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A Complementary Thermodynamic Limit for Classical Coulomb Matter

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The canonical equilibrium measure of classical two-component Coulomb matter with regularized interactions is analyzed in a finite volume. It is shown that, in the mean-field regime, the one-particle density is inhomogeneous on a new characteristic length scale λ_{inh}. For a system of N positive and N negative particles, λ_{inh} and the characteristic length scale of correlations λ_{corr} (= Debye screening length) are related via $\lambda_{\text{inh}} = (2N)^{1/2}\lambda_{\text{corr}}$. The major conceptual conclusion that is drawn from this is that one needs two nontrivial complementary thermodynamic limits to define the equilibrium thermodynamics of two-component Coulomb systems. One of them is the standard thermodynamic limit (infinite volume), where one takes $N \to \infty$, λ_{corr} fixed. Its complementary limit is characterized by $N \to \infty$, λ_{inh} fixed, and is a finite-volume inhomogeneous mean-field limit. The most prominent new feature in the mean-field thermodynamic limit, which is absent in the standard thermodynamic limit, is an anomalous first-order phase transition where the Coulomb system explodes or implodes, respectively. The phase transition is connected with the existence of a metastable plasma phase far below the ionization temperature.

KEY WORDS: Coulomb systems; classical point particles; canonical ensemble; equilibrium states; complementary thermodynamic limits; first-order phase transition.

1. INTRODUCTION

Given certain stability conditions on the Hamiltonian of a system, the limit of (average) particle number $N \to \infty$, volume $|\Lambda| \to \infty$, $N/|\Lambda| = n$ fixed, exists for the Gibbs equilibrium measures and the average quantities like

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energy density, pressure, etc. This limiting sequence is well known as the standard thermodynamic limit. It is one of the most important concepts of equilibrium statistical mechanics. See, e.g., refs. 1 and 2 for its construction for Hamiltonians with stable short-range forces, and refs. 3–5 for the multicomponent Coulomb problem, both classical and quantum mechanical. It has served as a principal working hypothesis that the equilibrium thermodynamics of a physical system had to be defined in terms of its equilibrium statistical mechanics in the standard thermodynamic limit.[1,2] That standpoint seems natural if one observes its impressive successes in explaining the thermodynamics of matter of ordinary size and in states we experience typically in our everyday lives. Defining thermodynamics on the basis of the standard thermodynamic limit implies, however, that all systems for which the standard thermodynamic limit does not exist are ruled out from thermodynamics. This applies essentially to systems with unstable interactions, examples of which are systems of cosmic size with dominant gravitational interactions and the many-electron atom, a one-component Coulomb system in the field of a localized external charge distribution. Until recently it was in fact a widespread belief that there is no thermodynamics for these systems, although approaches to apply thermodynamic ideas to gravitating systems, for example, go back at least as far as Lord Kelvin,[6] and were extensively discussed, for instance, in ref. 7 and 8. In recent years, the picture has somewhat changed, mainly because it was recognized that the asymptotic behavior as N becomes large of both the Gibbs equilibrium measures (the states) and the thermodynamic functions of systems with unstable interactions can appropriately be investigated in terms of what has become known as an inhomogeneous mean-field thermodynamic limit. See refs. 9–14 for this limit for fermions with either gravostatic or a mixture of both gravo- and electrostatic interactions, and ref. 15 for electrons in the field of infinitely massive nuclei. References 16 and 17 give comprehensive overviews over the basic methods and results of this so called "temperature-dependent Thomas–Fermi limit." One might also be interested in the corresponding ground-state problem.[18,19] Furthermore, ref. 20 deals with more general, unstable one-component quantum Hamiltonians, with special emphasis on spin systems. A classical mean-field limit of the canonical ensemble of one-component systems with fairly general unstable interactions was established in ref. 21, and thouroughly discussed for regularized Newton interactions (including the limiting case of exact Newton interactions) in ref. 22. As is the case in the standard thermodynamic limit, the equilibrium measures in an inhomogeneous mean-field thermodynamic limit are determined by the global minima of a suitable thermodynamic potential. It seems therefore natural to interpret the results derived from the inhomogeneous mean-field thermodynamic limit as pertaining to the equilibrium thermodynamics of the systems with unstable pair interactions. Precisely that has actually been done in the cited literature, and the present article is based on this standpoint as well.

The above discussion seems to point to the conclusion that the standard thermodynamic limit and the inhomogeneous mean-field thermodynamic limit would divide physical systems into two classes, each class associated with its own type of thermodynamic limit which defines the thermodynamics of the system under consideration. However, the aim of this and a subsequent paper is to show that there exist physically important systems for which both the standard and the inhomogeneous mean-field thermodynamic limits can be constructed as nontrivial limits. In such a case both limits are incompatible; they describe complementary asymptotic (as $N \to \infty$) properties of the same large but finite system. In other words, both limits can be regarded as forming *a pair of nontrivial complementary thermodynamic limits for one and the same system.*

In particular, such a situation occurs for classical two-component Coulomb systems with regularized interactions. The standard thermodynamic limit for these systems was constructed in ref. 3 for the thermodynamic functions and in ref. 4 for the measures as well. As will be shown here and in a forthcoming paper,[23] there also exists a nontrivial inhomogeneous mean-field thermodynamic limit. It is interesting in itself to mention that the equations of the mean-field limit of two-component Coulomb matter are formally identical to the mean-field equations of classical one-component Newton matter with regularized interactions.[21,22] In fact, there is a natural analogy between Coulomb and Newton systems in the many-body case, which will play a central role in the considerations given below. Clearly, some typical bulk properties of the Coulomb system obtained from its inhomogeneous mean-field thermodynamic limit cannot be obtained from its standard thermodynamic limit, and vice versa. In this sense, for two-component Coulomb matter the inhomogeneous mean-field thermodynamic limit is a nontrivial complementary thermodynamic limit with respect to the standard one, and vice versa.

The most prominent new feature which we shall find in the new mean-field thermodynamic limit is a first-order phase transition describing an explosion or implosion, respectively, of the Coulomb system. This result is particularly interesting in view of a "no-phase-transition theorem" which has been stated[4] for the standard thermodynamic limit of the here-considered Coulomb systems with regularized interactions.

The main aim of the present paper is to introduce the new concept of complementary thermodynamic limits for classical two-component Coulomb matter, with special emphasis on the discussion of the properties of the new mean-field thermodynamic limit and its possible implications for physical matter. The equations which determine the mean-field thermodynamic limit will be stated without proof. Only the basic ideas of the proof are presented, as well as some nonrigorous but intuitive plausibility reasoning. The technical aspects of the rigorous proof will be dealt with in a subsequent article.[23]

It remains to outline the structure of this paper. The next section contains some plausibility arguments on why it is natural to look for nontrivial complementary thermodynamic limits at all, and especially why classical Coulomb matter is a promising candidate for finding them. In Section 3 it is shown that to the mean-field regime of Coulomb matter there pertains a so far unknown length scale which is incompatible with the Debye scale. This scale is derived (i) by means of an analogy between classical Newton and Coulomb gases and (ii) by means of a variational principle which governs the isothermal equilibrium of finite classical systems with smooth long-range forces in the mean-field approximation. The variational principle is applied to classical Newton and Coulomb systems, both with regularized interactions, and it is shown that formally the results coincide. Section 4 anticipates that the new length scale has associated with it a limit where $N \to \infty$, which preserves this scale. It will be claimed that this limit is a nontrivial complementary thermodynamic limit (with respect to the standard one) for two-component Coulomb systems. We find that the set of equations derived in Section 3 already describes the Coulomb bulk properties in the new limit, which confirms that it is in fact a thermodynamic mean-field limit. The properties of Coulomb matter in the new limit are discussed in Section 5, emphasizing the possible implications for physical matter. Concluding remarks are given in Section 6.

2. CHARACTERISTIC SCALES AND THERMODYNAMIC LIMITS

Once one accepts that there is some type of thermodynamic behavior also for systems with unstable interactions, which may be described (or defined) in terms of an inhomogeneous mean-field thermodynamic limit, with a view toward unification of the notions of equilibrium thermodynamics of systems with stable and with unstable interactions, it is desirable to have an approach that treats the various thermodynamic limits on an equal footing. To achieve this, one has to look for some characteristic many-body features of physical systems which, to some extent, do not depend on whether one has stable or unstable interactions, and which can be used to characterize a thermodynamic limit.

The key notion that might help us in our efforts is that of characteristic bulk length scales. These scales measure typical many-body structures which emerge as the result of the simultaneous interaction of a large number of particles. More importantly, it seems that each of the known thermodynamic limits for nontrivial systems has naturally associated with it a characteristic structural length scale λ_{typ} which plays the role of a characteristic invariant as $N \to \infty$. [The trivial case of the perfect gas (no interactions) will not be considered here explicitly.]

The structures which are measured by some scale λ_{typ} can occur in the one-particle density or in the (higher) correlation functions, or in both. For the systems for which the standard thermodynamic limit (infinite volume) exists, the characteristic bulk scale which is an invariant for that limit is typically a characteristic scale of the two- or more-particle correlation functions. In particular, if the state in the standard thermodynamic limit is a homogeneous system, e.g., a gas, then it has no structure in the one-particle density, and some correlation scale is the only characteristic invariant scale of the standard thermodynamic limit. The equilibrium state might, however, be an infinite crystal. One or several crystal-lattice spacing(s) might then be considered as characteristic invariant(s) as well. In any case, the existence of the typical scales allows one to characterize the standard thermodynamic limit alternatively as the limit $N \to \infty$ of the properly normalized Gibbs measures which keeps certain typical scales λ_{typ} fixed, such that mean quantities such as energy per particle, entropy per particle, etc., have well-defined limits almost everywhere.

