; v) \tag{4.1}$$

with

$$\mathcal{Q}^{(N)}(\beta; \Lambda; v) = \int_{\Lambda^N} \exp\{-\beta[U_{\mathrm{R}}^{(N)}(v^{1/3}X) + v^{-1}U_{\mathrm{A}}^{(N)}(X) + \Phi(X)]\}\, m(d^{3N}x) \tag{4.2}$$

Here,

$$U_{\mathrm{A}}^{(N)}(X) = \sum_{1 \leqslant i < j \leqslant N} V_{\mathrm{A}}(x_i - x_j) \tag{4.3}$$

The factor $1/v$ in front of U_{A} in the partition functions compensates for the nonextensive $\langle U_{\mathrm{A}}(X)\rangle \sim \langle N\rangle^2$, which results through our "hydrodynamic" scaling $v^{-1}\langle N\rangle \approx \text{const}$ (= physical "number" of particles in Λ), and $v^{-1}\langle U_{\mathrm{R}}^{(N)}(v^{1/3}X)\rangle \approx \text{const}$ (= physical internal potential energy of the reference system).

Theorem 4.1. The limit grand potential

$$\Omega(\mu, \beta; \Lambda) = \lim_{v \to \infty} \Omega(\mu, \beta; \Lambda; v) \tag{4.4}$$

exists and is given by

$$\Omega(\mu, \beta; \Lambda) = \min_{\varrho} G[\varrho] \tag{4.5}$$

where

$$G[\varrho] = \int_{\Lambda} \{-\tfrac{1}{2}\varrho(x)(V_{\mathrm{A}} * \varrho)(x) - p_{\mathrm{R}}[\mu_{\mathrm{loc}}(x), \beta]\}\, d^3x \tag{4.6}$$

with

$$\mu_{\mathrm{loc}}(x) = \mu - \phi(x) - (V_{\mathrm{A}} * \varrho)(x) \tag{4.7a}$$

$$(V_{\mathrm{A}} * \varrho)(x) = \int_{\Lambda} V_{\mathrm{A}}(x-y)\, \varrho(y)\, d^3y \tag{4.7b}$$

the minimum being taken with respect to the measures $\varrho \in C^0(\Lambda)^*$ [the notation $\varrho(x)$ is symbolic]. The grand canonical pressure $p(\mu, \beta; \Lambda) = -|\Lambda|^{-1}\, \Omega(\mu, \beta; \Lambda)$ is positive, and βp is convex as a function of both β and μ, and increasing in μ.

To obtain the particle density at given μ, β, Λ, and ϕ, we again have to take into account that $p_{\mathrm{R}}(\mu, \beta)$ may not be everywhere C^1, but may have kinks associated with first-order phase transitions of the underlying reference system's particle distributions. By convexity of $\mu \mapsto p_{\mathrm{R}}(\mu, \beta)$, at most countably many kinks can exist for a reference system, and by the known analyticity at small fugacity,[3] for each β there is a finite smallest such μ at which a kink can occur. Molecular dynamics simulations[29] indicate that solid–fluid phase transitions indeed do occur at high μ for various reference systems with repulsive interactions. The liquid–vapor transition typically exists for much lower values of μ for which $\mu \mapsto p_{\mathrm{R}}(\mu, \beta)$ does not have a kink. In that regime, $p_{\mathrm{R}}[\mu_{\mathrm{loc}}(x), \beta]$ is differentiable w.r.t. to the first entry variable for each $x \in \Lambda$.

Let the $\mu^{(k)}(\beta)$, $k = 1, 2, \ldots$, denote all points at which $\mu \mapsto p_{\mathrm{R}}(\mu, \beta)$ has a kink. We assume they can be ordered as $\mu^{(1)} < \mu^{(2)} < \cdots$. For given ρ, the corresponding level sets $\mu_{\mathrm{loc}}(x) = \mu - \phi(x) - (V_{\mathrm{A}} * \rho)(x) = \mu^{(k)}$ partition Λ into a countable set of disjoint open subsets $\Lambda^{(k)}$, $k = 1, 2, \ldots$, given by

$$\Lambda^{(k)} = \{x \in \Lambda \mid \mu_{\mathrm{loc}}(x) < \mu^{(k)}\} \backslash \overline{\Lambda^{(k-1)}} \tag{4.8}$$

with $\Lambda^{(0)} \equiv \varnothing$. Clearly, the closure of $\bigcup_k \Lambda^{(k)}$ is the closure of Λ.

Theorem 4.2. Let $\rho(x)$ be a particle density for which $G(\mu, \beta; \Lambda)[\rho]$ is the global minimum of G, given μ, β, Λ. In each subdomain $\Lambda^{(k)}$, $\rho(x)$ is a solution of

$$\rho(x) = \partial_\mu p_{\mathrm{R}}[\mu - \phi(x) - (V_{\mathrm{A}} * \rho)(x), \beta] \tag{4.9}$$

We have displayed $\mu_{\mathrm{loc}}(x)$ here to make it manifest that (4.9) is a nonlinear integral equation. It may typically have many solutions, not all of which are minimizers. If more than one global minimizer exists, the ensemble is sitting at a first-order phase transition. Each member system, however, has one of the globally minimizing densities. In case a reference system's phase transition is encountered, we face the interesting additional complication that with $(V_A * \rho)(x)$, hence $\mu_{\mathrm{loc}}(x)$, also $\Lambda^{(k)}$ is not known *a priori.* In that case (4.9) poses a free boundary problem.

We consider next the equation of state. Wherever the following limits exist, the average number of physical particles in Λ is defined as

$$\mathcal{N}(\mu, \beta; \Lambda) = \lim_{v \to \infty} v^{-1} \langle N \rangle_v \tag{4.10}$$

the overall interaction energy due to the power k term in (1.2) as

$$\mathcal{V}_{\mathrm{R},k}(\mu, \beta; \Lambda) = \lim_{v \to \infty} v^{-1} \langle U_{\mathrm{R},k}^{(N)}(v^{1/3} X) \rangle_v \tag{4.11}$$

where $U_{\mathrm{R},k}$ is defined in an obvious way analogously to (2.2), and the "cohesion" energy due to the tail interactions as

$$\mathcal{V}_{\mathrm{A}}(\mu, \beta; \Lambda) = \lim_{v \to \infty} v^{-2} \langle U_{\mathrm{A}}^{(N)}(X) \rangle_v \tag{4.12}$$

The grand ensemble average $\langle \cdot \rangle_v$ at parameter v is given by

$$\langle K(N, X) \rangle_v = e^{v\beta\Omega} \sum_{N \in \mathbb{N}_0} e^{\beta\mu N} N!^{-1} v^N \int_{\Lambda^N} K(N, X)\, \mathcal{M}_v^{(N)}(d^{3N}x) \tag{4.13}$$

the measure $\mathcal{M}_v^{(N)}(d^{3N}x)$ being the integrand of $\mathcal{Q}^{(N)}$.

Theorem 4.3. Given Λ and ϕ, for almost all μ and β the quantities $\mathcal{N}$, $\mathcal{V}_{\mathrm{R},k}$, and $\mathcal{V}_{\mathrm{A}}$ exist. In these cases the grand pressure satisfies the equation of state

$$|\Lambda|\, p = \mathcal{N} k_{\mathrm{B}} T + \mathcal{V}_{\mathrm{A}} + \sum_{k=4}^{K} \frac{k}{3} \mathcal{V}_{\mathrm{R},k} \tag{4.14}$$

We conjecture that the following is true also, and we outline a proof. However, a rigorous proof must be given in future work.

Conjecture 4.4. Under the same conditions as in Theorem 4.3, we have the identifications

$$\mathcal{N} = \int_{\Lambda} \rho(x)\, d^3x \tag{4.15}$$

$$\mathcal{V}_{\mathrm{A}} = \frac{1}{2} \int_{\Lambda} \int_{\Lambda} \rho(x)\, V_{\mathrm{A}}(x - y)\, \rho(y)\, d^3x\, d^3y \tag{4.16}$$

$$\sum_{k=4}^{K} \frac{k}{3} \mathcal{V}_{\mathrm{R},k} = \int_{\Lambda} \{ p_{\mathrm{R}}[\mu_{\mathrm{loc}}(x), \beta] - k_{\mathrm{B}} T \rho(x) \}\, d^3x \tag{4.17}$$

where ρ is a global minimizer of (4.6).

