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Well-posedness of the Iterative Boltzmann Inversion

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Abstract The iterative Boltzmann inversion is a fixed point iteration to determine an effective pair potential for an ensemble of identical particles in thermal equilibrium from the corresponding radial distribution function. Although the method is reported to work reasonably well in practice, it still lacks a rigorous convergence analysis. In this paper we provide some first steps towards such an analysis, and we show under quite general assumptions that the associated fixed point operator is Lipschitz continuous (in fact, differentiable) in a suitable neighborhood of the true pair potential, assuming that such a potential exists. In other words, the iterative Boltzmann inversion is well-defined in the sense that if the kth iterate of the scheme is sufficiently close to the true pair potential then the $k+1$st iterate is an admissible pair potential, which again belongs to the domain of the fixed point operator.

On our way we establish important properties of the cavity distribution function and provide a proof of a statement formulated by Groeneveld concerning the rate of decay at infinity of the Ursell function associated with a Lennard-Jones type potential.

Keywords Statistical mechanics · cluster expansion · grand canonical ensemble · radial distribution function · cavity distribution function · Fréchet derivative

Mathematics Subject Classification (2000) 82B21 · 82B80

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1 Introduction

Numerical simulations of complex materials in physical chemistry are so time-consuming, even with today's computing power at hand, that it is necessary to implement subprocesses on a meso-scale by means of "coarse-graining" the atomistic structure of (parts of) the associated molecules. The coarse-grained "beads" are simulated by using effective potentials for their interactions. These effective potentials have to be determined a priori, and this is often done so as to match some given structural data.

Here we consider the case where this structural information consists of measurements of the so-called *radial distribution function* $g^\dagger$ of the beads; see (3.2) for a formal definition of this function. The effective potential $u^\dagger$ is then chosen in such a way that

$$F(u^\dagger) \,=\, g^\dagger\,, \tag{1.1}$$

where F is the function which maps a potential u (out of a predetermined family of suitable functions) onto the corresponding radial distribution function of the associated *grand canonical ensemble* under well-defined physical conditions. The question of existence and uniqueness of a solution $u^\dagger$ of (1.1) for a given $g^\dagger$ is referred to as the *inverse Henderson problem*, because Henderson [9] was the first to investigate the identifiability problem associated with (1.1), i.e., whether the radial distribution function is enough data to uniquely recover the underlying pair potential; see Kuna, Lebowitz, and Speer [11] for a more rigorous mathematical treatment of the uniqueness problem.

A popular method for solving numerically the inverse Henderson problem is the *iterative Boltzmann inversion* (IBI) suggested by Soper [15]. This method, which is available in pertinent public domain software like VOTCA[1] [12] starts from an initial guess u_0 and determines recursively an iterative sequence $(u_k)_{k\geq 0}$ of approximate solutions of (1.1) via

$$u_{k+1} \,=\, u_k \,+\, \gamma \log \frac{F(u_k)}{g^\dagger}\,, \qquad k = 0,1,2,\dots\,. \tag{1.2}$$

Here $\gamma > 0$ is a relaxation parameter that is usually chosen to be

$$\gamma \,=\, 1/\beta\,, \tag{1.3}$$

where $\beta > 0$ is the inverse temperature.

A mathematical analysis of the IBI method is still lacking although the method seems to be fairly robust. In his original paper [15] Soper provided a heuristic argument why IBI might be expected to converge, however, there is little hope to turn this argument into a rigorous proof.

From a mathematical point of view a possible framework for studying (1.2) is fixed point iteration theory, where

$$\Phi(u) \,=\, u \,+\, \gamma \log \frac{F(u)}{g^\dagger}$$

[1] `http://www.votca.org`

is the corresponding fixed point operator. This is the point of view taken in this paper. Note, however, that currently we are not yet able to prove existence of a fixed point of Φ under reasonable assumptions on $g^\dagger$ and the set of admissible pair potentials, although this is evidently a necessary requirement for convergence of (1.2); see [1,10,11] for preliminary results concerning the existence of solutions of the inverse Henderson problem.

Instead we stipulate that a solution $u^\dagger$ of (1.1) exists, and that it belongs to the class of *Lennard-Jones type potentials*. Then, assuming further that the system is in the so-called *gas phase* we can introduce a norm $\|\cdot\|_{\mathscr{V}_{u^\dagger}}$ and establish that the fixed point operator Φ is well-defined in a neighborhood of $u^\dagger$ with respect to this norm. Moreover, Φ is locally Lipschitz, i.e.,

$$\|\Phi(u) - \Phi(u^\dagger)\|_{\mathscr{V}_{u^\dagger}} \;\leq\; C_\Phi \|u - u^\dagger\|_{\mathscr{V}_{u^\dagger}} \tag{1.4}$$

for some $C_\Phi > 0$ and all u sufficiently close to $u^\dagger$; see Theorem 6.1 for the precise statement and the corresponding assumptions. Therefore, assuming that the kth iterate u_k is sufficiently close to $u^\dagger$, it follows from (1.4) that the $k+1$st iterate of IBI satisfies

$$\|u_{k+1} - u^\dagger\|_{\mathscr{V}_{u^\dagger}} \;=\; \|\Phi(u_k) - \Phi(u^\dagger)\|_{\mathscr{V}_{u^\dagger}} \;\leq\; C_\Phi \|u_k - u^\dagger\|_{\mathscr{V}_{u^\dagger}}\,,$$

and hence, $F(u_{k+1})$ and the next iterate u_{k+2} are well-defined.

We mention that in order to prove (1.4) we need to establish positive lower bounds for the radial distribution function $g = F(u)$ near the origin and tight upper bounds for $|g-1|$ near infinity.

In practice IBI is usually started with the initial guess

$$u_0 \;=\; -\frac{1}{\beta}\log g^\dagger\,, \tag{1.5}$$

i.e., the potential of mean force. Our analysis shows, in particular, that the potential of mean force is a Lennard-Jones type potential and that the resulting iterate u_1 of (1.2) is also well-defined; see Remark 6.5.

The outline of this paper is as follows. In the following section we specify our requirements on the family of admissible pair potentials and introduce the norm $\|\cdot\|_{\mathscr{V}_{u^\dagger}}$. We then review in Section 3 the necessary background concerning the associated grand canonical ensemble and its thermodynamical limit, and investigate in more detail the so-called *cavity distribution function* which is needed for the aforementioned lower bounds. Section 4 contains an auxiliary result on autoconvolution products of a certain class of functions which include the *Mayer function*. This will be applied in Section 5 to discuss the rate of decay of the *Ursell function* for large radii, and to improve upon our earlier results in [6] on the derivative of the Ursell function with respect to the pair potential. This provides the required upper bound of $|g-1|$ near infinity. Finally, in Section 6 we return to IBI and present the proof of (1.4).

We mention that although we treat IBI in the context of a grand canonical ensemble, it is possible to extend this analysis to a canonical ensemble, which is the more usual setting of numerical simulations in practice.

2 Setting

We start by considering an ensemble of identical classical particles in thermal equilibrium within a bounded cubical box $\Lambda \subset \mathbb{R}^3$ centered at the origin. We assume that the interaction of the particles can be described by a pair potential $u : \mathbb{R}^+ \to \mathbb{R}$, which only depends on the distance of the interacting particles, and that this potential satisfies

$$\begin{aligned} |u(r)| \,&\leq\, Cr^{-\alpha}\,, \qquad r \geq r_0\,, \\ u(r) \,&\geq\, cr^{-\alpha}\,, \qquad r \leq r_0\,, \end{aligned} \tag{2.1}$$

for some $\alpha > 3$, $r_0 > 0$, and constants c, C satisfying $C_0 > C > c > c_0 > 0$; here, α, r_0, c_0, and C_0 are fixed parameters, and we denote by $\mathscr{U} = \mathscr{U}(\alpha, r_0, c_0, C_0)$ the family of potentials u satisfying (2.1). Following Ruelle [14] potentials $u \in \mathscr{U}$ are called Lennard-Jones type pair potentials.