An analogous characterization can be given for systems with unstable interactions. A typical many-body feature of systems with unstable interactions is generally a large-scale inhomogeneity in the one-particle density. Let us pick the particular example of an isothermal self-gravitating gas, which will also play a central role in the considerations in the next sections. The characteristic inhomogeneity length scale $\lambda_{\text{inh}}^{(\mathscr{G})}$ for a self-gravitating gas is known as the Jeans length.[24,25] For a finite isothermal system of $N_{\mathscr{G}}$ gravitating particles in a hollow sphere of radius R it reads

$$\lambda_{\text{inh}}^{(\mathscr{G})} = [k_{\text{B}} T R^3 / 3(N_{\mathscr{G}} - 1)\, G m^2]^{1/2} \tag{2.1}$$

where k_{B} is Boltzmann's constant, G is Newton's constant, T is the temperature, and m is the mass of a particle. The inhomogeneous mean-field thermodynamic limit for a self-gravitating gas, consisting either of quantum particles with Fermi statistics or of classical particles with regularized interactions, can in fact be characterized as the limit $N_{\mathscr{G}} \to \infty$ of the Gibbs probability measures which keeps $\lambda_{\text{inh}}^{(\mathscr{G})}$ fixed, such that the energy per particle, etc., has a limit almost everywhere.

It should be noted that the requirement that the mean quantities exist is crucial. The requirement $N_{\mathscr{G}} \to \infty$ with $\lambda_{\text{inh}}^{(\mathscr{G})}$ fixed alone does not rule out the *formal* standard thermodynamic-limit sequence $N_{\mathscr{G}} \to \infty$, $R^3 \sim |\Lambda| \to \infty$, $N_{\mathscr{G}}/|\Lambda| = n$ (more precisely: $(N_{\mathscr{G}} - 1)/|\Lambda| = n$ fixed). But this sequence gives no thermodynamically meaningful limit because the extensivity of the energy, etc., does not hold for systems with gravitational interactions. Recall that in a given volume the classical ground-state energy (=minimum of the potential energy of systems with regularized interactions) diverges to minus infinity proportional to $-N^2$. This means that doubling the system does not imply doubling the energy. Similarly, the quantum mechanical ground-state energy for fermions with exact Newton interactions[26] goes like $-N^{7/3}$. The thermodynamically relevant limit $N_{\mathscr{G}} \to \infty$, $\lambda_{\text{inh}}^{(\mathscr{G})}$ fixed may be performed in a fixed volume, which for the measures implies that either the temperature has to be scaled like $T \sim (N_{\mathscr{G}} - 1)\, T_0$, with T_0 fixed, or the two-particle coupling constant Gm^2 has to be scaled $\sim (N_{\mathscr{G}} - 1)^{-1}[Gm^2]_0$. For details see, e.g., refs. 21 and 22 for the classical systems and refs. 9–17 for the quantum case. It turns out that this scaling of the coupling constant keeps the total (negative) potential energy extensive, i.e., formally proportional to the particle number N. For classical systems this is already sufficient for quantities such as the mean potential energy, etc., to exist, because of the decoupling of the momentum and configurational space contributions. So the mean-field thermodynamic limit for classical self-gravitating matter can be defined as the finite-volume limit $N_{\mathscr{G}} \to \infty$ of the Gibbs probability measure in configurational space, which keeps $\lambda_{\text{inh}}^{(\mathscr{G})}$ fixed. In the quantum case an additional scaling is required for the kinetic energy term. For details see, e.g., refs. 16 and 17.

Besides providing us with the possibility of treating the standard and the inhomogeneous mean-field thermodynamic limit on an equal footing, the characterization of thermodynamic limits by means of their typical length scales has an interesting conceptual spinoff. It is in fact only a small step to come to the conclusion that one should look for systems for which equilibrium thermodynamics may be defined (at least) in terms of a pair of nontrivial complementary thermodynamic limits. Such a situation would occur if the typical structural length scales of the various marginal measures of the Gibbs measure of a finite system would have different N dependences, such that not all length scales could be kept fixed simultaneously along a sequence $N \to \infty$. Such length scales will be called "incompatible." This presents us with the following interesting question: Is it possible at all that a physically meaningful system exists which has at least two incompatible characteristic bulk scales, such that both the thermodynamic limit and perhaps a kind of inhomogeneous mean-field thermodynamic limit exist as nontrivial limits? In that case it would be natural to consider both limits as representing complementary thermodynamic bulk properties of the system.

What we need is a system which as minimum requirement combines the following two properties: (1) The interactions must be stable, which is a sine qua non for the existence of a nontrivial thermodynamic limit[1] in the usual sense; and (2) the interactions must also be sufficiently long range, as sine qua non for a nontrivial kind of thermodynamic mean-field behavior.

Classical Coulomb systems with regularized interactions fulfill both these requirements. Recall that the overall neutrality and the regularization of the interactions guarantee the stability of the classical Coulomb system.[27,28] (Stability also holds in the quantum mechanical case with exact Coulomb interactions if all, or at least all negative particles, are fermions.[29,30]) So the first of our above requirements is fulfilled. The interactions are clearly long range; hence the second requirement holds, too.

The situation with these systems is even more promising. As we already know, the standard thermodynamic limit exists. The proof, both for classical systems with regularized interactions and for fermions, was given in ref. 3 for the thermodynamic functions (see also ref. 31 for a review), and in ref. 4 for all the correlation functions and the observables in the grand canonical ensemble. The standard thermodynamic limit for Coulomb matter is also nontrivial in the physical sense because it has associated with it a characteristic bulk scale which is kept fixed along the standard thermodynamic-limit sequence. This scale is the well-known Debye length, which for a two-species Coulomb system reads

$$\lambda_{\mathrm{corr}}^{(\mathscr{E})} = (\varepsilon_0 k_{\mathrm{B}} T / n_{\mathscr{E}} q^2)^{1/2} \tag{2.2}$$

where ε_0 is the vacuum permittivity, q is the absolute value of the electric charge carried by each particle, and $n_{\mathscr{E}}$ is the total average particle density. The Debye length is a measure for the range of the equilibrium correlations in electrolytes[32,33] and in a plasma,[34] which cluster exponentially with the Debye length as characteristic scale (for a rigorous proof see ref. 35). To see whether, in addition to the standard one, there might also exist a nontrivial complementary thermodynamic limit we have now first of all to investigate whether the long-range character of the Coulomb interactions gives rise to some nontrivial mean-field behavior that has associated with it another bulk scale which is incompatible with the Debye scale.

3. A NEW LENGTH SCALE FOR COULOMB GASES

3.1. Heuristic Estimation

A systematic search for another bulk length scale in two-component Coulomb gases requires investigating finite systems. Clearly, it makes no sense to investigate a system in its standard thermodynamic limit, hoping to find a length scale which is incompatible with that limit. So the problem has to be handled with some care, since in a finite system there can exist many different characteristic lengths which are caused by the interactions of the particles with the confining walls of the container. Most of them, however, will be of no thermodynamic relevance for the bulk system. For instance, that will be the case if only a small group of particles is involved instead of all particles, which form the bulk system. The problem is to find out whether there exists a *bulk* scale in two-component Coulomb systems distinct from the length scale of the correlations. A comparison with the behavior of self-gravitating matter will help us in our efforts. Since the Jeans length measures a large-scale inhomogeneity of gaseous self-gravitating matter in the mean-field regime, and since this regime is caused by the long-range character of the Newtonian gravity force and not by its unstable character, we should not be surprised to find a similar large-scale inhomogeneity in the one-particle density for a finite Coulomb plasma.

Remark. At first glance it may seem that the last claim runs counter to common textbook knowledge; however, a detailed examination of what is usually stated in textbooks reveals that it does not. In the literature one usually finds the statement that in thermal equilibrium a plasma is homogeneous,[34,36,37] but some place in the quoted textbooks it is always explicitly postulated that the thermal equilibrium is defined by the standard thermodynamic limit, a then natural assumption. In this infinite-volume limit a plasma is in fact homogeneous (in the absence of any external charge distribution), but this is not in conflict with the reasoning given here. The goal here is to see whether it is appropriate to define the thermodynamics of two-component Coulomb matter merely in terms of the standard thermodynamic limit or whether a nontrivial complementary limit might be needed.

The following, nonrigorous argument will show that it is indeed likely that there exists a (however, tiny) large-scale inhomogeneity of classical gaseous Coulomb matter in a finite volume. It will also yield a first estimate for the scale itself. (We shall see below that this estimate is even exact!) As pointed out above, the argument makes use of a very close relationship between systems with (regularized) gravostatic interactions and overall neutral systems with (regularized) electrostatic interactions. Hence, let us consider both a self-gravitating system with $N_{\mathscr{G}}$ particles and an overall neutral two-component plasma with $N_{\mathscr{E}}$ positive and $N_{\mathscr{E}}$ negative particles. Each system is confined to a spherical domain of radius R and in thermal equilibrium of temperature T. A nontrivial mean-field behavior can be found by estimating the behavior of both systems under the assumption that correlations can be neglected. This leads to the following picture. In the self-gravitating system each particle will be attracted by all $N_{\mathscr{G}} - 1$ remaining particles. That means that the average gravitational force acting on a particle seems to come from a spherically smeared-out distribution of matter of total mass equal to $N_{\mathscr{G}} - 1$ times the mass of a single particle. For symmetry reasons this resulting average force is directed toward the sphere's center. In equilibrium it is counterbalanced by a thermal pressure gradient which is associated with the large-scale inhomogeneity that lives on the Jeans length scale. In the Coulomb system, on the other hand, there are $N_{\mathscr{E}}$ attractive and $N_{\mathscr{E}} - 1$ repulsive forces acting on each particle of the system, such that on the average every particle sees the remaining system as if it were only a *singly*, oppositely charged fluid. Because of the spherical symmetry of the problem the resulting average attractive force again is directed toward the sphere's center. To balance this resulting average force a pressure gradient is required. This is equivalent to having a large-scale inhomogeneity. Since both the regularized electrostatic and gravostatic forces are essentially $1/r^2$ forces, at least their relevant long-range part, it is plausible that qualitatively the two inhomogeneities will look alike. We can thus guess the scale of the inhomogeneity in Coulomb matter by replacing the gravitational "many-particle coupling constant" $(N_{\mathscr{G}} - 1)\, Gm^2$ in (2.1) by $q^2/4\pi\varepsilon_0$. That way we get

$$\lambda_{\text{inh}}^{(\mathscr{E})} = (\varepsilon_0 k_B T 4\pi R^3/3q^2)^{1/2} \tag{3.1}$$

as a first guess for the inhomogeneity scale in classical gaseous Coulomb matter. Essentially the same argument should apply to slightly nonneutral systems. Because of electrostatic repulsion, any excess charge will aggregate within a thin spherical boundary layer. By Newton's theorem such a layer does not influence the locally essentially neutral interior, where the above line of reasoning applies.