We come to the proofs of our results. To prove Theorem 4.1, we need the representation of a canonical equilibrium density for V_A in terms of Gaussian function space integrals.[30] We introduce a family of cutoffs $\chi^\varepsilon_\Lambda(x) \in C_0^\infty(\Lambda)$ which in Λ (an open set) converge pointwise from below to the characteristic function $\chi_\Lambda(x)$ of Λ as $\varepsilon \to 0$, and which deviate from χ_Λ only in a small shell of thickness ε. Now introduce the linear symmetric operator W_ε with integral kernel

$$W_\varepsilon(x, y) = -\chi^\varepsilon_\Lambda(x)\, \beta V_A(x-y)\, \chi^\varepsilon_\Lambda(y) \tag{4.18}$$

This operator maps distributions into $C_0^0(\Lambda)$, and therefore $C_0^0(\Lambda)$ into itself. W_ε is positive definite with positive inverse on $\mathrm{Ran}(W_\varepsilon)$. We can now construct a nested sequence of Hilbert spaces H_n. Each H_n is the completion of $C_0^\infty(\Lambda)$ w.r.t. to the canonical norm $\|u\|_n^2 = \langle u, (I + W_\varepsilon^{-1})^n u\rangle$, where $\langle \cdot, \cdot \rangle$ is the canonical $L^2(\Lambda)$ scalar product. The Hilbert space $H_\infty = \bigcap_{n=-\infty}^{\infty} H_n$ is a nuclear space which consists of C^∞ functions for W_ε^{-1}, and $H_{-\infty}$ is its weak dual (i.e., with respect to the pairing $\langle \cdot, \cdot \rangle$) which consists of the distributions for W_ε^{-1}.[30] By duality, elements of H_∞ are linear functionals on $H_{-\infty}$, i.e., $\Theta\colon f \mapsto \Theta(f) \in \mathbb{R}$ for $f \in H_\infty$.

By Minlos' theorem, there exists a mean-zero Gaussian measure $d\gamma_\varepsilon(\Theta)$ on $H_{-\infty}$ with mass 1,

$$\int d\gamma_\varepsilon(\Theta) = 1 \tag{4.19}$$

and covariance kernel $v^{-1} W_\varepsilon(x, y)$, so that

$$\int d\gamma_\varepsilon(\Theta)\, e^{-\Theta(f)} = e^{(1/2v)\langle f,\, W_\varepsilon f\rangle} \equiv S(f) \tag{4.20}$$

for $f \in H_\infty$. Here,

$$\langle f, W_\varepsilon f \rangle = \tfrac{1}{2} \iint f(x)\, W_\varepsilon(x, y)\, f(y)\, d^3x\, d^3y \tag{4.21}$$

The functional $S(if)$ is the characteristic functional of $d\gamma_\varepsilon$. The self-energy terms are taken care of by Wick ordering,

$$:e^{-\Theta(f)}: = e^{-(1/2v)\langle f,\, W_\varepsilon f\rangle} e^{-\Theta(f)} \tag{4.22}$$

Since $S(f)$ is continuous in its natural H_{-1} topology induced by $\langle \cdot, W_\varepsilon \cdot \rangle$, the measure $d\gamma_\varepsilon$ is concentrated on the subspace H_1 of $H_{-\infty}$. Since our W_ε is itself C_0^0, the space H_{-1} contains singular measures; thus H_1 is equivalent to functions which are themselves C^0. We may thus take $f \to \delta_x$, and we write $\beta\psi(x)$ for $\Theta(\delta_x)$. Choosing in particular $f \to \sum_{i=1}^{N} \delta_{x_i}$ yields the convenient representation

$$\exp[-(1/2v)\,\beta U_{\mathrm{A},\varepsilon}^{(N)}(X)] = \int d\gamma_\varepsilon(\Theta) \prod_{i=1}^{N} :\exp[-\beta\psi(x_i)]: \tag{4.23}$$

with

$$:\exp[-\beta\psi(x_i)]: = \exp[(1/2v)\,\beta V_{\mathrm{A}}(0)\,\chi_\Lambda^\varepsilon(x_i)^2 - \beta\psi(x_i)] \tag{4.24}$$

where the additional subscript ε at U_{A} indicates that $\chi_\Lambda^\varepsilon(x)\,V_{\mathrm{A}}(x-y)\,\chi_\Lambda^\varepsilon(y)$ is used instead of V_{A}. In the following, a subscript ε will stand for exactly this replacement.

Proof of Theorem 4.1. Using (4.23), we write

$$\beta\Omega_\varepsilon(\mu, \beta; \Lambda; v) = -\frac{1}{v} \ln \int d\gamma_\varepsilon(\Theta) \sum_{N \in \mathbb{N}_0} \frac{e^{\beta\mu N}}{N!} v^N \mathcal{Q}_{\mathrm{R}, \Upsilon_\varepsilon}^{(N)}(\beta; \Lambda; v) \tag{4.25}$$

which states that $\exp(-v\beta\Omega_\varepsilon)$ is a Gaussian average of grand canonical partition functions, each of which represents a reference system in a given external continuous potential field

$$\Upsilon_\varepsilon(x) = \phi(x) + \psi(x) - (1/2v)\,V_{\mathrm{A}}(0)\,\chi_\Lambda^\varepsilon(x)^2 \tag{4.26}$$

i.e.,

$$\beta\Omega_\varepsilon(\mu, \beta; \Lambda; v) = -\ln\left\{\int d\gamma_\varepsilon(\Theta) \exp(-v\beta\Omega_{\mathrm{R}, \Upsilon_\varepsilon}[\mu, \beta; \Lambda; v])\right\}^{1/v} \tag{4.27}$$

Because the covariance $\sim v^{-1}$, the Gaussian measure concentrates sharply as $v \to \infty$. Formally we have

$$d\gamma_\varepsilon(\Theta) = \exp[-(v/2)\langle \beta\psi, W_\varepsilon^{-1} \beta\psi\rangle]\, D\psi$$

Taking the limit $v \to \infty$ gives

$$\lim_{v \to \infty} \Omega_\varepsilon(\mu, \beta; \Lambda; v) = \inf_\psi \left\{\frac{\beta}{2}\langle \psi, W_\varepsilon^{-1} \psi\rangle + \Omega_{\mathrm{R}, \phi+\psi}(\mu, \beta; \Lambda)\right\} \tag{4.28}$$

We show the infimum is a minimum. We need only control the asymptotic behavior of $\Omega_{\mathrm{R},\phi+\psi}$ as ψ becomes large negative, because then $\Omega_{\mathrm{R},\phi+\psi}$ becomes large negative, too. For our reference systems, a scaling argument reveals that the free energy density (2.17) scales as $f_{\mathrm{R}}(\rho) \sim \rho^\alpha$ at large density ρ, with $\alpha > 2$. By convex duality, $p_{\mathrm{R}}(\mu) \sim \mu^{\alpha^*}$, with

$1/\alpha + 1/\alpha^* = 1$ for μ large, whence $p_R(\mu) = o(\mu^2)$ for μ large. Thus $\Omega_{R,\phi+\psi} = o(\|\psi\|^2_{L^2})$ for ψ large negative. Since $\langle f, W_\varepsilon f\rangle^{1/2} \leqslant \|W_\varepsilon\|_\infty \|f\|_{L^2}$, by topological duality the norm $\langle \psi, W_\varepsilon^{-1}\psi\rangle^{1/2}$ dominates the L^2 norm of ψ. Hence our functional is continuous and coercive in the norm $\langle \psi, W_\varepsilon^{-1}\psi\rangle^{1/2}$, whence a finite minimum of (4.28) exists.

For any $\psi \in H_{-\infty}$,

$$\psi(x) = \chi^\varepsilon_\Lambda(x)(V_A * [\chi^\varepsilon_\Lambda \varrho])(x) \tag{4.29}$$

has the inverse in H_∞

$$\varrho(x) = -\beta W_\varepsilon^{-1}[\psi](x) \tag{4.30}$$

In general, ϱ here need not be positive. We can thus eliminate ψ in (4.28) in favor of ϱ. Because V_A is C^0, we may let ϱ be a (signed) measure and use the topology of weak* convergence (for ϱ). The functional in braces in (4.28) becomes then our (4.6).

Finally, we have to let $\varepsilon \downarrow 0$. Clearly, $W_\varepsilon \uparrow -\beta V_A$, and monotone convergence proves part one of Theorem 4.1.

The convexity and monotonicity properties follow immediately from the fact that for finite v, $\Omega(v)$ has these properties. Q.E.D.

Proof of Theorem 4.2. By the piecewise differentiability of $\mu \mapsto p_R(\mu, \beta)$, the global minimum is a stationary point of $G[\varrho]$ with respect to infinitesimal w^* variations of ϱ that leave the $\mu^{(k)}$ level sets unchanged (the converse is generally not true). Upon taking the w^* functional derivative of $G[\varrho]$ with respect to the $\mu^{(k)}$ level set preserving ϱ, we find our hydrostatic/mean-field equation for the stationary points ϱ_{stat}. Clearly, by (4.9) and the monotonic increase of p_R with μ, any solution of (4.9) is positive. Since $-|\Lambda|^{-1}\Omega = p$ is the grand pressure, and $\mu - \phi - V_A * \varrho$ the local chemical potential for p_R, the local thermodynamic relation $\rho = \partial_\mu p$ now shows that the minimizing ϱ is indeed the particle density ρ. Q.E.D.

We remark that when a unique minimizer exists (absence of a first-order phase transition), at points of μ differentiability of p_R the sequence of finite-v densities converges to the globally minimizing solution of (4.9). This can be established by convexity arguments. At points of phase transition, the finite-v densities generally do not converge to a single minimizer.