Under this assumption it is known (cf. Fisher and Ruelle [2]) that there exists $B > 0$ such that

$$U_N(\boldsymbol{R}_N) \,:=\, \sum_{1 \leq i < j \leq N} u(|R_i - R_j|) \,\geq\, -BN \tag{2.2}$$

for every configuration of N particles in free space and every $N \in \mathbb{N}$; here we denote by $R_i \in \mathbb{R}^3$ the coordinates of the ith particle, and by $\boldsymbol{R}_N = (R_1, \ldots, R_N) \in (\mathbb{R}^3)^N$ the configuration of the first N particles.

Associated with $u \in \mathscr{U}$ and the inverse temperature $\beta > 0$ is the Mayer function

$$f(R) \,=\, e^{-\beta u(|R|)} - 1\,, \tag{2.3}$$

which is considered to be -1 at the origin $R = 0$. Because of (2.1) the Mayer function is absolutely integrable, i.e., there exists $c_\beta > 0$ such that

$$\int_{\mathbb{R}^3} |f(R)| \, \mathrm{d}R \,<\, c_\beta\,. \tag{2.4}$$

By virtue of (2.2) and (2.4) every Lennard-Jones type potential is *stable* and *regular* in the sense of [14]. As worked out in the proof of [5, Proposition 2.1], for every $u \in \mathscr{U}$ the same constants B and c_β can be used in (2.2) and (2.4), respectively.

Associated with the parameter α in (2.1) is the weight function

$$\varrho(r) \,=\, (1 + r^2)^{\alpha/2}\,, \qquad r \geq 0\,. \tag{2.5}$$

For every $u \in \mathscr{U}$ we can use this weight function to define a corresponding Banach space $\mathscr{V}_u$ of *perturbations*, consisting of all functions $v : \mathbb{R}^+ \to \mathbb{R}$, for which the associated norm

$$\|v\|_{\mathscr{V}_u} \,=\, \max\bigl\{\|v/u\|_{(0,r_0]}, \|\varrho v\|_{[r_0,\infty)}\bigr\} \tag{2.6}$$

is finite. Clearly, for every $u \in \mathscr{U}$ there exists $\delta_0 = \delta_0(u) \in (0,1)$ sufficiently small such that $u + v \in \mathscr{U}$ for every $v \in \mathscr{V}_u$ with $\|v\|_{\mathscr{V}_u} \leq \delta_0$. Later, compare (5.11) and (5.12), we will reduce the size of $\delta_0(u)$ somewhat further to ensure additional properties of $u + v$ for all $v \in \mathscr{V}_u$ with $\|v\|_{\mathscr{V}_u} \leq \delta_0$.

3 The grand canonical ensemble

Let $u \in \mathscr{U}$ be the pair potential that determines the interaction of the particles. In the grand canonical ensemble the number of particles and their coordinates within Λ are random variables, and the probability of observing an ensemble with exactly N particles in an infinitesimal volume $\mathrm{d}\boldsymbol{R}_N$ at the coordinates $\boldsymbol{R}_N \in \Lambda^N$ (up to permutations) is given by

$$\frac{1}{\Xi_\Lambda(z)}\,\frac{z^N}{N!}\,e^{-\beta U_N(\boldsymbol{R}_N)}\,\mathrm{d}\boldsymbol{R}_N\,,$$

where $z > 0$ is the so-called *activity*, $U_N(\boldsymbol{R}_N)$ is defined in (2.2), and

$$\Xi_\Lambda(z) \;=\; \sum_{N=0}^{\infty}\frac{z^N}{N!}\int_{\Lambda^N} e^{-\beta U_N(\boldsymbol{R}_N)}\,\mathrm{d}\boldsymbol{R}_N$$

is the grand canonical partition function. We consider this grand canonical ensemble under specified physical conditions, i.e., we assume that the activity z and the inverse temperature β are given (and fixed), and that they satisfy the inequality

$$0 < z < \frac{1}{c_\beta e^{2\beta B+1}}\,, \tag{3.1}$$

where c_β and B are the constants in (2.4) and (2.2), respectively. This regime is known as the gas phase of the ensemble, cf. [14].

For $m \in \mathbb{N}$ and $\boldsymbol{R}_m \in \Lambda^m$ the m-particle distribution function is given by

$$\rho_\Lambda^{(m)}(\boldsymbol{R}_m) \;=\; \frac{1}{\Xi_\Lambda(z)}\sum_{N=m}^{\infty}\frac{z^N}{(N-m)!}\int_{\Lambda^{N-m}} e^{-\beta U_N(\boldsymbol{R}_N)}\,\mathrm{d}\boldsymbol{R}_{m,N}\,,$$

where $\boldsymbol{R}_{m,N} = (R_{m+1},\dots,R_N)$; $\rho_\Lambda^{(m)}$ determines the probability distribution for snap shots with m particles (up to permutations) at coordinates $R_1,\dots,R_m \in \Lambda$.[2] The grand canonical partition function Ξ_Λ can be seen to be an entire function of $z \in \mathbb{C}$, which is free of zeros for

$$z \in \mathcal{Z} \;=\; \Bigl\{\, z \in \mathbb{C} \,:\, |z| \,<\, \frac{1}{c_\beta e^{2\beta B+1}} \,\Bigr\}\,,$$

compare [14, Theorem 4.2.3], and similarly, the m-particle distribution functions all are analytic functions of $z \in \mathcal{Z}$. On the other hand, the m-particle distribution functions may encounter singularities for positive values of z outside the interval (3.1); those are understood to correspond to physical phase transitions.

As shown in [14] the m-particle distribution function has a well-defined *thermodynamical limit*, i.e., $\rho_\Lambda^{(m)}$ converges to some $\rho^{(m)} \in L^\infty\bigl((\mathbb{R}^3)^m\bigr)$ as $|\Lambda| \to \infty$, uniformly on every compact subset of $(\mathbb{R}^3)^m$ and for activities z from every compact subset of $\mathcal{Z}$, this being true for every $m \in \mathbb{N}$; here, $|\Lambda|$

[2] If $R_i = R_j$ for different indices $i,j \in \{1,\dots,m\}$ then $\rho_\Lambda^{(m)}(\boldsymbol{R}_m)$ is set to be zero.

denotes the volume of the box. In particular, for $m = 1$, the thermodynamical limit

$$\rho^{(1)}(R) \;=\; \rho_0 \;\in \mathbb{R}_0^+$$

is independent of $R \in \mathbb{R}^3$ and provides the counting density of the ensemble; for $m = 2$, $\rho^{(2)}(R_1, R_2)$ only depends on the distance $r = |R_1 - R_2| \geq 0$. Given these two functions the radial distribution function, referred to in the introduction, is defined to be

$$g(r) \;=\; \frac{1}{\rho_0^2}\,\rho^{(2)}(R, 0)\,, \qquad |R| = r \geq 0\,. \tag{3.2}$$

For $m \in \mathbb{N}_0$ and z as in (3.1) the function $\rho^{(m)}$ is Fréchet differentiable with respect to u, i.e., with respect to perturbations $v \in \mathscr{V}_u$ of u, cf. [5]. The derivative is a bounded linear operator $\partial\rho^{(m)} \in \mathscr{L}\big(\mathscr{V}_u, L^\infty((\mathbb{R}^3)^m)\big)$. A similar result (see [5, Remark 3.4] for details) applies to certain weighted copies of the particle distribution functions, which include the cavity distribution function (cf. Hansen and McDonald [7])

$$y(r) \;=\; e^{\beta u(r)} g(r)\,, \qquad r > 0\,, \tag{3.3}$$

as a special case; the following result elaborates on this.

Proposition 3.1 *For $u \in \mathscr{U}$ and $z \in \mathcal{Z}$ the cavity distribution function y of (3.3) is a bounded function of $r > 0$, which is analytic with respect to $z \in \mathcal{Z}$ and uniformly bounded on every compact subset of $\mathcal{Z}$. Moreover, y is Fréchet differentiable with respect to u with derivative $\partial y \in \mathscr{L}(\mathscr{V}_u, L^\infty(\mathbb{R}^+))$. If*

$$0 < z < \frac{1}{1+e}\,\frac{1}{c_\beta e^{2\beta B + 1}}\,, \tag{3.4}$$

then the cavity distribution function is strictly positive, i.e., there exists $c > 0$ (depending only on z, c_β, and B) such that

$$y(r) \;\geq\; c\,, \qquad r > 0\,, \tag{3.5}$$

for all $u \in \mathscr{U}$.