Expressing $\lambda_{\text{inh}}^{(\mathscr{E})}$ in terms of the length scale $\lambda_{\text{corr}}^{(\mathscr{E})}$ of the correlations, which for a finite system formally reads

$$\lambda_{\text{corr}}^{(\mathscr{E})} = (\varepsilon_0 k_B T 2\pi R^3/3N_{\mathscr{E}} q^2)^{1/2} \tag{3.2}$$

[set $n_{\mathscr{E}} = 2N_{\mathscr{E}}/|\Lambda|$ with $|\Lambda| = 4\pi R^3/3$ in (2.2)] yields the relation

$$\lambda_{\text{inh}}^{(\mathscr{E})} = (2N_{\mathscr{E}})^{1/2}\ \lambda_{\text{corr}}^{(\mathscr{E})} \gg \lambda_{\text{corr}}^{(\mathscr{E})} \tag{3.3}$$

Relation (3.3) reveals that, if the guess (3.1) is correct (it is, as will be shown), then the inhomogeneity of a finite Coulomb system in thermal equilibrium is a collective effect, since it extends far beyond the Debye scale. In this sense it is indeed a *plasma* phenomenon, according to the definition introduced by Langmuir.[38] More importantly, the inhomogeneity scale is in fact incompatible with the correlation scale as $N \to \infty$. In the standard thermodynamic limit, $\lambda_{\text{inh}}^{(\mathscr{E})}$ diverges.

The above reasoning suggests that a classical finite Coulomb plasma with regularized interactions has some mean-field features in common with a classical self-gravitating gas. Of course, the above arguments are far from rigorous; in fact, we are far from having proved anything about a complementary thermodynamic limit. Nevertheless, the results obtained in this subsection fit well together; so we shall move on with confidence. In the following subsection the analogy between classical Coulomb and Newton systems will be based on a firmer ground. Before doing so, however, it is appropriate to add the following:

Warning. It should be observed that from (3.1)–(3.3) it follows that, for temperatures above typical ionization temperatures the inhomogeneity is so tiny that it is most probably unobservable by any direct experimental means. One might therefore be tempted to conjecture that the inhomogeneity, and hence any effect associated with it, would be completely unimportant for the thermodynamics. This attitude is, however, erroneous. It overlooks that the inhomogeneity is rather a qualitative indicator that there are some collective interactions at work in a Coulomb system which could give rise to so far unknown but measurable phenomena. This possibility is worth considering. Apart from that, from an academic point of view it is interesting to observe that the inhomogeneity is itself a bulk effect, in the sense that all particles of the plasma are involved and not merely a small subgroup, for example, particles in a thin boundary layer.

3.2. Variational Approach to the Mean-Field Regime

The aim now is to verify, in a sense to be made precise below, the above estimation that formally the overall mean-field structure of the number density of a finite Coulomb gas in equilibrium is the same as that of a classical self-gravitating gas. Standard, however nonrigorous, techniques of theoretical physics are employed. The idea is to apply to a classical Coulomb system the type of variational principle which has already proved useful in determining the mean-field structure of a self-gravitating gas in thermal equilibrium. Thereby one obtains formally the same equations for the mean-field structure of a weakly coupled Coulomb gas as for a classical self-gravitating gas.

It is convenient to treat the gravostatic (= regularized Newton) and the electrostatic (=regularized Coulomb) systems together, specializing to each situation at a later stage of the calculations. Let

$$H^{(N)} = \sum_{i=1}^{\sigma N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{1 \leqslant i < j \leqslant \sigma N} V_{\alpha,\alpha'}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{3.4}$$

be the Hamiltonian of a finite system of σ species of classical point particles in a container $\Lambda \subset \mathbb{R}^3$. Each species consists of N identical particles. The $\mathbf{r}_i \in \Lambda$ are the particle coordinates and the $\mathbf{p}_i \in \mathbb{R}^3$ are the particle momenta. The mass of particle i is m_i. The particles interact via conservative, long-range, central forces. The potential energy $V_{\alpha,\alpha'}(|\mathbf{r}_i - \mathbf{r}_j|)$ between particle i of species α and particle j of species α' is assumed to be bounded. By $\Gamma = \mathbb{R}^{3\sigma N} \times \Lambda^{\sigma N}$ we denote the phase space, and by $f^{(N)}$ the density of a probability measure on Γ. The system is in thermal contact with a heat bath of temperature T. The goal is to estimate the overall structure of the particle density in the mean-field regime.

The basic idea is very simple. It starts from the well-known fact that the canonical probability density $f^{(N;\mathrm{can})}$ of the classical canonical equilibrium measure, given by

$$f^{(N;\mathrm{can})} = (N!^\sigma Z)^{-1} \exp(-\beta H) \tag{3.5}$$

with

$$Z(\Lambda, N, \beta) = (N!)^{-\sigma} \int_\Gamma \exp(-\beta H)\, d\tau \tag{3.6}$$

and $\beta = (k_{\mathrm{B}} T)^{-1}$, can be constructed from the Gibbs variational principle, which is based on the second law of thermodynamics. Explicitly, $f^{(N;\mathrm{can})}$ is the unique minimizer of the free-energy functional

$$\tilde{F}^{(N)}[f] = \langle H^{(N)} \rangle + k_{\mathrm{B}} T \langle \ln(f^{(N)}/f_0^{(N)} N!^\sigma) \rangle \tag{3.7}$$

In (3.7), $\langle \cdot \rangle = \int_\Gamma \cdot f^{(N)}\, d\tau$ denotes the phase space expectation functional taken with Liouville measure[39] $d\tau$, and $f_0^{(N)}$ is some normalizing constant. A slightly modified version of the above variational principle applies to the mean-field regime. Observe that correlations between the particles play a minor role in that regime. In a first approximation correlations might therefore be neglected completely for the calculation of the overall equilibrium properties, which in fact is a characteristic ingredient of any mean-field approximation. This suggests to replace the above variational principle for the construction of $f^{(N;\mathrm{can})}$ by a constrained variational principle and to look for the global minimum of (3.7) only on that subspace of the probability densities on Γ which consists of the α-symmetric products of one-particle densities. Here, "α-symmetric" means symmetric under permutations of the particle indices within species α. Clearly, the momentum part of the canonical equilibrium density is already an α-symmetric product density. Thus, it suffices to consider only the corresponding configurational free-energy functional $F^{(N)}[g]$, which reads

$$F^{(N)}[g] = \langle U^{(N)} \rangle + k_B T \langle \ln(|\Lambda_0|^{2N} g^{(N)}) \rangle \tag{3.8}$$

where $U^{(N)}$ is the interaction Hamiltonian, defined on the configurational subspace $\Omega(N) \subset \Gamma$; g is the configurational probability density, and $|\Lambda_0|$ a fixed reference volume. The constrained variational principle leads to a coupled system of σ integral equations for the configurational one-particle densities of the various species. These equations have to be solved *together* with the condition that a solution (-vector) has to be a global minimizer of the restriction of (3.8) to the α-symmetric subspace of the configurational product probability densities.

The constrained variational principle obviously provides us with the best upper bound to the canonical free energy that can be obtained by means of an uncorrelated probability density. This alone does not guarantee that the corresponding one-particle density is close to the exact one. It should be noted, however, that for the self-gravitating systems the constrained variational principle yields precisely the equations which are recovered in the classical mean-field limit.[21,22] Hence we should also expect the accurate mean-field equations to come out for the more general type of systems described by (3.4). As we shall see, the equations obtained from this variational principle have all the features of the usual mean-field picture.

Let us now compare the equations obtained from the constrained variational principle for a Coulomb system with those obtained for a Newton system. It is convenient to derive both sets of equations here. Let model system ($\mathscr{G}$) be a system of $N_{\mathscr{G}}$ identical classical particles which interact via regularized gravostatic forces. This means $\sigma = 1$ in (3.4). The interaction Hamiltonian of ($\mathscr{G}$) reads

$$U_{\mathscr{G}} = \sum_{1 \leqslant i < j \leqslant N_{\mathscr{G}}} V_{\mathscr{G}}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{3.9}$$

with $V_{\mathscr{G}} = -Gm^2 V < 0$, where $V > 0$ is of positive type[40] and a regularization of $1/|\mathbf{r}_i - \mathbf{r}_j|$. Thus, $V_{\mathscr{G}}$ is a regularization of the Newtonian interaction potential between two points, given by

$$V_{\mathscr{N}} = -\frac{Gm^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{3.10}$$

As $(\mathscr{G})$ contains only one species, the α-symmetric subspace of the configurational product densities consists of densities of the form

$$g(\mathbf{r}_1,..., \mathbf{r}_{N_{\mathscr{G}}}) = \prod_{k=1}^{N_{\mathscr{G}}} \rho(\mathbf{r}_k) \tag{3.11}$$

where ρ is a one-particle probability density on Λ. The free-energy functional (3.8) reduces to the functional

$$\begin{aligned}\mathscr{F}_{\mathscr{G}}[\rho] = &\frac{N_{\mathscr{G}}(N_{\mathscr{G}}-1)}{2} \int_{\Lambda \times \Lambda} \rho(\mathbf{r})\, \rho(\mathbf{r}')\, V_{\mathscr{G}}(|\mathbf{r}-\mathbf{r}'|)\, d^3r\, d^3r' \\ &+ N_{\mathscr{G}} \beta^{-1} \int_{\Lambda} \rho(\mathbf{r}) \ln[|\Lambda_0|\, \rho(\mathbf{r})]\, d^3r\end{aligned} \tag{3.12}$$

The global minimizers of $\mathscr{F}_{\mathscr{G}}$ form a subset of the stationary (or critical) points of $\mathscr{F}_{\mathscr{G}}$, where the first variation of $\mathscr{F}_{\mathscr{G}}$ with respect to ρ vanishes. Thus, one has to find all the solutions of the Euler–Lagrange equation

$$\rho(\mathbf{r}) = \frac{\exp[-(N_{\mathscr{G}}-1)\, \beta (V_{\mathscr{G}} * \rho)(\mathbf{r})]}{\int_{\Lambda} \exp[-(N_{\mathscr{G}}-1)\, \beta (V_{\mathscr{G}} * \rho)(\mathbf{r})]\, d^3r} \tag{3.13}$$

for which (3.12) takes its global minimum. In (3.13), $(V_{\mathscr{G}} * \rho)(\mathbf{r})$ is the convolution product of $V_{\mathscr{G}}$ and ρ.