Proof of Theorem 4.3. The equation of state follows from de l'Hospital's rule and the characterization of the limit pressure by the variational principle, Theorem 4.1. Knowing that the limit $v \to \infty$ exists for $\Omega(v)$, and from the fact that $\Omega(v)$ is differentiable, we obtain by de l'Hospital

$$-\Omega(\mu, \beta; \Lambda) = \lim_{v \to \infty} v^{-1} \langle N k_B T - v\, \partial_v U_R^{(N)}(v^{1/3} X) + v^{-1} U_A^{(N)}(X) \rangle_v \qquad (4.31)$$

For U_R we substitute (1.2). Since $-\Omega(\mu, \beta; \Lambda, v)$ is convex in μ, $\sigma_R^{(k)}$, and σ_A separately, the same is true for its limit $v \to \infty$. Therefore, given ϕ and Λ, for almost all μ, β the individual limits (4.10)–(4.12) exist as derivatives of $-\Omega(\mu, \beta; \Lambda)$ with respect to either μ or one of the coupling constants. By linearity of the finite-v expectation functional we can thus replace (4.31) by (4.13) wherever the individual limits exist. Q.E.D.

We finally outline a proof of Conjecture 4.4. The identification of $\mathcal{N}$ with $\int \rho$ is correct by Theorem 4.2. The identification of $\mathcal{V}_A$ with the bilinear form $(1/2) \int \rho V_A * \rho$ is more subtle. By assumption, the individual limits exist and so we are not at a first-order phase transition. Therefore a unique global minimum exists. In the limit $v = \infty$, the space of infinite sequences of exchangeable measures carries the weak limit points of the finite-v n-particle densities. By de Finetti's theorem, all limit measures are expressible as averages of product measures. In case of a unique global minimum the average *ought to be* a singleton, resulting in our identification for $\mathcal{V}_A$. The identification (4.17) now follows from the others and Theorem 4.1; clearly, (4.17) is the negative excess grand potential due to the short-range interactions.

5. ON THE PETIT- AND MICROCANONICAL ENSEMBLES

Our hydrostatic/mean-field limit is conceptually very close to the classical mean-field limits of refs. 15–19 and also to the quantum mean-field limits of Thomas–Fermi[20,21] and of Boltzmann type,[22] where local thermodynamics is always that of the ideal gas, modulo statistics. In particular, the works of Eyink and Spohn, Messer, and Thirring *et al.* discuss equivalence of micro and petit ensembles and show that, unlike the standard bulk limit, the ensembles are generally *not* equivalent in the neighborhood of a first-order phase transition. The reason is simply that the microcanonical ensemble may contain a region with the "wrong" convexity of the entropy as a function of the energy. Although the canonical ensemble is still obtained from the microcanonical one via the Legendre transformation (2.11), with S_R replaced by the relevant entropy function of the mean-field limit, it is not generally true that the microcanonical ensemble is obtained from the canonical one by the inverse of (2.11). Indeed, the region with the wrong convexity of $S(E)$ is a region with negative specific heat and is bridged by a first-order phase transition in the canonical ensemble, obtained correctly from the Legendre transform $S(E) \to \beta F(\beta)$. The inverse Legendre transform $\beta F(\beta) \to \mathrm{conv}[S(E)]$ gives the convex hull of the original $S(E)$. The region of negative specific heat is not recovered, but replaced by a straight line.

Although we have not rigorously constructed the canonical and the microcanonical counterparts of our grand-canonical hydrostatic/mean-field limit, we firmly believe that the same principles as found by Eyink and Spohn and others relate the various ensembles here, too. In the following we assume this is true. The hydrostatic/mean-field limits in the petit and the microcanonical ensembles are then *not* obtained from the limit of the grand canonical ensemble. However, they *are* obtained from the functionals defining the grand ensemble limit if we go beyond the global minimizers of (4.6) and consider all stationary points of (4.6). This brings multiple-valued mappings with it. Hence, we need to be slightly more pedantic with the notation.

For all solutions $\rho(x; \mu, \beta)$ of (4.9), we compute $\tilde{G}(\mu, \beta) = G[\rho(x; \mu, \beta)]$. Notice that $\tilde{G}$ is a multiple-valued map of its arguments whenever (4.9) has several solutions for the same β and μ. However, locally each branch of $\tilde{G}$ is well defined and differentiable w.r.t. μ and β modulo a set of singular exceptional points. For each branch of $\tilde{G}$, we define the (locally) unique function

$$\tilde{N}_A(\mu, \beta) = -\partial_\mu \tilde{G}(\mu, \beta) \tag{5.1}$$

wherever the derivative exists, and the (locally) unique function

$$\tilde{F}(\mu, \beta) = \tilde{G}(\mu, \beta) + \mu \tilde{N}_A(\mu, \beta) \tag{5.2}$$

Clearly, viewed globally as functions of μ and β, both $\tilde{N}_A$ and $\tilde{F}$ are multiple-valued. For each μ, β local branch, we now eliminate, via (5.1) and (5.2), the variable μ in favor of a new variable N_A. Set $N_A = \tilde{N}_A(\mu, \beta)$ locally, which upon inversion for fixed β gives $\mu = \tilde{N}_A^{-1}(N_A, \beta)$ locally. Inserting this in (5.2) defines locally a new function $\hat{F}(N_A, \beta)$. When viewed globally, $\hat{F}$ in general is a multiple-valued function of its arguments. The free energy F of the canonical ensemble is then determined by

$$F(N_A, \beta) = \min \hat{F}(N_A, \beta) \tag{5.3}$$

where the minimum is taken with respect to the various branches of $\hat{F}$ for given values of N_A and β. The corresponding canonical particle densities are solutions of (4.9) for which the free energy is the global minimum in the sense of (5.3).

In a similar way the microcanonical ensemble is found. For each branch of the multiple-valued $\hat{F}(N_\Lambda, \beta)$ we define locally

$$\hat{E}(N_\Lambda, \beta) = \partial_\beta \beta \hat{F}(N_\Lambda, \beta) \tag{5.4}$$

where the partial derivative is to be understood for fixed N_Λ, and also

$$k_{\mathrm{B}}^{-1} \hat{S}(N_\Lambda, \beta) = \beta \hat{E}(N_\Lambda, \beta) - \beta \hat{F}(N_\Lambda, \beta) \tag{5.5}$$

Globally these are in general multiple-valued mappings. Locally we introduce a new variable via $E = \hat{E}(N_\Lambda, \beta)$, which can be inverted for fixed N_Λ to give $\beta = \hat{E}^{-1}(E, N_\Lambda)$. Inserting this in (5.5) defines locally a new function $\check{S}(N_\Lambda, E)$. Viewed globally, $\check{S}(N_\Lambda, E)$ might be a multiple-valued function of its arguments. The entropy of the microcanonical ensemble is determined by

$$S(N_\Lambda, E) = \max \check{S}(N_\Lambda, E) \tag{5.6}$$

where the maximum is taken with respect to the various branches of $\check{S}$ for given values of N_Λ and E. The microcanonical particle densities are those solutions of (4.9) which generate $S(N_\Lambda, E)$.

6. HARD BALLS WITH $-r^{-6}$ INTERACTIONS

We now study the nonlinear hydrostatic/mean-field equation (4.9), assuming a reference system of many hard balls of volume $|b| = 4\pi a^3/3$. They interact with $V_A(r)$ given by (1.3), which behaves as $\sim -r^{-6}$ for large r, thus mimicking attractive van der Waals interactions. These specifications allow us to prove some quantitative estimates which can be tested against particle simulation data. Most of our results in this section are, however, obtained by numerically solving (4.9). We also intend to compare our results with measured data of the noble gases in some future work. For this purpose we include here the quantum of phase volume h^3 in the usual heuristic manner. We set $\phi \equiv 0$ in most of the following. However, if one wants to take wetting or nonwetting of the container walls into account, $\phi \neq 0$ is necessary. We stress that several of our qualitative statements will not sensitively depend on our choice of p_{R} and V_{A}.

6.1. Hydrostatics of the Reference System

In the fluid phase of the hard-ball reference system, a very good and also handy approximation for the pressure $p_{\mathrm{R}}(\mu, \beta)$ is given in parameter representation,

$$|b|\ \beta p_{\mathrm{R}}=\frac{\eta+\eta^2+\eta^3-\eta^4}{(1-\eta)^3}\equiv g_1(\eta) \tag{6.1}$$

$$\ln \zeta \equiv \beta\mu-\ln\frac{\lambda^3}{|b|}=\ln \eta+\frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3}\equiv g_2(\eta) \tag{6.2}$$

with $0\leqslant \eta\leqslant \eta_F<0.5$. We shall call ζ the effective fugacity. The particle density of the reference system

$$\rho_{\mathrm{R}}(\mu)=\partial_\mu p_{\mathrm{R}}(\mu) \tag{6.3}$$

and the auxiliary quantity η are related by

$$|b|\ \rho_{\mathrm{R}}=\eta=g_2^{-1}(\ln \zeta) \tag{6.4}$$

whence η is a dimensionless particle density. The few known terms of the virial expansion for the exact equation of state of a hard-ball fluid are reproduced by (6.1) to within a few percent, and it has been reported to deviate from the numerical simulation data by less than 1 % over the whole fluid range $0<\eta<\eta_F\approx\eta_*=0.49$.[31,32,29]

The numerical fit alone is not enough, though, to be acceptable as a thermodynamic pressure. The gap is filled by the following.