Proof The function

$$\sigma^{(2)}(R, 0) \;=\; \rho_0^2\, y(|R|)$$

is the second entry of the semi-infinite vector $\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathbb{R}^3}$ considered in [5, Remark 3.4]. There it is shown that $\boldsymbol{\sigma}$ satisfies a system

$$(I - zB)\boldsymbol{\sigma} \;=\; z\boldsymbol{e_1}\,, \qquad B = KD\,, \tag{3.6}$$

of Kirkwood-Salsburg integral equations, and that $\boldsymbol{\sigma}$ has certain differentiability properties. These properties readily imply differentiability of y with respect to z and u as stated above.

In (3.6) we have adopted notation of [5]: K is a semi-infinite matrix of integral operators, D a diagonal multiplication operator, and I the corresponding identity operator; $\boldsymbol{e_1}$ is a vector of constant functions, its first entry being identically one, and all other entries being zero. To establish the lower bound (3.5) for the specific real interval of activity parameters z given in (3.4), we first note that $I - zB$ can be developed into a Neumann series, and hence we can rewrite (3.6) in the form

$$\boldsymbol{\sigma} \;=\; z\boldsymbol{e_1} \;+\; z^2 B\boldsymbol{e_1} \;+\; \boldsymbol{h}\,, \tag{3.7}$$

where

$$\boldsymbol{h} \;=\; (h^{(m)})_m \;=\; z^3(I - zB)^{-1}BKD\boldsymbol{e_1} \;=\; z^3(I - zB)^{-1}BK\boldsymbol{e_1}\,,$$

because the $(1,1)$-entry of D is an identity operator. Looking at the second entry of the vector identity (3.7) we conclude that

$$\sigma^{(2)}(R,0) - z^2 \;=\; h^{(2)}(R,0)\,, \tag{3.8}$$

because the second entry b_{21} of $B\boldsymbol{e_1}$ is again a constant, i.e., $b_{21} = 1$; compare [5]. For $z \in \mathcal{Z}$ the right-hand side of (3.8) can be bounded as in [5], which gives

$$\|h^{(2)}\|_{L^\infty((\mathbb{R}^3)^2)} \;\leq\; z^3 e\,\frac{c_\beta e^{2\beta B+1}}{1 - zc_\beta e^{2\beta B+1}}\,.$$

Therefore, assuming (3.4), there holds

$$y(r) \;=\; \frac{\sigma^{(2)}(R,0)}{\rho_0^2} \;\geq\; \frac{z^2}{\rho_0^2}\Bigl(1 - ze\,\frac{c_\beta e^{2\beta B+1}}{1 - zc_\beta e^{2\beta B+1}}\Bigr) \;\geq\; c$$

with an appropriate choice of $c > 0$, valid for every $r > 0$ and every $R \in \mathbb{R}^3$ with $|R| = r$. □

4 An auxiliary inequality for autoconvolution products

Before we continue we define the Banach space $L^\infty_\varrho(\mathbb{R}^3)$ of functions $v \in L^\infty(\mathbb{R}^3)$ with finite norm

$$\|w\|_{L^\infty_\varrho(\mathbb{R}^3)} \;=\; \sup_{R\in\mathbb{R}^3} \varrho(|R|)|w(R)|\,, \tag{4.1}$$

where ϱ is as in (2.5). We mention that the Mayer f-function defined in (2.3) belongs to this space by virtue of (2.1). Note that $L^\infty_\varrho(\mathbb{R}^3)$ is continuously embedded in $L^1(\mathbb{R}^3)$ and $L^\infty(\mathbb{R}^3)$, because the parameter α in (2.1) is assumed to satisfy $\alpha > 3$. It readily follows that the convolution $w * w'$ of two functions $w, w' \in L^\infty_\varrho(\mathbb{R}^3)$ is an absolutely integrable function. In fact, we show next that the result belongs to $L^\infty_\varrho(\mathbb{R}^3)$ again.

Proposition 4.1 *Let $w, w' \in L^\infty_\varrho(\mathbb{R}^3)$. Then $w * w' \in L^\infty_\varrho(\mathbb{R}^3)$ with*

$$\|w * w'\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\leq\; c_\varrho 2^{\alpha+1}\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\|w'\|_{L^\infty_\varrho(\mathbb{R}^3)}\,, \tag{4.2}$$

where c_ϱ is the embedding constant for the embedding of $L^\infty_\varrho(\mathbb{R}^3)$ into $L^1(\mathbb{R}^3)$.

Proof For $R \in \mathbb{R}^3$ and $0 < \varepsilon < 1$ we consider the ball $\mathcal{B}_{\varepsilon|R|}(R) \subset \mathbb{R}^3$ of radius $\varepsilon|R|$ around R. Depending on whether R' is inside or outside this ball, there holds

$$1 + |R'|^2 \;\geq\; (1-\varepsilon)^2(1+|R|^2)\,, \qquad R' \in \mathcal{B}_{\varepsilon|R|}(R)\,, \tag{4.3a}$$

$$1 + |R'-R|^2 \;\geq\; \varepsilon^2(1+|R|^2)\,, \qquad R' \in \mathbb{R}^3 \setminus \mathcal{B}_{\varepsilon|R|}(R)\,. \tag{4.3b}$$

Using (4.3a) it follows for every $R \in \mathbb{R}^3$ that

$$\begin{aligned}
&\varrho(|R|)\left|\int_{\mathcal{B}_{\varepsilon|R|}(R)} w(R-R')w'(R')\,\mathrm{d}R'\right| \\
&\quad\leq \int_{\mathcal{B}_{\varepsilon|R|}(R)} \frac{\varrho(|R|)}{\varrho(|R'|)}\,\bigl|w(R-R')\bigr|\,\varrho(|R'|)\,\bigl|w'(R')\bigr|\,\mathrm{d}R' \\
&\quad\leq \frac{1}{(1-\varepsilon)^\alpha}\,\|w'\|_{L^\infty_\varrho(\mathbb{R}^3)} \int_{\mathcal{B}_{\varepsilon|R|}(R)} \bigl|w(R-R')\bigr|\,\mathrm{d}R' \\
&\quad\leq \frac{1}{(1-\varepsilon)^\alpha}\,\|w\|_{L^1(\mathbb{R}^3)}\|w'\|_{L^\infty_\varrho(\mathbb{R}^3)}\,,
\end{aligned}$$

while (4.3b) implies that

$$\begin{aligned}
&\varrho(|R|)\left|\int_{\mathbb{R}^3\setminus\mathcal{B}_{\varepsilon|R|}(R)} w(R-R')w'(R')\,\mathrm{d}R'\right| \\
&\quad\leq \int_{\mathbb{R}^3\setminus\mathcal{B}_{\varepsilon|R|}(R)} \frac{\varrho(|R|)}{\varrho(|R-R'|)}\,\varrho(|R-R'|)\,\bigl|w(R-R')\bigr|\,\bigl|w'(R')\bigr|\,\mathrm{d}R' \\
&\quad\leq \frac{1}{\varepsilon^\alpha}\,\|w\|_{L^\infty_\varrho(\mathbb{R}^3)} \int_{\mathbb{R}^3\setminus\mathcal{B}_{\varepsilon|R|}(R)} \bigl|w'(R')\bigr|\,\mathrm{d}R' \;\leq\; \frac{1}{\varepsilon^\alpha}\,\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\,\|w'\|_{L^1(\mathbb{R}^3)}\,.
\end{aligned}$$

Adding these two inequalities we thus conclude that

$$\begin{aligned}
&\|w * w'\|_{L^\infty_\varrho(\mathbb{R}^3)} \\
&\quad\leq \frac{1}{(1-\varepsilon)^\alpha}\,\|w\|_{L^1(\mathbb{R}^3)}\|w'\|_{L^\infty_\varrho(\mathbb{R}^3)} \;+\; \frac{1}{\varepsilon^\alpha}\,\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\,\|w'\|_{L^1(\mathbb{R}^3)} \qquad (4.4)\\
&\quad\leq \Bigl(\frac{1}{(1-\varepsilon)^\alpha} + \frac{1}{\varepsilon^\alpha}\Bigr)c_\varrho\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\|w'\|_{L^\infty_\varrho(\mathbb{R}^3)}\,,
\end{aligned}$$

where c_ϱ is the embedding constant for the embedding $L^\infty_\varrho(\mathbb{R}^3) \subset L^1(\mathbb{R}^3)$. By choosing $\varepsilon = 1/2$ we finally obtain (4.2). □

Proposition 4.1 implies that we can rescale the norm of $L^\infty_\varrho(\mathbb{R}^3)$ to make $L^\infty_\varrho(\mathbb{R}^3)$ a commutative Banach algebra with respect to convolution.