It should be observed that (3.13) is in fact a mean-field equation. This is readily seen by rewriting (3.13) in the familiar form of the well-known Boltzmann factor of a gas which is subject to a potential ϕ,

$$\rho(\mathbf{r}) = \frac{\exp[-\beta \phi(\mathbf{r})]}{\int_{\Lambda} \exp[-\beta \phi(\mathbf{r})]\, d^3r} \tag{3.14a}$$

where the potential ϕ is not arbitrary, but has to be computed self-consistently from the equation

$$\phi(\mathbf{r}) = (N_{\mathscr{G}}-1) \int_{\Lambda} \rho(\mathbf{r}')\, V_{\mathscr{G}}(|\mathbf{r}-\mathbf{r}'|)\, d^3r' \tag{3.14b}$$

This is the usual mean-field picture. Thus, we can conclude that in the mean-field regime the overall structure of the thermodynamic equilibrium of regularized Newton systems is fairly accurately approximated by those solutions $\rho^{(0)}(\mathbf{r})$ for which (3.12) takes its global minimum.

Remark 1. Instead of eliminating ϕ in (3.14a) via (3.14b), which immediately results in (3.13), one may also eliminate ρ from (3.14b) via (3.14a) to obtain a closed equation for ϕ. It is interesting to note that this equation for ϕ can alternatively be derived from the configurational integral by a method based on Jensen's inequality.[41]

Remark 2. Formally, as $V_{\mathscr{G}} \to V_{\mathscr{N}}$ *together* with the requirement that the normalizing integral $\int_\Lambda \exp[-(N_{\mathscr{G}}-1)\,\beta(V_{\mathscr{G}} * \rho)(\mathbf{r})]\,d^3r$ remains finite, (3.13) becomes the well-known (Lane–) Emden equation of the isothermal gas spheres,[7,8] when Λ is a spherical domain. In addition (3.13) has solutions[22] which converge *-weakly to the Dirac delta measure as $V_{\mathscr{G}} \to V_{\mathscr{N}}$. The Dirac measure is in fact the statistical mechanics equilibrium measure of exact (i.e., nonregularized) classical self-gravitating matter. Only with regularization there is a *small* high-temperature regime where the statistical mechanics equilibrium state is given by gaseous solutions of the Emden type. For a thorough discussion of this and related points see ref. 22.

We come now to the consideration of Coulomb systems. Let model $(\mathscr{E})$ describe a system of classical particles with regularized electrostatic interactions. There are $N_{\mathscr{E}}$ identical positively charged and $N_{\mathscr{E}}$ identical negatively charged classical particles, such that the system is totally neutral. The interaction Hamiltonian of $(\mathscr{E})$ reads

$$U_{\mathscr{E}} = \sum_{1 \leqslant i < j \leqslant 2N_{\mathscr{E}}} (-1)^{i+j}\, V_{\mathscr{E}}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{3.15}$$

where $V_{\mathscr{E}} = (q^2/4\pi\varepsilon_0)\,V > 0$, with the same V as in $V_{\mathscr{G}}$, is a regularization of the Coulomb interaction potential

$$V_{\mathscr{C}} = \frac{q^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{3.16}$$

In (3.15), particles of one species carry an even subscript and particles of the other species an odd one. For $(\mathscr{E})$, $\sigma = 2$; hence,

$$g(\mathbf{r}_1,\ldots,\mathbf{r}_{2N_{\mathscr{E}}}) = \prod_{k=1}^{N_{\mathscr{E}}} \rho_+(\mathbf{r}_{2k})\,\rho_-(\mathbf{r}_{2k-1}) \tag{3.17}$$

where ρ_- and ρ_+ are the one-particle probability densities of the negative and positive species. (Positive [negative] particles now carry even [odd] subscripts.) The right-hand side of (3.8) becomes the free-energy functional

$$\begin{aligned} \mathscr{F}_{\mathscr{E}}[\rho_+, \rho_-] = {} & \frac{N_{\mathscr{E}}(N_{\mathscr{E}}-1)}{2} \int_{\Lambda \times \Lambda} [\rho_+(\mathbf{r})\,\rho_+(\mathbf{r}') + \rho_-(\mathbf{r})\,\rho_-(\mathbf{r}')] \\ & \times V_{\mathscr{E}}(|\mathbf{r}-\mathbf{r}'|)\,d^3r\,d^3r' \\ & - N_{\mathscr{E}}^2 \int_{\Lambda \times \Lambda} \rho_+(\mathbf{r})\,\rho_-(\mathbf{r}')\,V_{\mathscr{E}}(|\mathbf{r}-\mathbf{r}'|)\,d^3r\,d^3r' \\ & + N_{\mathscr{E}}\beta^{-1} \int_\Lambda \rho_+(\mathbf{r}) \ln[|\Lambda_0|\,\rho_+(\mathbf{r})]\,d^3r \\ & + N_{\mathscr{E}}\beta^{-1} \int_\Lambda \rho_-(\mathbf{r}) \ln[|\Lambda_0|\,\rho_-(\mathbf{r})]\,d^3r \end{aligned} \tag{3.18}$$

The first integral describes the part of the potential energy which stems from the electrostatic interactions of each of the species with itself; the second integral is the analog of the first one for the interactions between the two species; the last two integrals are the negative configurational entropies. The corresponding Euler–Lagrange equations for the stationary points of $\mathscr{F}_{\mathscr{E}}[\rho_+, \rho_-]$ read

$$\rho_+(\mathbf{r}) = \frac{\exp[-(N_{\mathscr{E}}-1)\,\beta(V*\rho_+)(\mathbf{r}) + N_{\mathscr{E}}\beta(V*\rho_-)(\mathbf{r})]}{\int_\Lambda \exp[-(N_{\mathscr{E}}-1)\,\beta(V*\rho_+)(\mathbf{r}) + N_{\mathscr{E}}\beta(V*\rho_-)(\mathbf{r})]\,d^3r} \tag{3.19a}$$

$$\rho_-(\mathbf{r}) = \frac{\exp[-(N_{\mathscr{E}}-1)\,\beta(V*\rho_-)(\mathbf{r}) + N_{\mathscr{E}}\beta(V*\rho_+)(\mathbf{r})]}{\int_\Lambda \exp[-(N_{\mathscr{E}}-1)\,\beta(V*\rho_-)(\mathbf{r}) + N_{\mathscr{E}}\beta(V*\rho_+)(\mathbf{r})]\,d^3r} \tag{3.19b}$$

One has to find those solution pairs $[\rho_+^{(0)}(\mathbf{r}), \rho_-^{(0)}(\mathbf{r})]$ of the system of Euler–Lagrange equations (3.19a) and (3.19b) for which $\mathscr{F}_{\mathscr{E}}[\rho_+, \rho_-]$ takes its global minimum.

Lemma 1. If $[\rho_+^{(0)}(\mathbf{r}), \rho_-^{(0)}(\mathbf{r})]$ is a solution pair of the system (3.19a) and (3.19b), then $\rho_+^{(0)}(\mathbf{r}) = \rho_-^{(0)}(\mathbf{r}) \equiv \rho^{(0)}(\mathbf{r})$ for all $\mathbf{r}$.