Proposition 6.1. Extend the representation (6.1), (6.2) to all $\eta\in(0,1)$. Then the mappings $\mu\mapsto p_{\mathrm{R}}(\mu,\beta)$ and $\beta\mapsto\beta p_{\mathrm{R}}(\mu,\beta)$ are positive, convex, and C^∞ for all $\mu\in\mathbb{R}$ and all $\beta\in\mathbb{R}^+$. The first one is also increasing.

Proof. For $\eta\in(0,1)$, the mapping $\eta\mapsto g_1(\eta)$ is C^∞, positive, increasing by $\partial_\eta g_1>0$, and convex by $\partial_{\eta\eta} g_1>0$. For $\eta\in(0,1)$, the mapping $\eta\mapsto g_2(\eta)$ is C^∞, onto $\mathbb{R}$, and by

$$\partial_\eta g_2(\eta)=\frac{1}{\eta}\partial_\eta g_1(\eta)>0 \tag{6.5}$$

also increasing. As such, the inverse mapping $\eta=g_2^{-1}[\ln\zeta]$ is well defined, positive, and increasing. Therefore the mapping

$$\beta\ |b|\ p_{\mathrm{R}}(\mu,\beta)=g_1(g_2^{-1}[\ln\zeta]) \tag{6.6}$$

is C^∞, positive, increasing in μ, and convex in both variables. Q.E.D.

The restriction to the regime $\eta<\eta_F$ gives therefore acceptable functions $\beta p_{\mathrm{R}}(\mu,\beta)$ and $\rho_{\mathrm{R}}=\partial_\mu p_{\mathrm{R}}(\mu,\beta)$. They both share with the exact expressions of a hard-ball fluid a dependence on μ and β only through the

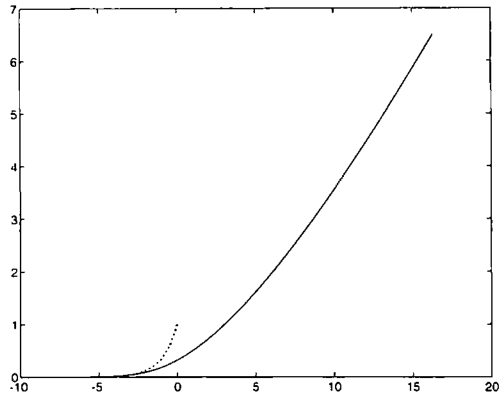

Fig. 1. The dimensionless pressure $\beta\,|b|\,p_R$ of a hard-ball system without attractive interactions as a function of $\ln\zeta$. The dotted curve gives the asymptotic low-density law of the ideal Boltzmann gas.

combination $\ln\zeta = \beta\mu - \ln(\lambda^3/|b|)$; see (6.2). We take η_* as definition of the maximal fluid density, for which $\ln\zeta = 15.208...$.

For comparison with later results, we display the pressure and the density of the hard-ball fluid without attractive interactions as functions of the logarithm of the fugacity in Fig. 1 and 2, respectively.

We see in Fig. 2 that there is a point of maximum slope for the map $\ln\zeta \mapsto \eta$. We shall make use of this fact by proving the uniqueness of the high-temperature phase. Our observation is made precise by the following:

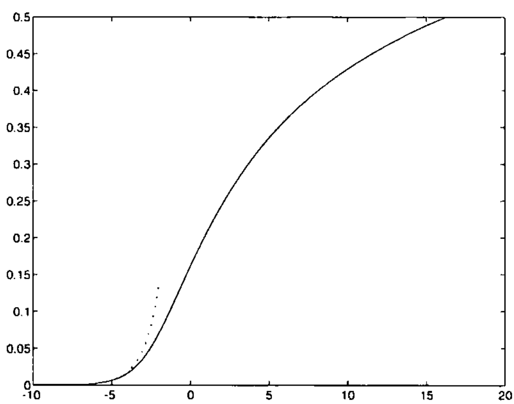

Fig. 2. The dimensionless density $\eta = |b|\,\rho_R$ of a hard-ball system without attractive interactions as a function of $\ln\zeta$, together with the low-density law of the ideal Boltzmann gas.

Proposition 6.2. For $p_R(\mu, \beta)$ defined by (6.1), (6.2), a global maximum of $\partial_{\mu\mu} p_R$ occurs for

$$\ln \zeta_M = -0.67244 \tag{6.7}$$

at which

$$\eta_M \equiv g_2^{-1}(\ln \zeta_M) = 0.130444 \tag{6.8}$$

and

$$\partial_{\mu\mu} p_R|_{\mu_M} = 0.047164\,|b|^{-1}\,\beta \tag{6.9}$$

where $\mu_M(\beta)$ is related to $\ln \zeta_M$ by (6.2).

Proof. For convenience we extend (6.1), (6.2) to all $\eta \in (0, 1)$. By (6.6), a maximum of $\partial_{\mu\mu} p_R(\mu)$ corresponds to an η at which $\partial_\eta g_2(\eta)$ takes a minimum. By

$$\lim_{\eta \downarrow 0} \partial_\eta g_2 = +\infty = \lim_{\eta \uparrow 1} \partial_\eta g_2 \tag{6.10}$$

and the continuity of (6.2), a global minimum of $\partial_\eta g_2(\eta)$ exists for some $\eta \in (0, 1)$, at which $\partial_{\eta\eta} g_2(\eta) = 0$. This happens at a fixed point in (0, 1) of

$$\eta \mapsto \left[\frac{1}{6}\frac{(1-\eta)^5}{5-\eta}\right]^{1/2} \tag{6.11}$$

This mapping is a contraction on (0, 1), whence a unique and stable fixed point exists and is easily found via iteration. It is given by (6.8). Therefore the global maximum sits in the fluid regime. The rest of our claim now follows. Q.E.D.

We are chiefly interested in the fluid regime. However, to determine the global minimizers of $G[\varrho]$ which are all-fluid, we have to control the solid regime to some extent, too. Equation (6.1) is not a good approximation to the equation of state for $\eta_F < \eta < \eta_{cp}$, with η_{cp} the normalized close packing density for hard spheres. Between η_F and some $\eta_S \approx 0.54$ there seems to be a coexistence region for a solid–fluid phase transition.[33] For $\eta > \eta_S$, g_1 and g_2 have to be replaced by g_3 and g_4, say. In particular, $g_4(\eta)$ has to be larger than 15.208..., monotonic increasing, and diverge $\uparrow +\infty$ for $\eta \uparrow \eta_{cp}$. This is all we need know about the solid regime; we do not have to specify $p_R(\mu, \beta)$ in the solid regime of the reference system.

6.2. The Hydrostatic/Mean-Field System

We now discuss the complete system. Solutions of interest for fluid studies exist in a restricted (μ, β) regime. Since we do not specify $p_{\mathrm{R}}(\mu, \beta)$ in the solid regime, we can identify the global minimizers of $G[\varrho]$ only in an even smaller domain of the (μ, β) plane for which we are sure that no solution exists which is not all-fluid. In the next proposition we summarize two results which discriminate the fluid from the solid phase. For their proofs, see ref. 34.

Proposition 6.3. Let $p_{\mathrm{R}}(\mu, \beta)$ be given by (6.1), (6.2). Let $V_{\mathrm{A}}(r)$ be given by (1.3). Let Λ be a ball of radius R, with $R \gg r_0$. Let β be given. Then at least one all-fluid solution of (4.9) exists for

$$\ln \zeta < 15.2 - \frac{\pi^2}{8} \frac{\beta \sigma_{\mathrm{A}}}{|b|\, r_0^3} + O\left(\frac{r_0}{R}\right) \tag{6.12}$$

For

$$\ln \zeta < 15.2 - \frac{3\pi^2}{16} \frac{\beta \sigma_{\mathrm{A}}}{|b|\, r_0^3} + O\left(\frac{r_0}{R}\right) \tag{6.13}$$

no solution of (4.9) exists which is not all-fluid.

Having thus sorted the solids from the fluids, we are finally ready to inquire into the fluid regime. We begin with the following more general result.

Theorem 6.4. Let $\mu \mapsto p_{\mathrm{R}}(\mu, \beta)$ be the positive, increasing, and convex pressure of a reference system [not necessarily (6.1), (6.2)], and let $\partial_{\mu\mu} p_{\mathrm{R}}$ have a global maximum at $\mu = \mu_M$ with respect to those μ for which the reference system is in the fluid phase. Let $\partial_{\mu\mu} p_{\mathrm{R}}(\mu_M, \beta) = M(\beta)$ be the global maximum. If

$$M(\beta)\, \| V_{\mathrm{A}} * 1 \|_{L^\infty} < 1 \tag{6.14}$$

then there is at most one solution of (4.9) with density entirely in the fluid regime of p_{R}.