For $w \in L^\infty_\varrho(\mathbb{R}^3)$ and $n \in \mathbb{N}$ let W_n be the n-fold autoconvolution of w, i.e.,

$$W_1 = w\,, \qquad W_{n+1} = w * W_n\,, \quad n \geq 1\,. \tag{4.5}$$

By virtue of Proposition 4.1 each W_n belongs to $L^\infty_\varrho(\mathbb{R}^3)$, and there holds

$$\|W_n\|_{L^1(\mathbb{R}^3)} \;\leq\; \|w\|^n_{L^1(\mathbb{R}^3)}\,, \qquad n \geq 1\,. \tag{4.6}$$

Proposition 4.2 *Assume that $w \in L^\infty_\varrho(\mathbb{R}^3)$ satisfies*

$$\|w\|_{L^1(\mathbb{R}^3)} \;=\; q \;<\; 1\,, \tag{4.7}$$

and let $\overline{q} \in (q,1)$. Then the autoconvolution products W_n defined in (4.5) *satisfy*

$$\|W_n\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\leq\; C_*\,\overline{q}^n \|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\,, \qquad n \in \mathbb{N}\,, \tag{4.8}$$

for some constant $C_* > 0$ depending only on α, q, and $\overline{q}$.

Proof We are going to prove by induction the inequality

$$\|W_n\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\leq\; \frac{1}{\varepsilon^\alpha}\,\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\,\frac{1-(q/\overline{q})^n}{1-q/\overline{q}}\,\overline{q}^{n-1}\,, \tag{4.9}$$

where we let

$$\varepsilon \;=\; 1-(q/\overline{q})^{1/\alpha}\,, \tag{4.10}$$

which is a positive number; this readily implies (4.8). The induction base $n = 1$ of (4.9) is obviously correct because $\varepsilon < 1$ according to (4.10). For the induction step from n to $n+1$, $n \geq 1$, we apply inequality (4.4) from the proof of Proposition 4.1 with $w' = W_n$ and ε of (4.10) to obtain

$$\|W_{n+1}\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\leq\; \overline{q}\,\|W_n\|_{L^\infty_\varrho(\mathbb{R}^3)} \;+\; \frac{1}{\varepsilon^\alpha}\,\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\,\|W_n\|_{L^1(\mathbb{R}^3)}\,.$$

Inserting (4.6), (4.7), and the induction hypothesis (4.9) this yields

$$\|W_{n+1}\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\leq\; \frac{1}{\varepsilon^\alpha}\,\|w\|_{L^\infty_\varrho(\mathbb{R}^3)}\Big(\frac{1-(q/\overline{q})^n}{1-q/\overline{q}} \;+\; (q/\overline{q})^n\Big)\overline{q}^n\,,$$

which coincides with the bound (4.9) for the norm of W_{n+1}. $\square$

Corollary 4.3 *Under the assumptions of Proposition 4.2 the infinite series*

$$W_\Sigma \;=\; \sum_{n=1}^\infty W_n \tag{4.11}$$

converges in $L^\infty_\varrho(\mathbb{R}^3)$.

5 The Ursell function

The Ursell function (relative to the origin) of a grand canonical ensemble with pair potential $u \in \mathscr{U}$ (see Section 3) is defined to be

$$\omega_\Lambda(R) \;=\; \rho_\Lambda^{(2)}(R,0) - \rho_\Lambda^{(1)}(R)\rho_\Lambda^{(1)}(0)\,, \qquad R \in \Lambda\,. \tag{5.1}$$

For $z \in \mathcal{Z}$ the Ursell function can be expanded into an absolutely convergent power series

$$\omega_\Lambda(R) \;=\; \sum_{N=2}^{\infty} a_{N,\Lambda}(R) z^N, \tag{5.2}$$

the coefficients of which depend on u via the Mayer function f defined in (2.3). They can be represented in the form

$$a_{N,\Lambda}(R) \;=\; \frac{1}{(N-2)!}\int_{\Lambda^{N-2}} \sum_{\mathcal{C}\in\mathfrak{C}_N} \prod_{(i,j)\in\mathcal{C}} f(R_i - R_j)\, \mathrm{d}\boldsymbol{R}_{2,N}\,, \tag{5.3a}$$

cf. Stell [16], where $R_1 = R$ and $R_2 = 0$, $\mathfrak{C}_N$ is the set of connected graphs with N vertices, labeled $1,\dots,N$, and the product in (5.3a) runs over all bonds in $\mathcal{C}$: the notation (i,j) refers to a bond connecting vertices i and j, where we use the convention that $i < j$ for $(i,j) \in \mathcal{C}$. For $N = 2$ the representation (5.3a) is to be read as

$$a_{2,\Lambda}(R) \;=\; f(R)\,. \tag{5.3b}$$

According to (5.1) and the discussion in Section 3 there holds

$$\omega_\Lambda(R) \;\longrightarrow\; \omega(R) \;:=\; \rho^{(2)}(R,0) - \rho_0^2\,, \qquad |\Lambda| \to \infty\,, \tag{5.4}$$

uniformly on every compact subset for $R \in \mathbb{R}^3$ and for all activities z in a compact subinterval of (3.1). Likewise, if $\partial\omega_\Lambda \in \mathscr{L}\bigl(\mathscr{V}_u, L^\infty(\Lambda)\bigr)$ and $\partial\omega \in \mathscr{L}\bigl(\mathscr{V}_u, L^\infty(\mathbb{R}^3)\bigr)$ are the derivatives with respect to u of the Ursell function and of its thermodynamical limit, respectively, and if $v \in \mathscr{V}_u$ then

$$\bigl((\partial\omega_\Lambda)v\bigr)(R) \;\longrightarrow\; \bigl((\partial\omega)v\bigr)(R)\,, \tag{5.5}$$

uniformly on every compact subset for $R \in \mathbb{R}^3$.

The goal of this section is two-fold. First, we derive a sharp upper bound for the decay of this thermodynamical limit ω as $|R| \to \infty$. Subsequently, we extend this analysis to estimate its perturbation, given a perturbation of the potential. To begin with, we prove the following inequality.

Lemma 5.1 *Let $u \in \mathscr{U}$ and $\widetilde{u} = u + \zeta v$, where $v \in \mathscr{V}_u$ with $\|v\|_{\mathscr{V}_u} \le \delta_0(u)$ for some $\delta_0(u) > 0$ sufficiently small, and where $\zeta \in \mathbb{C}$ with $|\zeta| \le 1$. Associated with $\widetilde{u}$ is the (complex) Mayer function $\widetilde{f}$, and*

$$\widetilde{\varphi}_N(\boldsymbol{R}_N) \;=\; \sum_{\mathcal{C}\in\mathfrak{C}_N} \prod_{(i,j)\in\mathcal{C}} \widetilde{f}(R_i - R_j)\,, \qquad \boldsymbol{R}_N \in \Lambda^N\,. \tag{5.6}$$

If z satisfies (3.1), *where c_β and B are given by* (2.4) *and* (2.2), *respectively, then*

$$\int_{\Lambda^{N-2}} \bigl|\widetilde{\varphi}_N(\boldsymbol{R}_N)\bigr| \,\mathrm{d}\boldsymbol{R}_{2,N} \;\leq\; C_\Sigma\, e^{N\beta B} N^{N-2} c_\beta^{N-1} \frac{1}{\varrho(R_1 - R_2)} \tag{5.7}$$

with ϱ of (2.5) *and with some constant C_Σ, which only depends on u and $\delta_0(u)$.*