Proof. It is more convenient to discuss the stationarity properties of $\mathscr{F}_{\mathscr{E}}[\rho_+, \rho_-]$ in terms of ρ and γ, which are defined by

$$\frac{\rho_+(\mathbf{r}) + \rho_-(\mathbf{r})}{2} \equiv \rho(\mathbf{r}) \tag{3.20}$$

$$\frac{\rho_+(\mathbf{r}) - \rho_-(\mathbf{r})}{2} \equiv \gamma(\mathbf{r}) \tag{3.21}$$

These formulas are readily inverted to yield $\rho + \gamma = \rho_+$ and $\rho - \gamma = \rho_-$. In terms of ρ and γ, the free-energy functional $\mathscr{F}_{\mathscr{E}}[\rho_+, \rho_-]$ becomes

$$\begin{aligned}\mathscr{F}_{\mathscr{E}}^*[\rho, \gamma] = {} & -N_{\mathscr{E}} \int_{\Lambda\times\Lambda} \rho(\mathbf{r})\,\rho(\mathbf{r}')\,V_{\mathscr{E}}(|\mathbf{r}-\mathbf{r}'|)\,d^3r\,d^3r' \\ & + (2N_{\mathscr{E}}-1)\,N_{\mathscr{E}} \int_{\Lambda\times\Lambda} \gamma(\mathbf{r})\,\gamma(\mathbf{r}')\,V_{\mathscr{E}}(|\mathbf{r}-\mathbf{r}'|)\,d^3r\,d^3r' \\ & + N_{\mathscr{E}}\beta^{-1} \int_\Lambda (\rho+\gamma)(\mathbf{r})\ln[|\Lambda_0|(\rho+\gamma)(\mathbf{r})]\,d^3r \\ & + N_{\mathscr{E}}\beta^{-1} \int_\Lambda (\rho-\gamma)(\mathbf{r})\ln[|\Lambda_0|(\rho-\gamma)(\mathbf{r})]\,d^3r \end{aligned} \tag{3.22}$$

Stationary points of (3.18), i.e., solution pairs $[\rho_+^{(0)}(\mathbf{r}), \rho_-^{(0)}(\mathbf{r})]$ of (3.19a) and (3.19b) obviously correspond one-to-one with stationary points $[\rho^{(0)}(\mathbf{r}), \gamma^{(0)}(\mathbf{r})]$ of (3.22). Now observe that by symmetry of $V_{\mathscr{E}}$ we have

$\mathscr{F}_{\mathscr{E}}^{*}[\rho, \gamma] = \mathscr{F}_{\mathscr{E}}^{*}[\rho, -\gamma]$. This immediately implies that stationary points of $\mathscr{F}_{\mathscr{E}}^{*}[\rho, \gamma]$ must occur pairwise; i.e., if $[\rho^{(0)}(\mathbf{r}), \gamma^{(0)}(\mathbf{r})]$ is a stationary point of (3.22), so is $[\rho^{(0)}(\mathbf{r}), -\gamma^{(0)}(\mathbf{r})]$ for the same $\rho^{(0)}$ and $\gamma^{(0)}$. On the other hand, since $V_{\mathscr{E}}$ is of positive type, for given $\rho^{(0)}$ the functional $\mathscr{F}_{\mathscr{E}}^{*}[\rho^{(0)}, \gamma]$ is strictly convex with respect to variations of γ, which follows from Theorem 4 of ref. 21. This implies that, if $\rho^{(0)}$ belongs to a stationary point $[\rho^{(0)}, \gamma^{(0)}]$ of $\mathscr{F}_{\mathscr{E}}^{*}[\rho, \gamma]$, there is one and only one $\gamma^{(0)}$ such that $[\rho^{(0)}, \gamma^{(0)}]$ is a stationary point. Together with the above result that stationary points occur in pairs, this implies $\gamma^{(0)} = -\gamma^{(0)}$, which in turn implies $\gamma^{(0)} = 0$ identically. This proves the lemma. ∎

Lemma 1 states that $\mathscr{F}_{\mathscr{E}}[\rho_+, \rho_-]$ as given in (3.18) can be stationary only if the system which is described by the no-correlations approximation is locally charge neutral. This thus holds for the global minimum. Hence in the no-correlations approximation we recover the fact that there is no macroscopic average electric field in equilibrium, which holds for the system described by the exact Gibbs measure. Setting $\rho_+ = \rho_- \equiv \rho$ in (3.18) and abbreviating $\mathscr{F}_{\mathscr{E}}[\rho, \rho]$ by $\mathscr{F}_{\mathscr{E}}[\rho]$ gives the free-energy functional

$$\mathscr{F}_{\mathscr{E}}[\rho] = -N_{\mathscr{E}} \int_{\Lambda \times \Lambda} \rho(\mathbf{r})\, \rho(\mathbf{r}')\, V_{\mathscr{E}}(|\mathbf{r} - \mathbf{r}'|)\, d^3r\, d^3r' + 2N_{\mathscr{E}} \beta^{-1} \int_{\Lambda} \rho(\mathbf{r}) \ln[|\Lambda_0|\, \rho(\mathbf{r})]\, d^3r \tag{3.23}$$

This free-energy functional is proportional to $N_{\mathscr{E}}$; i.e., in this sense $\mathscr{F}_{\mathscr{E}}[\rho]$ is extensive. Similarly, the Euler–Lagrange equation for the stationarity of $\mathscr{F}_{\mathscr{E}}[\rho]$ becomes

$$\rho(\mathbf{r}) = \frac{\exp[\beta(V_{\mathscr{E}} * \rho)(\mathbf{r})]}{\int_{\Lambda} \exp[\beta(V_{\mathscr{E}} * \rho)(\mathbf{r})]\, d^3r} \tag{3.24}$$

which is independent of $N_{\mathscr{E}}$. Equation (3.24) can also be obtained directly from (3.19a) or (3.19b) by setting $\rho_+ = \rho_- \equiv \rho$ in either equation. Again, those solutions $\rho^{(0)}(\mathbf{r})$ for which (3.23) takes its global minimum are also the global minimizers of (3.18). These are the relevant mean-field densities which approximately describe the exact thermodynamic equilibrium state of a Coulomb system with regularized interactions.

It should now be observed that formally the free-energy functional (3.23) is the same as (3.12), and the Euler–Lagrange equation (3.24) is formally the same as (3.13). This was stated at the beginning of this section. Obviously, the analogous discussion as given below (3.13) also applies to (3.24). That means that (3.24) is a mean-field equation which gives the one-particle density as a Boltzmann factor in the self-consistent mean-field potential $-(V_{\mathscr{E}} * \rho)(\mathbf{r})$. The meaning of this self-consistent potential is that of an attractive (regularized) electrostatic potential which is experienced by every particle, independent of the sign of its charge. Although there is no *total* macroscopic electric field, every plasma particle sees the remaining plasma as a singly oppositely charged fluid of density $\rho(\mathbf{r})$. This is precisely the picture sketched in the preceding subsection.

The formal identity between the results obtained in the no-correlations approximations (in fact: mean-field approximations) of the Coulomb and Newton systems establishes that besides the characteristic scale of the correlations, there exists another bulk scale of a Coulomb plasma in the mean-field regime, which is precisely $\lambda_{\text{inh}}^{(\mathscr{E})}$ as given in (3.1). This follows immediately from the fact that (3.13) has inhomogeneous gaseous solutions. For spherical domains Λ these are the above-mentioned ("regularized") isothermal Emden gas spheres, which are inhomogeneous on the scale $\lambda_{\text{inh}}^{(\mathscr{G})}$ given by (2.1). The formal identity between (3.13) and (3.24) reveals, upon comparing the right sides of both equations, that (3.24) has gaseous solutions which are inhomogeneous on the scale $\lambda_{\text{inh}}^{(\mathscr{E})}$.

4. THE LIMIT $N \to \infty$; $\lambda_{\text{inh}} = \text{const}$

The inhomogeneity scale λ_{inh} of classical Coulomb matter with regularized interactions should have associated with it a nontrivial thermodynamic limit where $N \to \infty$ and λ_{inh} is fixed. (The index $\mathscr{E}$ on N, λ_{inh}, and λ_{corr} will be dropped in this section, as no confusion with the respective quantities for self-gravitating matter may occur.) In the present section it is anticipated that this limit exists, and further that the limit is mean-field. For the rigorous construction see ref. 23.

Consider the expression (3.1) for λ_{inh}. Although (3.1) is strictly valid only for spherical domains, one can interpret this formula as characterizing the large-scale inhomogeneity also in more general simply connected domains Λ, provided these domains do not deviate too much from a spherical domain. Then R is a typical radius. From (3.1) it can now be seen that the seemingly simplest way of performing a limit $N \to \infty$, $\lambda_{\text{inh}} = \text{const}$ is to put more and more particles of both species into the container Λ, thereby keeping the volume $|\Lambda|$, the temperature T, the charge q, the total charge Q $(=0$ here), and the physical constants fixed. The limit is then a finite-volume limit without any rescaling of particle quantities. This means that more and more particles will be contained in every volume element however small without having scaled the two-particle forces to vanish with $N \to \infty$. This is a peculiar limiting procedure. Taking a physical point of view, we have to bear in mind that in reality it is impossible to put an arbitrary equal number of positively and negatively charged particles into a given finite volume with the energy per particle, etc., being essentially fixed. Quantum effects come into play, and gravity would finally spoil the extensivity of the energy, the entropy, etc. So, given that the limit $N \to \infty$, $\lambda_{\text{inh}} = \text{const}$ exists mathematically for classical Coulomb systems with regularized interactions, if the particle number in a real system is too large for a given volume, the limiting quantities will clearly not describe the properties of the real system adequately. This type of problem, however, is not only characteristic of the present limiting procedure, but is well known also in the context of the standard thermodynamic limit. The standard thermodynamic limit is also not realizable by any real physical system, in a strict sense, because of gravity. Hence, analogous to the philosophy of corresponding states[2] associated with the standard thermodynamic limit, the physical meaning of the limit $N \to \infty$, $\lambda_{\text{inh}} = \text{const}$ resides for the moment on the hope that the convergence to the limiting quantities is fast enough. There will then exist a regime of the physical parameters where the limiting quantities approximately apply. See also the next section.

The limiting procedure is of interest from a mathematical standpoint as well. Since the two-particle forces do not vanish as $N \to \infty$, there has to occur a subtle cancellation of attractive and repulsive terms in order that a meaningful limit exists. Since the limit is expected to be mean-field, this cancellation has even to go beyond that which gives rise to the standard thermodynamic limit.[3,4] Technically this mean-field problem is therefore *not* simply the many-species generalization of the classical inhomogeneous mean-field thermodynamic limit for one-component systems with unstable interactions,[21,22] where the two-particle forces are scaled to zero in the limit such that only the nonsaturated long-range part (i.e., the mean-field part) survives. Nevertheless, the following can be proved.