Proof. Let (6.14) be true. Assume there are two solutions of (4.9), $\rho_1 \neq \rho_2$, both entirely in the fluid regime of the reference system. By the fact that they are solutions of (4.9), $\mu_{\mathrm{loc}}(x)_i = \mu - V_{\mathrm{A}} * \rho_i$, $i = 1, 2$, takes everywhere in Λ only values for which $p_R[\mu_{loc}(x)_i, \beta]$ is in the fluid regime. Let $-V_A * \rho_i = \psi_i$. Then

$$\begin{aligned}
\|\rho_2-\rho_1\|_{L^1} &= \int_\Lambda |\partial_\mu p_R(\mu+\psi_2, \beta) - \partial_\mu p_R(\mu+\psi_1, \beta)| \, d^3x \\
&= \int_\Lambda \left| \int_{\psi_1}^{\psi_2} \partial_{\mu\mu} p_R(\mu+t, \beta)\, dt \right| d^3x \\
&\leqslant \int_\Lambda \int_{\min\{\psi_1,\psi_2\}}^{\max\{\psi_1,\psi_2\}} \partial_{\mu\mu} p_R(\mu+t, \beta)\, dt\, d^3x \\
&\leqslant M(\beta) \int_\Lambda \int_{\min\{\psi_1,\psi_2\}}^{\max\{\psi_1,\psi_2\}} dt\, d^3x \\
&= M(\beta) \int_\Lambda |\psi_2-\psi_1| \, d^3x \\
&\leqslant M(\beta) \, \|V_A * 1\|_{L^\infty} \, \|\rho_2-\rho_1\|_{L^1}
\end{aligned} \tag{6.15}$$

which, by (6.14), is a contradiction. Hence, there is at most one solution entirely in the fluid phase. Q.E.D.

This implies the following result for the hard-ball fluid with r^{-6} interactions.

Corollary 6.5. Let $p_R(\mu, \beta)$, $V_A(r)$, Λ, and r_0/R be as in Proposition 6.3. Let

$$\frac{\pi^2}{80} \frac{\beta\sigma_A}{|b|\, r_0^3} < 1 + O\left(\frac{r_0}{R}\right) \tag{6.16}$$

Then, if in addition μ satisfies the bound (6.12), there exists a unique solution of (4.9) which is fluid everywhere in Λ. If μ satisfies even the bound (6.13), then the unique all-fluid solution is the only solution of (4.9), whence it is the global minimizer of $G[\varrho]$.

Proof. We want to prove Corollary 6.5 as a corollary to Theorem 6.4. For $p_R(\mu, \beta)$ given by (6.1) and (6.2), by Proposition 6.2, (6.9), we have with $0.047164 < 0.05$ the estimate

$$M(\beta) < 0.05\beta\, |b|^{-1} \tag{6.17}$$

The sup norm of $V_A * 1$ is obtained from

$$-\frac{4r_0^3}{\pi\sigma_A}(V_A * 1)(r) = \frac{2Rr_0(R^2 - r_0^2 - r^2)}{(R^2 + r_0^2 + r^2)^2 - 4R^2r^2} + \sum_{n=1}^{2} \arctan\left(\frac{R + (-1)^n r}{r_0}\right) \tag{6.18}$$

with $r = |\mathbf{x}|$. The maximum is taken for $r = 0$, giving

$$\frac{2r_0^3}{\pi\sigma_A}\|V_A * 1\|_\infty = \arctan\left(\frac{R}{r_0}\right) + Rr_0\frac{R^2 - r_0^2}{(R^2 + r_0^2)^2} = \frac{\pi}{2} + O\left(\frac{r_0}{R}\right) \tag{6.19}$$

With (6.19) and (6.17), Theorem 6.4, (6.14), gives (6.16) as an estimate for the critical temperature above which at most one all-fluid solution exists.

To be in the fluid phase, (6.12) has to be satisfied by μ, and if (6.13) is satisfied, there is no other solution at all. Finally, if (4.9) admits only one solution, and if this is all-fluid, this is necessarily the global minimizer, as the global minimum is then a regular critical point of $G[\varrho]$. Q.E.D.

We remark that for $r_0/R \ll 1$, the correction term in (6.19), whence in (6.16), is small and can be discarded. (For concreteness: $R = 1$ cm and $r_0 = 1$ Å, so that $R = 10^8 r_0$.)

The uniqueness regime at high temperature has an interesting physical interpretation, which is suggested by the fact that the second derivative $\partial_{\mu\mu} p_R(\mu, \beta)$ has a global maximum for a $\mu = \mu_M(\beta) < \mu_{SF}(\beta)$, where μ_{SF} stands for the solid–fluid phase transition. This signals a nearby maximum in the fluid compressibility $\kappa(\mu) = \rho_R(\mu)^{-2}\,\partial_{\mu\mu} p_R$. In other words, if the attractive tail interactions cannot compress the fluid sufficiently under conditions of maximum compressibility, no transition between states of different density can occur.

We mention here that in ref. 34 we have obtained a more general control over the solution structure of (4.9) for the system discussed here. Based on fixed-point theorems and monotone iteration arguments, we show uniqueness for the low-fugacity phase, determine a regime with multiple solutions, prove a condensation phase transition, and give estimates for the spinodal points. We are not going to discuss this further here, but instead refer to ref. 34.

6.3. Numerical Results

In addition to the analysis of the previous section we have integrated (4.9) numerically for the reference system given by (6.1) and (6.2) and with

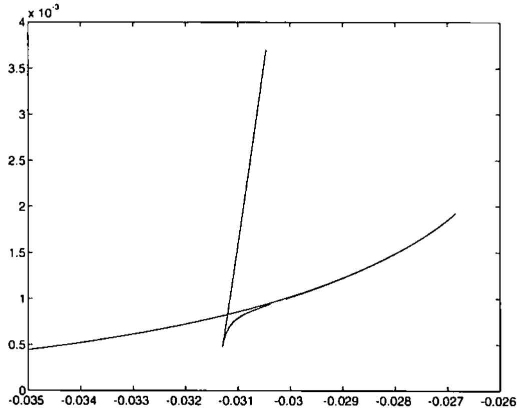

Fig. 3. For computed solutions ρ of (4.9), the negative dimensionless grand functional $-|\Lambda|^{-1}|b|\,\beta G[\rho]$ versus $\ln\zeta$. The proper grand ensemble is represented by the maximal part of the multiple-valued curve, which thus shows the dimensionless grand pressure $|b|\,\beta p$ as a function of $\ln\zeta$. The units are the same as in Fig. 1, for comparison. At the kink there is the traditional first-order condensation phase transition. The swallowtail structure is not accessible in the proper grand ensemble.

V_A given by (1.3). We have applied a combination of two complementary algorithms, both based on Picard and Newton iterations, to get the solutions in different parameter regimes. Details will appear elsewhere.[35] There is a critical set of parameters at which the different parts of the solution curve meet. There the convergence of both algorithms slows down

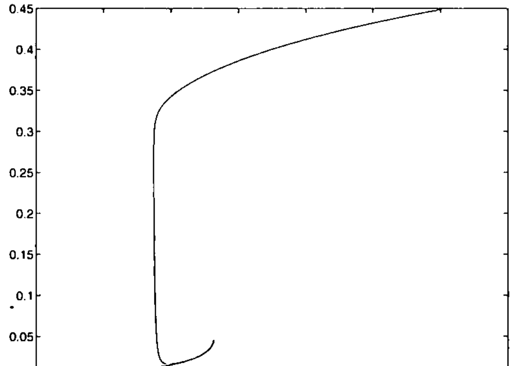

Fig. 4. For each computed solution of (4.9), $\bar{\eta}$ versus $\ln\zeta$. The horn at the right end of the lower branch actually consists of two nearby solution branches which merge smoothly in a turning point at the right tip. Units are as in Fig. 2, for comparison.

dramatically. We have stopped the calculations in a small neighborhood of the critical parameters. In some graphs there is therefore a small gap.

We have chosen a spherical container with radius equal to $50r_0$. This is of course much smaller than the typical $10^8 r_0$ that is relevant for experiments, but is roughly what can be handled numerically. We found that the interface structure depends very insensitively on its location in the container, which indicates that a realistically large domain will not alter the interface structure significantly. We have calculated a bifurcation sequence of (4.9) w.r.t. $\ln \zeta$ [see (6.2)] for $4\pi\beta\sigma_A/r_0^3\,|b| = 150$, which contains all radial decreasing stationary points of $G[\rho]$ for these parameters. To get a better feeling for the parameters, define an "almost critical" β_{acr} by setting left-hand side $(6.16) = 1$, i.e., $\pi^2\beta_{\mathrm{acr}}\sigma_A/|b|\, r_0^3 = 80$. Then our $\beta \approx 1.4726 \times \beta_{\mathrm{acr}}$, i.e., the temperature is somewhat below the almost critical one above which there is a unique solution for each μ. We have checked the quality of our estimate in Corollary 6.5 by performing a bifurcation run at $\beta' \approx 0.982\beta_{\mathrm{acr}}$, for which we did find a unique solution at each μ. However, the bifurcation diagram was quite steep in a certain range of μ, indicating the appearance of multiple solutions when β is increased somewhat beyond β_{acr}.