Proof Let u and $\widetilde{u} = u + \zeta v$ be as in the statement of this lemma, with $\delta_0(u)$ as specified in Section 2. Below, we may reduce the size of $\delta_0(u)$ somewhat further. We define $\widetilde{U}_N$, V_N, and $|V|_N$ as in (2.2), replacing u by $\widetilde{u}$, v and $|v|$, respectively, on the right-hand side. Using this notation it follows from (2.2) that $\widetilde{u}$ satisfies the stability bound

$$\begin{aligned} \mathrm{Re}\,\bigl(\widetilde{U}_N(\boldsymbol{R}_N)\bigr) \;&=\; U_N(\boldsymbol{R}_N) \,+\, \mathrm{Re}\,(\zeta)\, V_N(\boldsymbol{R}_N) \\ &\geq\; U_N(\boldsymbol{R}_N) \,-\, |V|_N(\boldsymbol{R}_N) \;\geq\; -NB \end{aligned} \tag{5.8}$$

for every coordinate vector $\boldsymbol{R}_N \in (\mathbb{R}^3)^N$, because $u - |v| \in \mathscr{U}$ by the definition of δ_0. Therefore the absolute value of the function $\widetilde{\varphi}_N$ of (5.6) can be estimated by means of the tree-graph inequality

$$|\widetilde{\varphi}_N(\boldsymbol{R}_N)| \;\leq\; e^{N\beta B} \sum_{\mathcal{T}\in\mathfrak{T}_N} \prod_{(i,j)\in\mathcal{T}} \bigl|\widetilde{f}(R_i - R_j)\bigr|\,, \tag{5.9}$$

where $\mathfrak{T}_N$ is the set of trees with N vertices; this particular version of the tree-graph inequality can be found in Ueltschi [17].

As far as the Mayer function is concerned there holds

$$\bigl|\widetilde{f}(R) - f(R)\bigr| \;\leq\; \beta e^{-\beta(u-|v|)(|R|)} \bigl|v(|R|)\bigr| \;\leq\; \begin{cases} \dfrac{1}{e(1-\delta_0)}\, \|v\|_{\mathscr{V}_u}\,, & |R| < r_0\,, \\[2ex] \dfrac{\beta e^{2\beta B}}{\varrho(|R|)}\, \|v\|_{\mathscr{V}_u}\,, & |R| \geq r_0\,, \end{cases}$$

and hence, it follows that

$$|\widetilde{f}(R)| \;\leq\; c_\beta w(R), \qquad R \in \mathbb{R}^3\,, \tag{5.10}$$

where c_β has been introduced in (2.4), and

$$w(R) \;=\; \frac{1}{c_\beta}\, |f(R)| \,+\, C_\beta\, \frac{\delta_0}{\varrho(|R|)} \tag{5.11}$$

for some suitably chosen constant $C_\beta > 0$; note that w is a positive function. Reducing the size of δ_0, when necessary, we can make sure that

$$q \;:=\; \int_{\mathbb{R}^3} w(R)\,\mathrm{d}R \;<\; 1 \tag{5.12}$$

by virtue of (2.4). We fix $\delta_0 = \delta_0(u)$ accordingly for the remainder of this paper. Note that (5.10) holds uniformly for all $\widetilde{u} = u + \zeta v$ with $\|v\|_{\mathscr{V}_u} \leq \delta_0$ and $\zeta \in \mathbb{C}$, $|\zeta| \leq 1$.

As we have already mentioned in Section 4 the Mayer function associated with u belongs to the Banach space $L^\infty_\varrho(\mathbb{R}^3)$ introduced in (4.1), hence the function w of (5.11) satisfies the assumptions of Proposition 4.2 and Corollary 4.3: As before we denote by $W_n, W_\Sigma \in L^\infty_\varrho(\mathbb{R}^3)$ the corresponding autoconvolutions (4.5) and their infinite series (4.11), respectively. Note that there exists $C_\Sigma > 0$, such that

$$0 \,<\, W_n(R) \,\leq\, W_\Sigma(R) \,\leq\, C_\Sigma \,\frac{1}{\varrho(R)} \tag{5.13}$$

for every $R \in \mathbb{R}^3$ and $n \in \mathbb{N}$, because w is a positive function and $W_\Sigma \in L^\infty_\varrho(\mathbb{R}^3)$.

By virtue of (5.10) we have the inequality

$$\int_{\Lambda^{N-2}} \prod_{(i,j)\in\mathcal{T}} \bigl|\widetilde{f}(R_i - R_j)\bigr| \,\mathrm{d}\boldsymbol{R}_{2,N} \,\leq\, \int_{\mathbb{R}^{N-2}} \prod_{(i,j)\in\mathcal{T}} c_\beta w(R_i - R_j)\,\mathrm{d}\boldsymbol{R}_{2,N} \tag{5.14}$$

for any fixed tree $\mathcal{T} \in \mathfrak{T}_N$. Such a tree consists of (i) a "backbone" with n bonds and $n-1$ inner vertices, where $1 \leq n \leq N-1$, which connects the vertices 1 and 2, and (ii) $n+1$ subtrees rooted at all vertices of this backbone. One can first integrate (5.14) over all $N-n-1$ vertices of these subtrees besides their roots, with each of these integrals being bounded by c_β according to (5.12); integrating over the inner vertices of the backbone thereafter constitutes an n-fold autoconvolution of $c_\beta w$, i.e.,

$$\int_{\Lambda^{N-2}} \prod_{(i,j)\in\mathcal{T}} \bigl|\widetilde{f}(R_i{-}R_j)\bigr|\,\mathrm{d}\boldsymbol{R}_{2,N} \,\leq\, c_\beta^{N-1} W_n(R_1{-}R_2) \,\leq\, C_\Sigma\, c_\beta^{N-1} \frac{1}{\varrho(R_1 - R_2)}\,,$$

where we have used (5.13) for the final inequality. Note that this estimate is independent of the particular form of the tree $\mathcal{T}$. Therefore, making use of Cayley's result that $\mathfrak{T}_N$ consists of exactly N^{N-2} different trees, we conclude that

$$\sum_{\mathcal{T}\in\mathfrak{T}_N} \int_{\Lambda^{N-2}} \prod_{(i,j)\in\mathcal{T}} \bigl|\widetilde{f}(R_i - R_j)\bigr|\,\mathrm{d}\boldsymbol{R}_{2,N} \,\leq\, C_\Sigma\, N^{N-2} c_\beta^{N-1} \frac{1}{\varrho(R_1 - R_2)}\,,$$

and hence, the inequality (5.7) follows from (5.9). □

Corollary 5.2 *Let $u \in \mathscr{U}$ and let z satisfy* (3.1), *where c_β and B are given by* (2.4) *and* (2.2), *respectively. Then the thermodynamical limit* (5.4) *of the Ursell function belongs to $L^\infty_\varrho(\mathbb{R}^3)$, i.e., there exists $c_\omega = c_\omega(u,z) > 0$ such that*

$$\bigl|\omega(R)\bigr| \,\leq\, c_\omega(1 + |R|^2)^{-\alpha/2} \tag{5.15}$$

for every $R \in \mathbb{R}^3$.

Proof From (5.2) and (5.3) we have

$$\omega_\Lambda(R) \,=\, \sum_{N=2}^\infty \frac{z^N}{(N-2)!} \int_{\Lambda^{N-2}} \varphi_N(\boldsymbol{R}_N)\,\mathrm{d}\boldsymbol{R}_{2,N}\,,$$

where $R_1 = R$ and $R_2 = 0$, and $\varphi_N(R)$ is defined as in (5.6) with $\widetilde{f}$ replaced by the Mayer function f associated with u. It therefore follows from Lemma 5.1 that

$$\begin{aligned}\big|\omega_\Lambda(R)\big| &\leq \frac{C_\Sigma}{c_\beta}\left(\sum_{N=2}^{\infty}\big(zc_\beta e^{\beta B}\big)^N \frac{N^{N-2}}{(N-2)!}\right)\frac{1}{\varrho(R)} \\ &\leq \frac{C_\Sigma}{c_\beta}\left(\sum_{N=2}^{\infty}\big(zc_\beta e^{\beta B+1}\big)^N\right)\frac{1}{\varrho(R)} \;=\; C_\Sigma\,\frac{z^2 c_\beta e^{2(\beta B+1)}}{1-zc_\beta e^{\beta B+1}}\,\frac{1}{\varrho(R)}\,.\end{aligned}$$

Now the assertion follows by turning to the thermodynamical limit $|\Lambda|\to\infty$, compare (5.4). □

Some comments on Corollary 5.2 are in order.