Theorem 1. Let $V_{\mathscr{E}}$ be of positive type. Consider the configurational equilibrium measure

$$\mu^{(N)}(d\omega) = \frac{\exp[-\beta \sum_{1 \leqslant i < j \leqslant 2N} (-1)^{i+j} V_{\mathscr{E}}(|\mathbf{r}_i - \mathbf{r}_j|)]}{\int_{\Lambda^{2N}} \exp[-\beta \sum_{1 \leqslant i < j \leqslant 2N} (-1)^{i+j} V_{\mathscr{E}}(|\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_j|)]\, d\tilde{\omega}}\, d\omega \tag{4.1}$$

of a finite system as a measure on the infinite Cartesian product Ω of the Λ of the totally neutral infinite system, whose restriction to $\Lambda^{2N} \subset \Omega$ is given by (4.1), with $d\omega$ the Lebesgue measure on Λ^{2N}. Let $\mathscr{M}$ denote the space of probability measures on Λ and let $\varrho(d^3r) = \rho(\mathbf{r})\, d^3r \in \mathscr{M}' \subset \mathscr{M}$ be absolutely continuous w.r.t. Lebesgue measure. The corresponding product measure on Ω is denoted by $\mu_\varrho = \varrho \otimes \varrho \otimes \cdots$. Let $\mathscr{M}^* \subset \mathscr{M}'$ denote the subset of probabilities ϱ for which the corresponding density ρ is a global minimizer of the free-energy functional $\mathscr{F}_{\mathscr{E}}[\rho]$ given in (3.23). Then any weak limit point of $\{\mu^{(N)} | N=1, 2,...\}$ on Ω is given by a linear convex superposition of those μ_ϱ for which $\varrho \in \mathcal{M}^*$.

Remark. It should be observed that any global minimizer $\rho^{(0)}$ of $\mathcal{F}_\mathcal{E}[\rho]$ is independent of N. It is thus also a global minimizer of the functional of the free energy per particle $(2N)^{-1}\mathcal{F}_\mathcal{E}[\rho] \equiv f_\mathcal{E}[\rho]$; explicitly,

$$f_\mathcal{E}[\rho] = -(1/2)\int_{\Lambda\times\Lambda} \rho(\mathbf{r})\,\rho(\mathbf{r}')\,V_\mathcal{E}(|\mathbf{r}-\mathbf{r}'|)\,d^3r\,d^3r' + \beta^{-1}\int_\Lambda \rho(\mathbf{r})\ln[|\Lambda_0|\,\rho(\mathbf{r})]\,d^3r \tag{4.2}$$

The proof of Theorem 1 requires, in a sense, a kind of hybridization of techniques developed originally for proving the standard thermodynamic limit for all the correlation functions of classical regularized Coulomb matter[4] on one side and for proving the inhomogeneous mean-field thermodynamic limit for classical matter with unstable regularized interactions[21] on the other. We note that Λ is compact and so is Ω (in the product topology). Any α-symmetric probability measure $\mu^{(N)}$ on Λ^{2N} (e.g., a canonical equilibrium measure of a finite system) can naturally be interpreted as an α-symmetric probability measure on Ω such that its restriction to $\Lambda^{2N} \subset \Omega$ is just $\mu^{(N)}$. By the compactness of Ω there exist weak limit points of $\{\mu^{(N)}\}$ as $N(k)\to\infty$ with $k\to\infty$ in the space of α-symmetric probability measures on Ω. The necessary regularity properties of all the marginal measures $\mu^{(N)}_{n_+,n_-}$ are implied by the regularity properties required for $V_\mathcal{E}$ and are proved with the aid of the functional Fourier transformation[4,39,42] (which was denoted the "Siegert transformation" in ref. 43). Subadditivity and weak upper semicontinuity of entropy imply then that the limit $N\to\infty$ of the free energy per particle [see (4.3) below] exists and that it coincides with the mean free energy of any weak limit point of $\{\mu^{(N)} | N=1, 2,...\}$. The latter quantity in turn equals the infimum of the mean free-energy functional defined on $\mathcal{P}$, the space of α-symmetric probability measures on Ω. The mean entropy is affine,[44] and so is the mean free energy. Any α-symmetric probability measure μ on Ω can be written as a convex superposition of the extreme points of $\mathcal{P}$, which is essentially an application of the Krein–Milman theorem (see refs. 1 and 45 for a general discussion). This implies that the mean free energy of μ can be written as the same convex superposition of the free energies of the extreme points. The extreme points of $\mathcal{P}$ turn out to be the product measures of the form $(\varrho_+\otimes\varrho_+\otimes\cdots)\otimes(\varrho_-\otimes\varrho_-\otimes\cdots)$, where the first factor contains all coordinates of the positive species and the second all coordinates of the negative species. This is proved by directly generalizing the proof of the representation theorem for permutation-invariant measures[46] to the α-symmetric case. Finally, by Lemma 1 only those extreme points are involved for which $\varrho_+ = \varrho_-$. For details of the proof we refer to ref. 23.

The following is immediate.

Corollary 1. For all β for which the global minimum of $\mathscr{F}_{\mathscr{E}}[\rho]$ (equivalently: $f_{\mathscr{E}}[\rho]$) is unique there exists a unique limit μ of $\{\mu^{(N)} \mid N = 1, 2,...\}$, which is a product measure. The length scale λ_{inh} given in (3.1) is kept fixed along the sequence $N \to \infty$.

By Theorem 1 the limit state is generally a superposition of mean-field states, i.e., a mixed state. It is of interest to know whether there are pure states. Corollary 1 tells us that if the global minimum of $F_{\mathscr{E}}[\rho]$ is unique, then the complementary thermodynamic equilibrium measure is correlation free, and thus a mean-field or pure state. The following theorem says that there exists a high-temperature regime of pure states.

Theorem 2. Let $(1/2)\, k_{\mathrm{B}} T > V_{\mathscr{E}}(0)$. Then the sequence $\{\mu^{(N)} \mid N = 1, 2,...\}$ converges to a unique product measure μ.

Proof. By Theorem 3 of ref. 21 the solution of (3.24) is unique for $\beta < 1/[2 \sup_{r \in \mathbb{R}^+} V_{\mathscr{E}}(r)]$. The potential $V_{\mathscr{E}}$ is of positive type. Hence[40] $\sup_{r \in \mathbb{R}^+} V_{\mathscr{E}}(r) = V_{\mathscr{E}}(0)$. Now Corollary 1 applies. ∎

The above theorems establish that the limit $N \to \infty$, $\lambda_{\mathrm{inh}} = \mathrm{const}$ exists and also that this limit is mean-field. From now on we may consider that limit as a nontrivial complementary thermodynamic limit, with respect to the standard thermodynamic limit, of classical Coulomb matter with regularized interactions.

The above considerations are somewhat technical, but some weaker results about the mean extensive quantities can be obtained by much simpler arguments. First of all, the existence of convergent subsequences of the mean extensive quantities is guaranteed by the Bolzano–Weierstrass theorem and the following inequalities. The canonical configuration free energy per particle, given by

$$(2N)^{-1} F^{(N,\mathrm{can})} = -(2N\beta)^{-1} \ln Q^{(N)} \tag{4.3}$$

with

$$Q^{(N)} = |\Lambda_0|^{-2N} \int_{\Lambda^{2N}} \exp\left[-\beta \sum_{1 \leqslant i < j \leqslant 2N} (-1)^{i+j} V_{\mathscr{E}}(|\mathbf{r}_i - \mathbf{r}_j|)\right] d\omega \tag{4.4}$$

being the configurational integral, is bounded via

$$\begin{aligned} -(1/2)\, V_{\mathscr{E}}(0) &\leqslant -(2N\beta)^{-1} \ln Q^{(N)} - \beta^{-1} \ln(|\Lambda_0|/|\Lambda|) \\ &\leqslant -(1/2)\, |\Lambda|^{-2} \int_{\Lambda \times \Lambda} V_{\mathscr{E}}(|\mathbf{r} - \mathbf{r}'|)\, d^3r\, d^3r' \end{aligned} \tag{4.5}$$

The first inequality was proved in ref. 27. The second inequality is a consequence of the Gibbs inequality and obtains by choosing a homogeneous configurational trial density. The potential energy per particle is bounded analogously by

$$-(1/2)\, V_{\mathscr{E}}(0) \leqslant (2N)^{-1}\, E^{(N)} \leqslant -(1/2)\, |\Lambda|^{-2} \int_{\Lambda \times \Lambda} V_{\mathscr{E}}(|\mathbf{r}-\mathbf{r}'|)\, d^3r\, d^3r' \tag{4.6}$$

The first inequality is again due to ref. 27. The second one obtains from noting that $\partial E^{(N)}/\partial\beta < 0$, which is well known from statistical mechanics, and then computing $\lim_{\beta \searrow 0} E^{(N)}(\beta)$, which is just the right side of (4.6). Clearly, from the identity $F^{(N)} = E^{(N)} - TS^{(N)}$ we obtain also N-independent upper and lower bounds for the entropy per particle $(2N)^{-1}\, S^{(N)}$ upon combining (4.5) and (4.6). The upper bound can, however, be improved by computing the maximum of $-\langle \ln(|\Lambda_0|^{2N}\, g^{(N)})\rangle$ in the space of probability measures with density g. Hence

$$\begin{aligned} -(1/2)\left[V_{\mathscr{E}}(0) - |\Lambda|^{-2} \int_{\Lambda \times \Lambda} V_{\mathscr{E}}(|\mathbf{r}-\mathbf{r}'|)\, d^3r\, d^3r' \right] \\ \leqslant (2N)^{-1}\, TS^{(N)} \leqslant -\beta^{-1} \ln(|\Lambda_0|/|\Lambda|) \end{aligned} \tag{4.7}$$

Although not sufficient to prove a limit, in analogy to the known situations encountered in the problem of constructing thermodynamic limits, the existence of weak limit points (i.e., convergent subsequences) as implied by the bounds (4.5)–(4.7) for the mean extensive quantities can be interpreted as good indicator that a meaningful limit exists for almost all β.