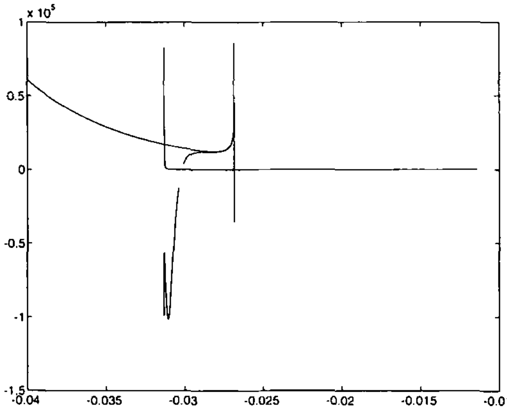

Fig. 5. The total mean compressibility κ of all solutions as a function of $\ln \zeta$. Two singularities, where the compressibility jumps from $-\infty$ to $+\infty$, correspond to the points with infinite slope in the previous diagram. These we call "spinodal points." The branch of pure vapor solutions enters from the left and is strictly convex and positive, diverging to $+\infty$ at the right spinodal point. The branch of the liquid solutions is also strictly convex and positive. It starts at $+\infty$ at the left spinodal point, drops quickly to almost zero, and leaves the figure to the right. Between the spinodal points is a third solution branch which is not convex and not everywhere positive. It comes from $-\infty$ at the left spinodal point and goes to $-\infty$ at the right spinodal point. It has three maxima and two minima. Clearly, the total compressibility takes on negative values on part of this branch.

We now discuss the grand ensemble first, starting with the thermodynamic functions (see Fig. 3–5).

Figures 3 and 4 are analogs of Fig. 1 and 2, respectively, now for the hard-ball system with attractive interactions. Notice that the figures show data for 'all' computed solutions of (4.9), i.e., not only for those which make up the grand ensemble. Notice also that the inclusion of attractive interactions now yields nonconstant particle densities $\rho(r)$. The quantities on the ordinate in Fig. 3 and 4 are mean quantities and do not give the local values at r. In particular, the dimensionless grand pressure $\beta\,|b|\,p$ is a mean quantity. The dimensionless mean density is $\bar{\eta} \equiv |\Lambda|^{-1} \int_\Lambda \eta\, d^3x$. Similarly, Fig. 5 shows the total mean compressibility κ for the computed solutions versus $\ln \zeta$. Notice that the compressibility is positive for the solutions which make up the grand ensemble. However, some solutions on the swallowtail structure have negative total compressibility. The points where κ diverges are called spinodal points.

We leave the thermodynamic functions and come to the particle densities. Figure 6 is a standard bifurcation diagram for (4.9).

In Fig. 7 and 8 we show the (radial) density profiles of various solutions. Obviously, the solutions which make up the grand ensemble (part of Fig. 7) are "wall-modified" traditional (=uniform) bulk phases. The large solution suffers a stronger distortion from uniformity, but the effect is confined to a small neighborhood of the container wall. Spinodal solutions are shown in Fig. 8. One of them has a more pronounced vapor atmosphere as compared to the stable liquid solution at the phase transition. In addition, there are completely unstable solutions, not shown here.

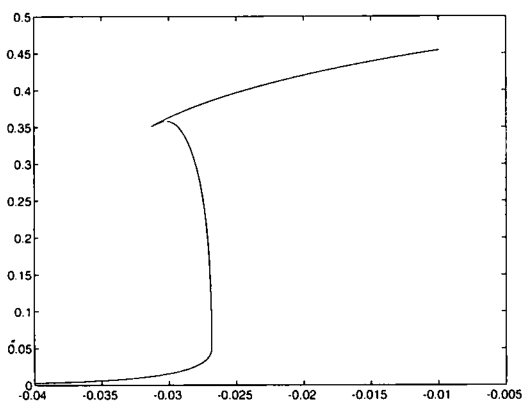

Fig. 6. The central dimensionless density $\eta(0)$ as a multiple-valued function of $\ln \zeta$. Left of the region with three solutions is the uniqueness regime of the vapor density solutions. To the right of the three-solutions regime is a uniqueness regime for large-liquid-density solutions. The condensation phase transition is situated in the three-solution regime.

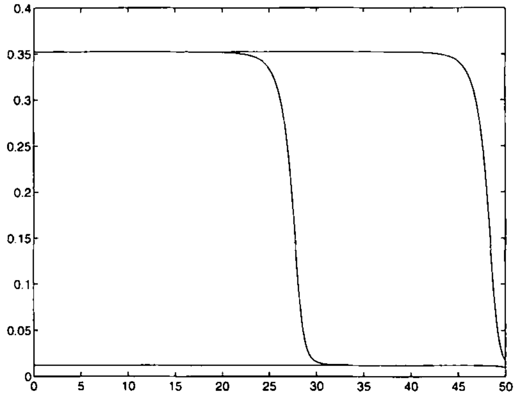

Fig. 7. The three solutions $\eta(r)$ of (4.9) which exist simultaneously at the point of condensation phase transition of the grand ensemble. The solutions are pointwise ordered; the small and the large ones are global minimizers of G for the same $\ln \zeta$ and β. The intermediate solution has proper interface structure, but sits on the swallowtail structure. It is grand canonically unstable.

We come to the generalized canonical bifurcation sequence and the canonical ensemble. We begin again with a thermodynamic function and discuss the free energy density as a function of the mean density (see Fig. 9). [Strictly speaking, since N_A should be an integer, our diagram should be read as a smooth interpolation of the discrete $F(N_A/|A|)$.]

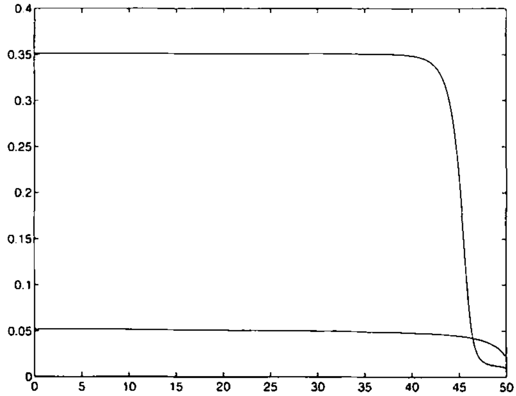

Fig. 8. The two solutions $\eta(r)$ which exist at the spinodal points. The low-density solution represents a strongly supersaturated vapor, the mainly high-density one represents a big liquid drop surrounded by a small vapor atmosphere. Both solutions mark the endpoints of the regions which contain local minimizers of G which are not global. These are presumably regions of metastability for the grand canonical contact conditions.

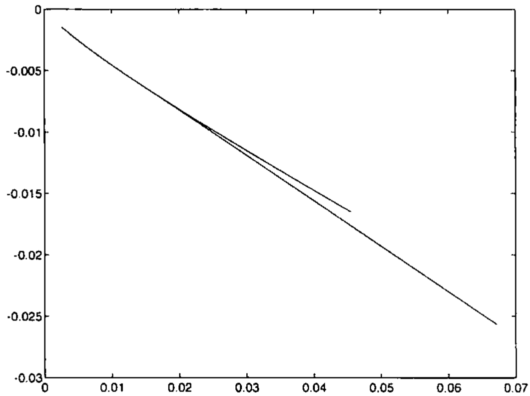

Fig. 9. For some computed solutions ρ of (4.9), the dimensionless free energy density functional $|b|\ \beta F[\rho]/|A|$ versus the mean density $\bar{\eta}$ for fixed β. Shown is only a small but interesting region of $\bar{\eta}$. The curve is not single-valued, but not really visible is the fact that it features a swallowtail structure. The branch which runs to the lower right contains proper interface solutions which merge smoothly with the liquid solutions way down to the lower right (outside the range shown). The pointwise minimal branch defines the proper canonical free energy density. The minimal curve has a kink at which a new phase transition of first order occurs.

The condensation phase transition of the grand ensemble appears as an almost straight portion of the free energy curve, running down to the right. Hardly visible here is the very interesting feature of "wrong convexity" of the canonical free energy in a certain range of $\bar{\eta}$ values. The corresponding states have negative total compressibility, as anticipated from Fig. 5. They are nevertheless stable in the canonical ensemble because no intrinsic number fluctuations of the system occur, and no fluctuations of the domain size. We call this "conditionally stable." The states with negative total compressibility are proper interface solutions (see below). They are "jumped" in the grand ensemble by the traditional condensation phase transition. Very interesting is also the new canonical phase transition of first order, which is embedded in the region of negative total compressibility. All this is better visible if we leave the thermodynamic functions and turn to the densities.