The estimate (5.15) can be found in a paper by Groeneveld [3] with similar assumptions on the pair potential[3], but it appears that he only published a proof for nonnegative potentials (in [4]). On the other hand, Ruelle included in his book [14] a proof of the weaker statement that $\omega \in L^1(\mathbb{R}^3)$; see also [13].

A common way of estimating the decay of the Ursell function consists in rewriting the Mayer function in (5.9) as

$$f(R) \;=\; \big(f(R)e^{a(R)}\big)e^{-a(R)}$$

in such a way that a satisfies a triangle inequality, and fe^a is bounded and absolutely integrable. In this case the integral over the backbone considered above can be estimated by $e^{-a(R)}$ times an autoconvolution of fe^a, and the former factor $e^{-a(R)}$ provides an estimate for the rate of decay. In our case this approach could be realized with

$$e^{a(R)} \;=\; |R|^{\alpha'-3} \qquad \text{for any}\quad 3<\alpha'<\alpha\,,$$

but the resulting bound for the Ursell function is evidently suboptimal.

The bound (5.15), on the other hand, is optimal up to multiplicative constants, as follows from the cluster expansion (5.2), which gives

$$\omega(R) \;=\; z^2 f(R) \,+\, O(z^3)\,, \qquad z\to 0\,,$$

according to (5.3b).

In the remainder of this section we treat the Ursell function as a function of the pair potential u and prove the following result.

Theorem 5.3 *Assume that z satisfies* (3.1)*. Then the thermodynamical limit of the Ursell function, considered a function of $u\in\mathscr{U}$, has a Fréchet derivative $\partial\omega \in \mathscr{L}(\mathscr{V}_u, L^\infty_\varrho(\mathbb{R}^3))$. More precisely, if ω and $\widetilde{\omega}$ denote the thermodynamical limits of the Ursell functions corresponding to u and $\widetilde{u} = u+v$,*

[3] The notation in [3] concerning the assumptions on u and the corresponding hypothesis is not fully clear, though.

respectively, then there exists $C_\omega = C_\omega(u,z)$*, such that*

$$\|\widetilde{\omega} - \omega\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\le\; C_\omega \|v\|_{\mathscr{V}_u}\,, \tag{5.16}$$

$$\|\widetilde{\omega} - \omega - (\partial\omega)v\|_{L^\infty_\varrho(\mathbb{R}^3)} \;\le\; C_\omega \|v\|^2_{\mathscr{V}_u}\,, \tag{5.17}$$

provided that $\|v\|_{\mathscr{V}_u}$ *is sufficiently small.*

Proof Let $u \in \mathscr{U}$ and $\delta_0 = \delta_0(u)$ be chosen as in the proof of Lemma 5.1. Fix a perturbation $v_0 \in \mathscr{V}_u$ with $\|v_0\|_{\mathscr{V}_u} \le \delta_0$ and an activity parameter z satisfying (3.1). In addition, let $R_1 = R \in \Lambda$ and $R_2 = 0$, and for $N \ge 2$ let $\boldsymbol{R}_{2,N} \in \Lambda^{N-2}$ be further $N-2$ points in Λ. With these variables fixed we define entire functions

$$f_{ij}(\zeta) \;=\; e^{-\beta\left(u(|R_i-R_j|)+\zeta v_0(|R_i-R_j|)\right)} - 1\,, \qquad 1 \le i < j \le N\,,$$

of $\zeta \in \mathbb{C}$, and

$$\varphi_N(\zeta) \;=\; \sum_{\mathcal{C}\in\mathfrak{C}_N} \prod_{(i,j)\in\mathcal{C}} f_{ij}(\zeta)\,.$$

Note that $f_{ij}(\zeta)$ coincides with $\widetilde{f}(R_i - R_j)$ and $\varphi_N(\zeta)$ coincides with $\widetilde{\varphi}(\boldsymbol{R}_N)$ of Lemma 5.1, when $R_1 = R$ and $R_2 = 0$; we switch to the new notation to highlight the dependency on ζ, rather than $\boldsymbol{R}_N$. Further note that φ_N is also an entire function of ζ, because the number of connected graphs with N vertices is finite. For $0 < \varepsilon \le 1/2$ we can therefore apply Cauchy's integral formula to deduce that

$$\bigl|\varphi_N(\varepsilon)-\varphi_N(0)\bigr| \;=\; \Bigl|\frac{\varepsilon}{2\pi\mathrm{i}}\int_{|\zeta|=1}\frac{\varphi_N(\zeta)}{\zeta(\zeta-\varepsilon)}\,\mathrm{d}\zeta\Bigr| \;\le\; \frac{\varepsilon}{\pi}\int_0^{2\pi}\bigl|\varphi_N(e^{\mathrm{i}\theta})\bigr|\,\mathrm{d}\theta \tag{5.18}$$

and

$$\begin{aligned}&\bigl|\varphi_N(\varepsilon)-\varphi_N(0)-\varepsilon\varphi_N'(0)\bigr| \\ &\qquad = \Bigl|\frac{\varepsilon^2}{2\pi\mathrm{i}}\int_{|\zeta|=1}\frac{\varphi_N(\zeta)}{\zeta^2(\zeta-\varepsilon)}\,\mathrm{d}\zeta\Bigr| \;\le\; \frac{\varepsilon^2}{\pi}\int_0^{2\pi}\bigl|\varphi_N(e^{\mathrm{i}\theta})\bigr|\,\mathrm{d}\theta\,.\end{aligned} \tag{5.19}$$

Integrating φ_N, $N \ge 2$, over the free parameters $\boldsymbol{R}_{2,N} \in \Lambda^{N-2}$, but keeping $R_1 = R$ and $R_2 = 0$ fixed, we can extend (5.3) and (5.2) to scalar functions of the complex variable ζ, namely

$$a_{N,\Lambda}(\zeta) \;=\; \frac{1}{(N-2)!}\int_{\Lambda^{N-2}} \varphi_N(\zeta)\,\mathrm{d}\boldsymbol{R}_{2,N}\,,$$

and

$$\omega_\Lambda(\zeta) \;=\; \sum_{N=2}^\infty a_{N,\Lambda}(\zeta) z^N\,. \tag{5.20}$$

For $\zeta = 0$ we recover the original definitions (5.3) and (5.2). Since φ_N is absolutely integrable with respect to $\boldsymbol{R}_{2,N} \in \Lambda^{N-2}$, cf. (5.7), and the integral is uniformly bounded for $|\zeta| \le 1$, it follows that a_N is also complex analytic for $|\zeta| \le 1$. Furthermore, from (5.19) and (5.7) we obtain

$$\begin{aligned} \bigl|a_{N,\Lambda}(\varepsilon) - a_{N,\Lambda}(0) - \varepsilon a'_{N,\Lambda}(0)\bigr| \;&\le\; 2C_\Sigma\,\varepsilon^2\,\frac{N^{N-2}}{(N-2)!}\,e^{N\beta B}c_\beta^{N-1}\frac{1}{\varrho(R)} \\ &\le\; C_\Sigma\,\frac{2\varepsilon^2}{c_\beta}\,(c_\beta e^{\beta B+1})^N\frac{1}{\varrho(R)} \end{aligned}$$

for $0 < \varepsilon \le 1/2$.