We also observe that each $\mu^{(N)}$ is the global minimizer of the free-energy functional (3.8) for the finite-N case. Hence, it is natural to expect that any weak limit point of $\{\mu^{(N)}\}$ is a global minimizer of the corresponding expression of the free-energy functional per particle in the infinite case.

Finally, one may also guess that the sequence $N \to \infty$, λ_{inh} fixed amounts to a mean-field limit from the following observation. The correlation length λ_{corr} shrinks to 0 as $N \to \infty$, λ_{inh} fixed, which follows from (3.3). So one might be tempted to argue that the volume λ_{corr}^3 within which particles are correlated with a given particle shrinks to zero. The number of particles ν with which a given particle is correlated is then roughly given by the product of λ_{corr}^3 with the average density $2N/|\Lambda|$ and is given by

$$\nu = (2N)^{-1/2}\, (\lambda_{\text{inh}}^3/|\Lambda|) \tag{4.8}$$

which vanishes as $N \to \infty$. There are then no particles with which a given particle is correlated. This mean-field regime is different from the usual Debye–Hückel mean-field regime,[47] where the number of correlated particles goes to infinity, but with the amplitude of the correlations shrinking rapidly to zero.

It should be noted that a similar type of argument goes through in $d > 3$ dimensions, but not for $d < 3$. (I thank B. Jancovici for drawing my attention to this point.) This clearly shows a weakness of this simple argument, since the proof of Theorem 1 seems not to involve the dimension d of space. Strictly speaking, there is also a little cheating in the argument because (3.2) applies as measure of the correlation length only if the interactions are dominated by the long-range electrostatic part, and even that has been proved only for the high-temperature, low-density regime.[35,48] The short-range interactions (i.e., the smoothing) come(s) into play in regions of space where the density becomes large, i.e., formally if $N \to \infty$ anyway, and physically also at low temperatures even if the formal average density $2N/|\Lambda|$ is small. On the other hand, it is reasonable to expect the regularized short-range part of the interactions to be harmless, such that the argument essentially applies. The correlation length, however, will not be given exactly by the Debye formula (3.2), but by some "modified Debye formula." In that sense, with the appropriate caution in mind, one could expect already from the above simple arguments that in the limit $N \to \infty$, λ_{inh} fixed, all correlations will be perfectly averaged out, except at points of phase transition.

5. APPLICATION TO PHYSICAL MATTER

It is appropriate first to discuss the system of equations [(3.23), (3.24)], which, by Theorem 1, govern the mean-field thermodynamic limit, and then to inquire into the range of physical parameter values where the results might apply. To facilitate the discussion, some notation will be introduced. A formal ionization temperature T^* may be defined by

$$(1/2)\, k_{\mathrm{B}} T^* = V_{\mathscr{E}}(0) \tag{5.1}$$

This is motivated by the fact that $V_{\mathscr{E}}$ is a regularized Coulomb potential, of positive type; hence, it vanishes $\sim r^{-1}$ with $r \to \infty$, but is bounded with $\sup_r V_{\mathscr{E}}(r) = V_{\mathscr{E}}(0)$. Thus, $(1/2)\, k_{\mathrm{B}} T^*$ is the amount of energy necessary to separate two initially tightly bound particles. It is also convenient to introduce a formal classical "atomic" radius a_0 by

$$(1/2)\, k_{\mathrm{B}} T^* = q^2/4\pi\varepsilon_0 a_0 \tag{5.2}$$

The notion of atomic radius corresponds to the picture that physically two-particle bound states will have a size roughly given by a_0 defined via (5.2). In this classical picture a_0 may also be interpreted as an effective cutoff length in the sense that for $r > a_0$ the potential $V_{\mathscr{E}}(r)$ is essentially identical to the exact Coulomb potential $V_{\mathscr{C}}(r)$, but for $r < a_0$ is roughly given by $V_{\mathscr{E}}(r) \approx V_{\mathscr{E}}(0) \approx V_{\mathscr{C}}(a_0)$. Of course, there is no need to stick to applications to systems consisting of classical elementary particles. We may feel free to choose a_0 of rather macroscopic than atomic size. This applies to so-called grain plasmas, which occur in space.

We may like to profit from some results proved in ref. 22; hence, let us add the requirement that $V_{\mathscr{E}}(r)$ is monotonically decreasing and strictly smaller than $V_{\mathscr{C}}(r)$ for all r. For simplicity let Λ be a ball B_R of radius $R \gg a_0$.

The following is a list of important properties of the set of equations [(3.23), (3.24)], respectively [(4.2), (3.24)]:

1. Any local minimizer of the free-energy functional $\mathscr{F}_{\mathscr{E}}[\rho]$ (equivalently, $f_{\mathscr{E}}[\rho]$) is spherically symmetric.

2. For temperatures $T > T^*$ there exists a unique solution ρ of (3.24) (cf. Theorem 2). This solution is thus the global minimizer of (3.23)/(4.2) and describes a pure phase with (formal) inhomogeneity scale λ_{inh} given in (3.1). For all practical purposes the solution can, however, be treated as being homogeneous because $T/T^* > 1$ and $R/a_0 \gg 1$ imply

$$\frac{\lambda_{\text{inh}}}{R} = \left(\frac{2\pi}{3}\right)^{1/2} \left(\frac{T}{T^*}\frac{R}{a_0}\right)^{1/2} \gg 1 \tag{5.3}$$

We shall therefore speak of "quasihomogeneity."

3. At a temperature $T_\updownarrow < T^*$ there exist (at least) two different global minimizers of $f_{\mathscr{E}}[\rho]$. For $T = T_\updownarrow$ the sequence $\{\mu^{(N)}\}$ of the measures (4.1) therefore has a convex continuum of weak limit points. Each weak limit point can be expressed as a convex superposition of the extreme points of that continuum. This corresponds to the existence of a first-order phase transition. If T is decreased from $T > T_\updownarrow$ to $T < T_\updownarrow$, at $T_\updownarrow$ the global minimizer of (3.23) collapses from a quasihomogeneous state to a strongly inhomogeneous state. The phase transition is connected with a jump in the energy and entropy of the system, and with a jump in the pressure at the boundary. In this sense it is an anomalous first-order transition. For the transition temperature one finds the estimate

$$2V_{\mathscr{E}}(0) > k_{\text{B}} T_\updownarrow > V_{\mathscr{E}}(2a_0)/6 \ln(R/a_0) \tag{5.4}$$

for a_0/R small enough.

Remark 1. The first inequality in (5.4) is exact; the second is asymptotically exact as $a_0 \to 0^+$. [Recall that $V_{\mathscr{E}}(0) \to \infty$ as $a_0 \to 0^+$ by construction.] The second inequality is, however, not optimal.

Remark 2. By Theorem 4.4 of ref. 4, a phase transition does not occur in the standard thermodynamic limit for two-component Coulomb systems with regularized classical interactions.

4. The phase transition is connected with the existence of metastable solutions of (3.24) below $T_{\updownarrow}$. A metastable solution is a local, but not global minimizer of $f_{\mathscr{E}}[\rho]$. The branch of the metastable solutions connects differentiably to the high-temperature uniqueness regime. These metastable solutions all are inhomogeneous on the scale λ_{inh}. As the temperature decreases, the inhomogeneity becomes more and more pronounced, although not as pronounced as for the collapsed solutions. There exists a critical temperature $T^{**} \approx (3/2)(a_0/R)\, T^* \ll T^*$ below which the metastable equilibria cease to exist. In particular, $T \approx T^{**}$ means $\lambda_{\text{inh}} \approx R$, which is the analog of the Jeans criterion for self-gravitating gases.

The properties listed in 1–4 are proved in ref. 22, which gives further details; however, there the interpretation of the corresponding formulas was given for self-gravitating systems, as ref. 22 only addresses such systems.

We come now to the possible applications to physical matter. The limit $N \to \infty$, λ_{inh} fixed cannot be realized exactly by a physical system, but only approximately. Even then it is only valid for certain ranges of the parameter values characterizing Coulomb systems. First of all, we can distinguish between two different kinds of solutions of (3.24). On one hand, there are the globally stable quasihomogeneous solutions above the ionization temperature T^*, which connect differentiably to the regime of metastable solutions which extends beyond $T_{\updownarrow}$. Their structure is essentially determined by the long-range part of the Coulomb interactions. On the other hand, there are the collapsed solutions, which are globally stable below $T_{\updownarrow}$. Their structure is determined essentially by the short-range regularization of the interactions. Hence we must not take the details of the collapsed solutions too seriously, although the mere existence of these solutions is of course important. In the following we shall therefore concentrate only on the quasihomogeneous and on the metastable Emden-type solutions.

To estimate the range of the physical parameters where these limit solutions apply, we have to consider the relevant smallness parameters of the problem. The complementary thermodynamic limit is mean-field with the formal condition that the number of correlated particles is small. As we do not have the exact expression for this smallness parameter, we take the number of particles ν in the Debye sphere (see the discussion in the preceding section). We are also working in a classical picture; hence, the ratio of the volume where thermal quantum effects play a role to the total volume must be small. Finally, there is the smoothing length a_0, which in the elementary-particle plasma approximately stands for the size that bound states would have. In the classical grain plasma it stands for the size of the particles. The role played by a_0 also depends on whether we are sufficiently far above or below T^*.