Figure 10 is the analog of Fig. 6. Now the bifurcation diagram for (4.9) shows $\eta(0)$ as multiple-valued function of $\bar{\eta}$. The canonically stable interfaces sit on the plateau. Notice that on the interface plateau, $\eta(0)$ in fact increases slightly with decreasing $\bar{\eta}$. The decreasing droplet volume means increasing curvature of the interfacial region which is responsible for the cohesive effect of the forces due to V_A. This compresses small droplets more than large ones and is in fact nicely seen in the diagram.

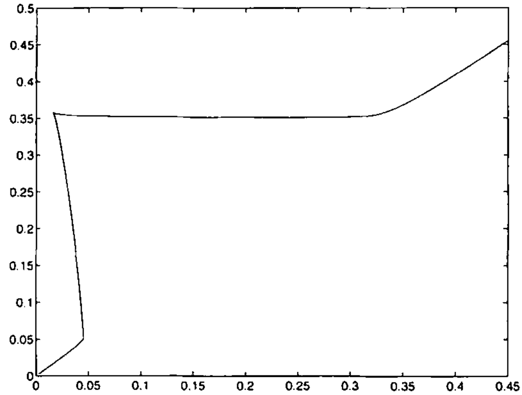

Fig. 10. Plot of $\eta(0)$ as a function of $\bar{\eta}$ for all solutions. For small and large $\bar{\eta}$, the solution curve is asymptotic to a straight diagonal line which would obtain for $V_A \equiv 0$. In an intermediate regime of $\bar{\eta}$, the cohesion due to V_A is too strong and forces the fluid to collapse to a liquid–vapor interface solution with high (liquid) density in the center and a vapor atmosphere. This is in the plateau regime. With increasing $\bar{\eta}$, the liquid drop simply grows in volume, almost without change of $\eta(0)$, until the container is filled with liquid. Any further increase of $\bar{\eta}$ will now increase $\eta(0)$.

Clearly seen in Fig. 10 is a three-solutions regime, which produces the swallowtail structure in the free energy diagram. In this region the new canonical phase transition happens. The canonical transition is different from the grand transition. A quasiuniform vapor solution and a droplet solution coexist; see Fig. 11, which is the analog of Fig. 7. Finally, Fig. 12

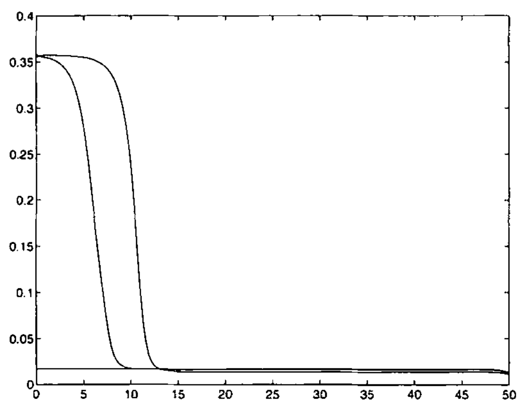

Fig. 11. The three solutions $\eta(r)$ which exist for the parameter values of the canonical phase transition. The vapor density solution and the drop-type solution with bigger radius are global minimizers of the free energy functional. They exist in the proper canonical ensemble. The droplike solution with smaller radius is canonically unstable and not accessible in the proper canonical ensemble

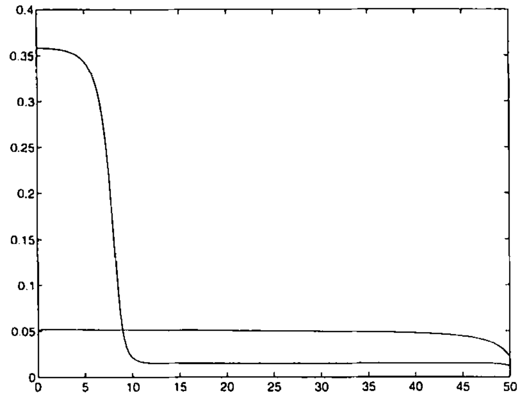

Fig. 12. The two solutions $\eta(r)$ which exist at the turning points (upper left and lower right) of the bifurcation graph (Fig. 10), which now are spinodal points under canonical contact conditions. The small one is clearly a supersaturated vapor. The large one is once more a droplet of liquid, surrounded by vapor. Both solutions represent the endpoints of domains where local minimizers of a canonical free energy functional (not constructed in this paper) exist which are not global.

is the analog of Fig. 8 and shows spinodal solutions under the canonical contact conditions.

We do not display diagrams for the microcanonical ensemble, but refer to ref. 35. However, we notice that the three solutions at the canonical phase transition mean that for these values of $N_A/|A|$ and β one also encounters the same phase transition point when we vary β and consider $N_A/|A|$ fixed. Generically, this transition therefore implies that the Legendre unfolding $\beta F \to S(E)$ will produce a region of negative specific heat in the microcanonical ensemble. If the van der Waals $-r^{-6}$ interactions are replaced by gravitational ones, then indeed there are ranges of N_A values where the diagram looks as expected here.[36] Regions with negative specific heat and negative compressibility are well known from simulations with finitely many particles in finite domains (see, e.g., ref. 29), and fall into the category "finite-size effects." An interesting aspect of our work is that such behavior does not vanish if one takes a continuum limit of infinitely many particles in a finite domain. We emphasize that it is such a limit which opens the possibility to speak properly of such objects as "thermodynamic states," "phase transitions," and the like.

We remark that a very brief speculation about a connection of the classical condensation phase transition with a region of negative specific heat in the microcanonical ensemble appeared in ref. 37 (see their last remark on p. 419). However, these authors seemed to have the bulk limit in mind, for which we know that no negative specific heat occurs. Nevertheless, our results show that their speculation came close.

Clearly, our results suggest some tempting conclusions regarding experiments with a real system. In an ideal situation one has a spherical container with a fixed number of particles not subjected to external gravity. In this case one may speculate that, under nonwetting conditions for the container walls, in the neighborhood of the canonical transition the predominant fluctuations are between a liquid drop surrounded by a vapor atmosphere and a quasiuniform gas state. In particular, we conjecture that wave scattering experiments should be able to confirm the existence of a "smallest droplet size" in the canonical setup.

For wetting conditions, the fluctuations may be rather between a gas phase and a vapor bubble immersed centrally in a liquid.[38] Further away from the canonical transition, in the plateau regime of Fig. 10, the system should always aim at staying stably in an interface structure, with relatively small fluctuations. The liquid drop as a whole, however, may easily wander about, as the vapor does not exhibit strong restoring pressure gradients.

7. ON VAN DER WAALS–MAXWELL–ORNSTEIN THEORY

We briefly show that we obtain the classical van der Waals–Maxwell–Ornstein theory from our finite-volume hydrostatic limit by performing a secondary singular scaling limit in which V_{A} tends to a Dirac delta function.

Although the variation in (4.5) can be taken for ϱ a measure (since V_{A} is continuous), we have seen from the Euler–Lagrange equation that the stationary points are continuous functions. For $V_{\mathrm{A}} = o(r^{-3})$ at infinity, we define

$$A = \int_{\mathbb{R}^3} V_{\mathrm{A}}(x)\, d^3x < 0 \tag{7.1}$$

For any given $\varrho \in C^0$, we can now take the limit

$$V_{\mathrm{A}}(x-y) \rightharpoonup A\delta(x-y) \tag{7.2}$$

in our functional $G[\varrho]$. In those cases where along with (7.2) the minimizer converges to a continuous function as well, we may exchange the limiting processes in the variational principle (4.5)–(4.7). This results in

$$\Omega^{(0)}(\mu, \beta) = \inf_{\varrho \in C^0} \int_{\Lambda} \left\{ -\frac{A}{2}\varrho^2(x) - p_{\mathrm{R}}[\mu - \phi(x) - A\varrho(x), \beta] \right\} d^3x \tag{7.3}$$

We consider the case without external ϕ. The continuous minimizers are now even constant in all of Λ. The infimum in (7.3) is taken for a subset of the solutions of

$$p = p_{\mathrm{R}}[\mu - A\rho, \beta] + \tfrac{1}{2}A\rho^2 \tag{7.4}$$

This is the grand canonical version of van der Waals' equation, with the modification of a more realistic local thermodynamic pressure (van der Waals took the equation of state of a one-dimensional system of hard rods, which becomes unrealistic in other dimensions at high densities). Equation (7.4), when extended to all values of constant ρ, produces the famous van der Waals loop with the artificial negative compressibility region. In our generalized grand canonical setup, such a negative compressibility loop shows up in the so-called swallowtail structure, similar to the one shown in Fig. 3. Clearly, this loop does not carry the continuous minimizers and is automatically avoided by (7.3). Also, this loop does *not* represent limit states of the hydrostatic/mean-field equation (4.9), but results from the additional restriction of the function space to the constant functions. No such restriction occurs in our setup; hence the reason for our swallowtail structure is in fact very different from the original van der Waals swallowtail, which is displayed in his thesis.[4]