Since the infinite series (5.20) converges uniformly for $\zeta \in \mathbb{C}$, $|\zeta| \le 1$ (for the same fixed parameters R, z, and the same perturbation $v_0 \in \mathscr{V}_u$), the complex extension (5.20) of the Ursell function is also an analytic function of ζ in a neighborhood of the unit disk with

$$\bigl|\omega_\Lambda(\varepsilon) - \omega_\Lambda(0) - \varepsilon\omega'_\Lambda(0)\bigr| \;\le\; C_\Sigma\,\varepsilon^2 z^2\,\frac{2c_\beta e^{2(\beta B+1)}}{1 - zc_\beta e^{\beta B+1}}\,\frac{1}{\varrho(R)} \tag{5.21}$$

for $0 < \varepsilon \le 1/2$. Accordingly, (5.21) implies that when choosing $v_0 \in \mathscr{V}_u$, z as in (3.1), and $R \in \Lambda$ as above then

$$\omega'_\Lambda(0) \;=\; \bigl((\partial\omega_\Lambda)v_0\bigr)(R)\,.$$

On the other hand, (5.21) is valid for every z as in (3.1), $R \in \Lambda$, and independent of the particular choice of $v_0 \in \mathscr{V}_u$ with $\|v_0\|_{\mathscr{V}_u} \le \delta_0$. Therefore, denoting by ω_Λ and $\widetilde{\omega}_\Lambda$ the Ursell functions (5.1) associated with the reference potential u and *any* perturbed potential $\widetilde{u} = u + v$ with $\|v\|_{\mathscr{V}_u} \le \delta_0/2$, we can rewrite (5.21) for

$$v_0 \;=\; \delta_0 v/\|v\|_{\mathscr{V}_u} \qquad \text{and} \qquad \varepsilon \;=\; \|v\|_{\mathscr{V}_u}/\delta_0$$

as

$$\begin{aligned} &\bigl|\widetilde{\omega}_\Lambda(R) - \omega_\Lambda(R) - \bigl((\partial\omega_\Lambda)v\bigr)(R)\bigr| \\ &\qquad\qquad \le\; C_\Sigma\,z^2\,\frac{2}{\delta_0^2}\,\frac{c_\beta e^{2(\beta B+1)}}{1 - zc_\beta e^{\beta B+1}}\,\|v\|_{\mathscr{V}_u}^2\,\frac{1}{\varrho(R)}\,, \end{aligned} \tag{5.22}$$

valid for every $R \in \Lambda$.

Starting from (5.18) the same line of argument leads to the corresponding estimate

$$\bigl|\widetilde{\omega}_\Lambda(R) - \omega_\Lambda(R)\bigr| \;\le\; C_\Sigma\,z^2\,\frac{2}{\delta_0}\,\frac{c_\beta e^{2(\beta B+1)}}{1 - zc_\beta e^{\beta B+1}}\,\|v\|_{\mathscr{V}_u}\,\frac{1}{\varrho(R)}\,, \tag{5.23}$$

valid for every $R \in \Lambda$ and every $v \in \mathscr{V}_u$ with $\|v\|_{\mathscr{V}_u} \le \delta_0/2$. Finally, (5.16) and (5.17) readily follow from (5.22) and (5.23), respectively, by turning to the thermodynamical limit $|\Lambda| \to \infty$, compare (5.4) and (5.5). $\square$

6 Iterative Boltzmann inversion

Now we turn to the fixed point operator

$$\Phi(u) \;=\; u \;+\; \gamma \log \frac{F(u)}{g^\dagger}$$

associated with the IBI method (1.2), where $\gamma > 0$ is a fixed parameter. Recall that F is the nonlinear operator (1.1) which takes a pair potential $u \in \mathscr{U}$ onto the corresponding radial distribution function g in (3.2). This operator is associated with the corresponding grand canonical ensemble at fixed (inverse) temperature $\beta > 0$ and fixed activity $z > 0$, where for technical reasons we slightly restrict the interval of admissible activity parameters, cf. (6.2) below. Note that Henderson [9] as well as Soper [15] considered the operator F for a canonical ensemble at fixed temperature and fixed (counting) density ρ_0; it is possible to redo the subsequent analysis also for this case with ρ_0 sufficiently small by using the equivalence of ensembles and treating the activity as a function of the counting density and the potential, i.e., $z = z(\rho_0, u)$.

For fixed radial argument $r > 0$ it is an immediate consequence of the results in [5] that the scalar function $u \mapsto (\Phi(u))(r)$ is differentiable with respect to u, and the corresponding derivative is given by

$$\Phi'(u)v \;=\; v \;+\; \gamma\, \frac{F'(u)v}{F(u)}\,, \tag{6.1}$$

pointwise for $r > 0$. However, since $F(u)$ – as a function of r – decays exponentially near $r = 0$ it is not at all obvious whether Φ' actually is a Fréchet derivative in $\mathscr{L}(\mathscr{V}_u, \mathscr{V}_u)$. This is the key assertion of our main result.

Theorem 6.1 *Let $u \in \mathscr{U}$, and let*

$$0 \;<\; z \;<\; \frac{1}{1+e}\,\frac{1}{c_\beta e^{2\beta B+1}}\,. \tag{6.2}$$

Then there exists $C_\Phi = C_\Phi(u,z) > 0$ such that

$$\|\Phi(\widetilde{u}) - \Phi(u)\|_{\mathscr{V}_u} \;\le\; C_\Phi \|\widetilde{u} - u\|_{\mathscr{V}_u} \tag{6.3}$$

for $\|\widetilde{u} - u\|_{\mathscr{V}_u}$ sufficiently small. Moreover, Φ is Fréchet differentiable with respect to u with $\Phi'(u) \in \mathscr{L}(\mathscr{V}_u, \mathscr{V}_u)$, and

$$\|\Phi(\widetilde{u}) - \Phi(u) - \Phi'(u)(\widetilde{u} - u)\|_{\mathscr{V}_u} \;\le\; C_\Phi \|\widetilde{u} - u\|_{\mathscr{V}_u}^2 \tag{6.4}$$

for $\|\widetilde{u} - u\|_{\mathscr{V}_u}$ sufficiently small.

To prepare for a proof of this theorem we investigate the core region $0 < r \le r_0$ and the remaining interval $r > r_0$ separately. We start with the core region.

Lemma 6.2 *Let $u \in \mathscr{U}$, and let z satisfy (6.2). Then there exists $C > 0$, depending on u and on z but independent of $r \in (0, r_0]$, such that*

$$\Big| \big(\Phi(\widetilde{u}) - \Phi(u)\big)(r) \Big| \;\leq\; C\, \|\widetilde{u} - u\|_{\mathscr{V}_u} u(r)\,, \tag{6.5}$$

$$\Big| \big(\Phi(\widetilde{u}) - \Phi(u) - \Phi'(u)(\widetilde{u} - u)\big)(r) \Big| \;\leq\; C\, \|\widetilde{u} - u\|_{\mathscr{V}_u}^2\,, \tag{6.6}$$

uniformly for $\widetilde{u} \in \mathscr{U}$, provided that $\|\widetilde{u} - u\|_{\mathscr{V}_u}$ is sufficiently small.

Proof Referring to the cavity distribution function y defined in (3.3) we have

$$F(u) \;=\; g \;=\; e^{-\beta u} y\,,$$

from which we deduce the representation

$$F'(u)v \;=\; -\beta e^{-\beta u} v y \;+\; e^{-\beta u}(\partial y)v\,, \tag{6.7}$$

pointwise for $0 < r \leq r_0$ and all $v \in \mathscr{V}_u$; here, ∂y denotes the Fréchet derivative of y with respect to u, compare Proposition 3.1.

Let $\widetilde{y}$ be the cavity distribution function associated with $\widetilde{u} = u + v$ for some $v \in \mathscr{V}_u$ sufficiently small. Then we have

$$\begin{aligned} \Phi(\widetilde{u}) - \Phi(u) \;&=\; v \;+\; \gamma\, \log \frac{F(\widetilde{u})}{F(u)} \;=\; (1 - \beta\gamma)v \;+\; \gamma\, \log \frac{e^{\beta \widetilde{u}} F(\widetilde{u})}{e^{\beta u} F(u)} \\ &=\; (1 - \beta\gamma)v \;+\; \gamma \log(\widetilde{y}/y)\,, \end{aligned}$$

and because y is bounded from below, cf. Proposition 3.1, we can use the estimate

$$\big|\log(1 + x) \;-\; x\big| \;\leq\; 2x^2\,, \qquad |x| < 1/2\,, \tag{6.8}$$

to obtain

$$\begin{aligned} \Phi(\widetilde{u}) - \Phi(u) \;&=\; (1 - \beta\gamma)v \;+\; \gamma\, \frac{\widetilde{y} - y}{y} \;+\; O(\|v\|_{\mathscr{V}_u}^2) \\ &=\; (1 - \beta\gamma)v \;+\; O(\|v\|_{\mathscr{V}_u})\,, \end{aligned} \tag{6.9}$$

uniformly for $0 < r \leq r_0$ and $\|v\|_{\mathscr{V}_u}$ sufficiently small. Because of (2.1) and the definition (2.6) of $\|\cdot\|_{\mathscr{V}_u}$ this implies assertion (6.5).