Let us first consider elementary-particle plasmas. Sufficiently far above the ionization temperature we need not take into account the role of a_0 as a measure of the size of bound states. Physically this means that the influence of bound states is small for $T > T^*$. This is also reflected in the fact that the equilibrium states in the uniqueness regime $T > T^*$ (see point 2 above) are essentially independent of the value of a_0, as long as this value is small. So the remaining conditions come from the requirement of the classical mean-field regime. With the abbreviations $T/T^* = \Theta$ and $2N(a_0/R)^3 = \gamma$, the mean-field condition $\nu \ll 1$ yields

$$A\Theta^{3/2}\gamma^{-1/2} \ll 1 \tag{5.5}$$

where A is a numerical constant. For $q = e$ (elementary charge) we have $A \approx 1.2 \times 10^{-1}$. We see that for $\Theta > 1$, condition (5.5) is fulfilled only in the ultrahigh-density regime $\gamma^{1/2} \gg 1$. Now the condition that the relative thermal de Broglie volume be small reads

$$B\Theta^{-3/2}\gamma \ll 1 \tag{5.6}$$

For the numerical factor one gets $B \approx 2.2 \times 10^{-2}$ upon inserting the electron mass in the expression for the thermal de Broglie wavelength and the Bohr radius for a_0. Note that a_0 comes in through the definition of Θ. From these crude estimates we see that, for $\Theta > 1$, the simultaneous fulfillment of both conditions (5.5) and (5.6) cannot be achieved satisfactorily. A satisfactory treatment requires the use of quantum mechanics. Clearly, it would be interesting to see whether for some $\Theta > 1$ the quantum mechanical high-density regime also becomes mean-field.

For temperatures sufficiently far below T^* the situation is more promising, although now we have to take into account that the interesting solutions are only metastable. In the classical model this means that small disturbances would initiate the collapse to states determined by the short-range regularized part of the interactions. An intuitive way to keep the influence of the short-range part small at these low temperatures is to require that the gas parameter γ now also must be small. So $\gamma \ll 1$ together with (5.5) and (5.6) must be required. This is indeed possible to achieve.

For instance, let $\Theta = 0.1$ and $\gamma = 0.01$; then the left side (LS) of (5.5) is ≈ 0.03 and LS(5.6) ≈ 0.02. Let $\Theta = 0.01$ and $\gamma = 10^{-3}$; then LS(5.5) $\approx$ 3×10^{-3} and LS(5.6) ≈ 0.05. These two examples show that sufficiently far below T^* the classical mean-field limit presumably applies. It predicts the existence of a regime of low-density, metastable, mean-field plasma equilibria.

Let us now come to grain plasmas. Here the particles are of macroscopic size a_0. This time we therefore have to require the condition $\gamma \ll 1$ for all temperatures. That means that condition (5.5) is violated above T^*; hence the mean-field limit does not apply there. However, sufficiently far below T^*, i.e., in the metastable regime, there are now fairly good mean-field conditions. For these very massive particles the thermal de Broglie wavelength is so small that condition (5.6) can be dropped. (The numerical factor B will now be much smaller than in the elementary-particle case.) The remaining mean-field condition (5.5) can be fulfilled for $\Theta \ll 1$ together with $\gamma \ll 1$. From this one may conjecture that the mean-field limit can approximately be realized in the form of metastable grain plasma states.

It remains to consider the intermediate-temperature regime, i.e., $T \approx T^*$. As the temperature is not high enough, we should keep the condition $\gamma \ll 1$. But $\gamma \ll 1$ together with (5.5) is impossible for $\Theta \approx 1$, although (5.6) still could be achieved. So roughly at the formal ionization temperature T^* the mean-field condition (5.5) becomes violated if we demand that the particles interact essentially by the Coulomb part of the interactions and also that quantum effects are small. It is interesting that in the complementary thermodynamic limit a phase transition occurs precisely at a temperature $T_\updownarrow$ somewhat below T^*.

It should be observed that the phase transition describes an implosion or explosion, respectively, of the system as a whole. There is no formation or dissociation of bound two-particle states! This is presumably a consequence of the high-density limit, where arbitrarily many particles are squeezed into the "natural" volume an isolated bound-particle state would have, such that these states lose their meaning. Nevertheless there are some implications for dilute physical systems. In a dilute metastable plasma phase below $T_\updownarrow$ there should be a strong affinity of the plasma to condense, i.e., collapse as a whole. The mechanism that drives such a phenomenon is the residual or collective electrostatic attraction described in Section 3. A collapse will happen as soon as suitable fluctuations are available. In reality such a collapse of a *dilute physical* system will lead to an increase of the central density, which at one point would most likely initiate the formation of atoms, or of larger aggregates of bound matter. One can conceive that such a collective collapse mechanism is perhaps at work in certain grain plasmas in space. It might be potentially important for the creation of very small celestial bodies. It should be observed that from the isomorphism established here between classical Coulomb and Newton gases it follows that in dilute, overall neutral systems of less than $\approx 10^{30}$ massive ($\approx 10^{3}$ a.u.) *charged* particles the Coulomb clustering in fact dominates over gravitational clustering.

6. CONCLUDING REMARKS

We have seen that both the standard thermodynamic limit, which is usually taken to define the thermodynamics of systems with stable interactions, and the inhomogeneous mean-field thermodynamic limit, which is usually taken to define the thermodynamics of systems with unstable interactions, can be treated on an equal footing. The basic idea is to characterize a limit by means of some generic structural length scale which is inherent in the physical situation under consideration and which serves as an invariant as $N \to \infty$. This method of characterization of a thermodynamic limit turns out to yield more than merely an umbrella for the two known types of limit. The major conceptual spinoff is the notion of complementary thermodynamic limits for classical two-component Coulomb systems with regularized interactions. As found in Section 3, these systems possess (at least) two characteristic structural length scales, (3.1) for the one-particle density and (3.2) for the higher correlation functions, which are incompatible in any limit where $N \to \infty$. Either length scale can be taken as a characteristic invariant for a thermodynamic limit sequence where $N \to \infty$. Choosing the correlation length λ_{corr} (the Debye screening length) as invariant, the corresponding thermodynamic limit $N \to \infty$, λ_{corr} fixed of the appropriately normalized Gibbs measures and of the mean extensive quantities turns out to be the well-known standard thermodynamic limit[3,4] (infinite-volume limit). Choosing the inhomogeneity scale λ_{inh} of the one-particle density as invariant, the corresponding thermodynamic limit $N \to \infty$, λ_{inh} fixed of the Gibbs probability measures and of the mean extensive quantities turns out to be an inhomogeneous mean-field thermodynamic limit in a fixed volume (Section 4 and ref. 23). In particular, as new phenomena in classical two-component Coulomb systems we find an anomalous first-order phase transition and a metastable plasma phase in the inhomogeneous mean-field thermodynamic limit (Section 5). Both phenomena do not occur[4] in the standard thermodynamic limit. So at least for these idealized systems one may say that the standard thermodynamic limit is incomplete, since it does not predict all bulk properties. The same conclusion holds of course for the inhomogeneous mean-field thermodynamic limit. In this sense it is suggestive to postulate that equilibrium thermodynamics of two-component classical Coulomb matter is to be defined (at least) in terms of two nontrivial complementary thermodynamic limits.

This shows that the relation between equilibrium thermodynamics and statistical mechanics is presumably more subtle than is expressed by the short-hand "thermodynamics = statistical mechanics in the standard thermodynamic limit," which is usually assumed to apply to systems for which the standard thermodynamic limit exists. (In this context, see also ref. 49.) One might need several different complementary limits to define the thermodynamics of one and the same system. The systems considered in this paper are of course very idealized, but it seems promising to invest future effort to see whether our findings carry over at least to a more realistic quantum mechanical treatment of the physical matter system. This means proving a corresponding mean-field thermodynamic limit for two-component fermion systems with exact Coulomb interactions.

From a mathematical technical point of view the inhomogeneous mean-field thermodynamic limit for two-component Coulomb matter is, in a sense, the analog but not a mere many-species generalization of the mean-field thermodynamic limit for one-component systems with unstable interactions. It should be noted that the Hamiltonian of classical two-component Coulomb matter with regularized interactions is stable.[27] This requires several new technical steps for proving the mean-field limit, as compared to the technique of proving the corresponding limit for classical unstable systems. A similar remark applies to quantum systems.

A by-result that is particularly interesting in itself is that the equations which govern the classical two-component Coulomb mean-field limit (Section 4) are formally identical to the mean-field equations of classical self-gravitating, one-component systems with regularized interactions.[21,22] Hence the nature of the first-order phase transitions in both types of systems is essentially the same. Assuming this analogy to hold in the quantum case, one can indeed easily write down the corresponding formal (!) Thomas–Fermi equations for two-component fermion systems with Coulomb interactions. These equations show the same phase transition as gravitating fermions[10–12] do. However, writing down the equations is one thing, proving them is another.

The two-component character of the Coulomb system seems to be crucial for this analogy between Coulomb and Newton systems. The fact that the Coulomb and Newton forces are both r^{-2} alone does not imply a general many-body isomorphism between Coulomb and Newton systems. As pointed out by the referees, the corresponding finite-temperature Thomas–Fermi limit of a one-component fermion gas in a fixed Coulombic background yields a unique equilibrium state[15–17] (see also footnote 13 of ref. 10); hence there is no phase transition in these systems. Although there is a phase transition in the mean-field thermodynamic limit of Bose jellium[50] (also a one-component Coulomb system in a fixed background), this phase transition is a modified Bose condensation, i.e., of a rather different nature.

The above results suggest that the various ensembles might not be equivalent for the Coulomb mean-field limit, which is known to hold for the gravitating systems,[13,51] and which might be a general feature of non-standard thermodynamic limits.[52]

In the first place the results presented in the present paper are of a conceptual nature. The application to physical matter is tempting, but has to be handled with care. Some rather crude estimates (Section 5) reveal that the classical metastable plasma phase could be present in physical matter. The verification of a metastable phase of massive grain plasmas by means of computer simulations might be possible. Here the application to space plasmas is of value. The verification of a metastable plasma phase below the ionization temperature would also mean an indirect "verification" that some first-order phase transition would be present in physical Coulomb matter. The collective mechanism responsible for the phase transition is presumably also at work in certain dilute space plasmas. Nevertheless, the estimates in Section 5 are rather heuristic than exact, and therefore far from final. Clearly, with a view toward applications to physical matter, the results of an infinite-density limit within the framework of classical statistical mechanics can only be considered as preliminary. Any justification has to come from a quantum mechanical treatment, perhaps even from a quantum field approach.

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