We go even further and show that the original swallowtail structure of Fig. 3 shrinks to a point at the location of the kink in the limit (7.1), (7.2). To see this, notice that the infimum with respect to the constant densities is not necessarily the infimum with respect to the wider class of piecewise continuous functions. They do not belong to the function space $C^0 \ni \varrho$ for which our singular limit originally makes sense. However, since $\Omega^{(0)}$ may prefer nonuniform minimizing sequences under the right circumstances, we want to include the limit points of the minimizing sequence as real minimizers. We now have to extend the functional in (7.3) to this larger space. We do not present details, but notice that this actually does not present the right order of limits when one starts from our variational principle (4.5)–(4.7). However, it does give Ornstein's variational principle, in which the infimum of the functional in (7.3) is taken with respect to $\varrho \in L^\infty$. We now notice that at $\mu_{LG}^{(0)}$, indeed all

$$\rho_{\mathrm{LG}} = \rho_{\mathrm{L}} \chi_{\Lambda_{\mathrm{L}}} + \rho_{\mathrm{G}} \chi_{\Lambda_{\mathrm{G}}} \tag{7.5}$$

with

$$\Lambda_{\mathrm{L}} \cup \Lambda_{\mathrm{G}} = \Lambda; \qquad \Lambda_{\mathrm{L}} \cap \Lambda_{\mathrm{G}} = \varnothing \tag{7.6}$$

are global minimizers of Ornstein's variational principle, too. The proof is elementary and omitted. Clearly, the minimization problem is hopelessly degenerate, which is a result of the wrong order of limits. The degeneracy disappears if we take the correct order. This shows that the presence of the container walls allows the weak but finite-range tail interactions to introduce a separation of the bulk phases, i.e., we have a kind of symmetry breaking. In fact, a Schwartz symmetrization argument shows that a minimizer has to be radial symmetric and decreasing, excluding the possibility of a quasirandom distribution of the two density levels of the bulk system.

Therefore, at $\mu = \mu_{\mathrm{LG}}^{(0)}$ the density jumps from the liquid density level

$$\rho_{\mathrm{L}} = -\partial_{\mu}^{+} \Omega^{(0)} \tag{7.7a}$$

to the gas density level ρ_{G}

$$\rho_{\mathrm{G}} = -\partial_{\mu}^{-} \Omega^{(0)} \tag{7.7b}$$

but all intermediate mixtures coexist as well.

For further discussions of the classical van der Waals–Maxwell–Ornstein theory see ref. 10. It should be remarked that in these and the works of Kac, Uhlenbeck, Hemmer, Lebowitz, and Penrose, the van der Waals–Maxwell theory was obtained by taking first the standard infinite-volume thermodynamic limit, then second the scaling limit for the weak tail interaction such that the range of V_{A} is sent to infinity and its strength goes to zero. In our finite-volume setup, the situation is clearly different.

8. OPEN PROBLEMS

We conclude with a brief list of open questions which should be answered in subsequent works. First of all, on the level of the hydrostatic/mean-field limit, it is of interest to construct the limit rigorously for the canonical and the microcanonical ensemble. Its evaluation should confirm our numerical results about the regions of negative compressibility and negative specific heat. A further important point is, of course, the quantitative comparison of the limit results with real or at least simulated data. In this respect, further numerical integration of our equations is of interest,[35] as done for gravitational rather than van der Waals interactions in ref. 36. A quantum version of our limit should be possible, too; cf. Lieb's[39] treatment of the uniform van der Waals–Maxwell theory.

Somewhat more challenging is the question of fluctuations. Previous considerations revealed some ambiguities,[13,14] but were also not rigorous. We expect that our setup allows us to construct a type of "central limit theorem" or its analog, and to clarify the nature of the equilibrium fluctuations around the hydrostatic/mean field states with liquid–vapor structure. Here an open question is whether the fluctuations are Gaussian or not. We hope to come back to this in a future work.

Finally, the interface dynamics should be addressed on a rigorous as well as numerical level. For recent progress in this respect see the preprint of De Masi *et al.* (see Note Added).

Note Added. When writing up our results, we received a preprint by A. De Masi, E. Orlandi, E. Presutti, and L. Triolo, Glauber evolution with Kac potentials. In their notable paper, Ising systems with finite-range potentials are studied with probabilistic methods in a related mean-field limit for lattice systems, performed after the bulk limit has been taken. We thank Anna De Masi for sending us their work prior to publication, and for some interesting discussions. In this context, we also learned of the work by M. Cassandro, E. Orlandi, and E. Presutti [Interfaces and typical Gibbs configurations for one-dimensional Kac potentials, *Prob. Theory Rel. Fields* **96**:57–96 (1993)], which discusses the distribution of 1D Ising interfaces in this limit.

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REFERENCES

1. J. K. Percus, in *The Liquid State of Matter*, E. W. Montroll and J. L. Lebowitz, eds. (North-Holland, Amsterdam, 1982).
2. M. H. Kalos, J. K. Percus, and M. Rao, *J. Stat. Phys.* **17**:111 (1977).
3. D. Ruelle, *Statistical Mechanics: Rigorous Results* (Benjamin, New York, 1969).
4. J. D. van der Waals, De Continuiteit van den Gas- en Vloeistoftoestand, Doctoral thesis, University of Leiden (1873) [English transl. in *Studies in Statistical Mechanics XIV*, J. L. Lebowitz and J. S. Rowlinson, eds. (North-Holland, Amsterdam, 1988)].
5. J. C. Maxwell, *Nature* **11**:358 (1875); *J. Chem. Soc.* **13**:493 (1875) [reprinted in *Scientific Papers*, Dover, New York].
6. L. S. Ornstein, Toepassing der Statistische Mechanica van Gibbs op molekulair-theoretische vraagstukken, Doctoral thesis, University of Leiden (1908).
7. M. Kac, *Phys. Fluids* **2**:8 (1959).
8. M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* **4**:216 (1963).
9. J. L. Lebowitz and O. Penrose, *J. Math. Phys.* **7**:98 (1966).
10. P. C. Hemmer and J. L. Lebowitz, in *Phase Transitions and Critical Phenomena*, Vol. 5b, C. Domb and M. S. Green, eds. (Academic Press, London, 1976).
11. J. K. Percus, *Trans. N. Y. Acad. Sci.* **26**:1062 (1964).
12. N. G. van Kampen, *Phys. Rev.* **135**:A362 (1964).
13. J. K. Percus, *Int. J. Quant. Chem.* **16**:33 (1982).
14. J. K. Percus, *J. Stat. Phys.* **52**:1157 (1988).
15. J. Messer and H. Spohn, *J. Stat. Phys.* **29**:561 (1982).
16. G. Eyink and H. Spohn, *J. Stat. Phys.* **70**:833 (1993).
17. S. Kusuoka and Y. Tamura, *J. Fac. Sci. Tokyo Univ.* **31**:223 (1984).

18. M. K.-H. Kiessling, *Commun. Pure Appl. Math.* **47**:27 (1993).
19. E. Caglioti, P. L. Lions, C. Marchioro, and M. Pulvirenti, *Commun. Math. Phys.* **143**:501 (1992).
20. W. Thirring, *Lehrbuch der Mathematischen Physik 4* (Springer, Vienna, 1980).
21. J. Messer, *Temperature-Dependent Thomas–Fermi Theory* (Lecture Notes in Physics 147, Springer, Berlin, 1981).
22. N. Angelescu, M. Pulvirenti, and A. Teta, *J. Stat. Phys.* **74**:147 (1994).
23. M. E. Fisher, *Arch. Rat. Mech. Anal.* **17**:377 (1967).
24. D. Ruelle, *Helv. Phys. Acta* **36**:183 (1963).
25. R. Dobrushin, *Teorija Verojatn. i ee Prim.* **9**:626 (1964).
26. J. Fröhlich and Y. M. Park, *J. Stat. Phys.* **23**:701 (1980).
27. R. S. Ellis, *Entropy, Large Deviations and Statistical Mechanics* (Springer, New York, 1985).
28. J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**:116 (1963).
29. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1976).
30. J. Glimm and A. Jaffe, *Quantum Physics* (Springer, New York, 1981).
31. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
32. R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975).
33. W. G. Hoover and F. H. Ree, *J. Chem. Phnys.* **49**:3609 (1968).
34. M. K.-H. Kiessling and J. K. Percus, *J. Math. Phys.*, submitted.
35. M. K.-H. Kiessling and J. K. Percus, In preparation (1994).
36. B. Stahl, M. K.-H. Kiessling, and K. Schindler, *Planet. Space Sci.*, to appear.
37. D. Lynden-Bell and R. M. Lynden-Bell, *Monthly Not. R. Astron. Soc.* **181**:405 (1977).
38. J. B. Keller, in *Cavitation in Real Liquids*, R. Davies, ed. (Elsevier, Amsterdam, 1964), p. 19.
39. E. H. Lieb, *J. Math. Phys.* **7**:1016 (1966).