Starting from (6.9) and inserting the representations (6.1) and (6.7) of $\Phi'(u)$ and $F'(u)$, respectively, it follows that

$$\begin{aligned} \Phi(\widetilde{u}) - \Phi(u) - \Phi'(u)v \;&=\; \gamma \Big(\frac{\widetilde{y} - y}{y} \;-\; \frac{F'(u)v}{F(u)} \;-\; \beta v \Big) \;+\; O(\|v\|_{\mathscr{V}_u}^2) \\ &=\; \frac{\gamma}{y} \big(\widetilde{y} - y - e^{\beta u} F'(u)v - \beta v y \big) \;+\; O(\|v\|_{\mathscr{V}_u}^2) \\ &=\; \frac{\gamma}{y} \big(\widetilde{y} - y - (\partial y)v \big) \;+\; O(\|v\|_{\mathscr{V}_u}^2) \;=\; O(\|v\|_{\mathscr{V}_u}^2) \end{aligned}$$

by virtue of Proposition 3.1, again, and this estimate also holds uniformly for $0 < r \leq r_0$. This proves assertion (6.6). □

Lemma 6.3 *Under the assumptions of Lemma 6.2 there exists $C > 0$, such that*

$$\Big|\big(\Phi(\widetilde{u}) - \Phi(u)\big)(r)\Big| \;\leq\; C\|\widetilde{u} - u\|_{\mathscr{V}_u}(1 + r^2)^{-\alpha/2}\,, \qquad (6.10)$$

$$\Big|\big(\Phi(\widetilde{u}) - \Phi(u) - \Phi'(u)(\widetilde{u} - u)\big)(r)\Big| \;\leq\; C\|\widetilde{u} - u\|^2_{\mathscr{V}_u}(1 + r^2)^{-\alpha/2}\,, \qquad (6.11)$$

uniformly for $r \geq r_0$, provided that $\|\widetilde{u} - u\|_{\mathscr{V}_u}$ is sufficiently small.

Proof Using (3.2) and (5.4) we readily obtain the representation

$$\big(F(u)\big)(r) \;=\; g(r) \;=\; 1 + \frac{1}{\rho_0^2}\,\omega(R)\,, \qquad r = |R| \geq 0\,, \qquad (6.12)$$

and therefore (5.15), (5.16), and the differentiability of ρ_0 with respect to u imply a local Lipschitz bound

$$\Big|\big(F(\widetilde{u}) - F(u)\big)(r)\Big| \;\leq\; C_F\|\widetilde{u} - u\|_{\mathscr{V}_u}(1 + r^2)^{-\alpha/2} \qquad (6.13)$$

with some $C_F = C_F(u, z) > 0$ for all $\|\widetilde{u} - u\|_{\mathscr{V}_u}$ sufficiently small and all $r \geq 0$. Moreover, for $r \geq 0$ and $R \in \mathbb{R}^3$ with $|R| = r$ we further deduce from (6.12) that

$$\big(F'(u)v\big)(r) \;=\; \partial\Big(\frac{1}{\rho_0^2}\,\omega(R)\Big)v\,,$$

where the right-hand side denotes the derivative of the scalar function $u \mapsto \omega(R)/\rho_0^2$ with respect to u in direction $v \in \mathscr{V}_u$. Again, using the differentiability of $\rho_0 = \rho_0(u)$, (5.15), and (5.17), we conclude that

$$\Big|\big(F(\widetilde{u}) - F(u) - F'(u)v\big)(r)\Big| \;\leq\; C_F'\|v\|^2_{\mathscr{V}_u}(1 + r^2)^{-\alpha/2}\,, \qquad (6.14)$$

for some $C_F' > 0$, all $v = \widetilde{u} - u \in \mathscr{V}_u$ sufficiently small, and all $r \geq 0$.

Since $F(u)$ is uniformly bounded from below for the given value of the activity and all $r \geq r_0$ according to Proposition 3.1 and (2.1), (6.13) implies that the fraction $(F(\widetilde{u}) - F(u))/F(u)$ is bounded by $1/2$ in absolute value, say, for $\|v\|_{\mathscr{V}_u}$ sufficiently small and all $r \geq r_0$. Accordingly,

$$\begin{aligned}\Big|\Phi(\widetilde{u}) - \Phi(u)\Big| \;&\leq\; |v| \,+\, \gamma\,\Big|\log\frac{F(\widetilde{u})}{F(u)}\Big| \\ &=\; |v| \,+\, \gamma\,\frac{|F(\widetilde{u}) - F(u)|}{F(u)} \,+\, 2\gamma\,\Big|\frac{F(\widetilde{u}) - F(u)}{F(u)}\Big|^2\end{aligned}$$

by virtue of (6.8). Using once again that $F(u)$ is bounded from below for the respective radii $r \geq r_0$, (6.13) and (2.6) imply the first assertion (6.10).

Using (6.1) the same argument as before yields

$$\begin{aligned}\big|\Phi(\widetilde{u}) - \Phi(u) - \Phi'(u)v\big| \;&=\; \gamma\,\Big|\log\frac{F(\widetilde{u})}{F(u)} \,-\, \frac{F'(u)v}{F(u)}\Big| \\ &\leq\; \gamma\,\Big|\frac{F(\widetilde{u}) - F(u) - F'(u)v}{F(u)}\Big| \,+\, 2\gamma\,\Big|\frac{F(\widetilde{u}) - F(u)}{F(u)}\Big|^2\end{aligned}$$

for $\|v\|_{\mathscr{V}_u}$ sufficiently small and all $r \geq r_0$. The second assertion (6.11) thus follows from (6.14) and (6.13). □

After these preparations we can readily finalize our theoretical analysis of the Iterative Boltzmann Inversion.

Proof of Theorem 6.1 Assembling the upper bounds (6.5) and (6.10) from Lemma 6.2 and Lemma 6.3 we obtain the first inequality (6.3). Likewise, (6.6) and (6.11) yield inequality (6.4). □

We conclude with two remarks.

Remark 6.4 For the particular choice $\gamma = 1/\beta$ of the relaxation parameter in IBI, compare (1.3), the first term on the right-hand side of (6.9) vanishes, and hence, in this particular case we have the stronger Lipschitz bounds

$$\begin{aligned} \|\Phi(\widetilde{u}) - \Phi(u)\|_{L^\infty_\varrho(\mathbb{R}^3)} \;&\leq\; C_\Phi \|\widetilde{u} - u\|_{\mathscr{V}_u}\,, \\ \|\Phi(\widetilde{u}) - \Phi(u) - \Phi'(u)(\widetilde{u} - u)\|_{L^\infty_\varrho(\mathbb{R}^3)} \;&\leq\; C_\Phi \|\widetilde{u} - u\|^2_{\mathscr{V}_u}\,, \end{aligned}$$

under the same assumptions as in Theorem 6.1. ◇

Remark 6.5 Since the cavity distribution function $y^\dagger = e^{\beta u^\dagger} g^\dagger$ associated with the true pair potential $u^\dagger$, compare (1.1), is bounded and strictly positive according to Proposition 3.1, we have

$$-\frac{1}{\beta}\log g^\dagger(r) \;=\; u^\dagger - \frac{1}{\beta}\log y^\dagger \;=\; u^\dagger + O(1)\,, \tag{6.15}$$

uniformly for $0 < r \leq r_0$. On the other hand it follows from Corollary 5.2 that there exists $c_g > 0$ with

$$\bigl|g^\dagger(r) - 1\bigr| \;\leq\; c_g (1 + r^2)^{-\alpha/2}\,,$$

which implies

$$\bigl|\log g^\dagger(r)\bigr| \;\leq\; C(1 + r^2)^{-\alpha/2} \tag{6.16}$$

by virtue of (6.8) for some $C > 0$ and r sufficiently large. Moreover, since $y^\dagger$ has strictly positive lower and upper bounds, the representation $g^\dagger = e^{-\beta u^\dagger} y^\dagger$ of the radial distribution function implies that (6.16) extends to all $r \geq r_0$ after increasing C appropriately, when necessary.

We thus conclude from (6.15) and (6.16) that the potential (1.5) of mean force is a Lennard-Jones type pair potential with the same parameter α, and therefore the first iteration of IBI is well-defined for this initial guess. ◇

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