**Computational Statistical Mechanics of a confined, three-dimensional Coulomb gas**

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(Dated: April 24, 2020)

The thermodynamic properties of systems with long-range interactions is still an ongoing challenge, both from the point of view of theory as well as computer simulation. In this work we study a model system, a Coulomb gas confined inside a sphere, by using the Wang-Landau algorithm. We have computed the configurational density of states (CDOS), the thermodynamic entropy and the caloric curve, and compared with microcanonical Metropolis simulations, while showing how concepts such as the configurational inverse temperature can be used to understand some aspects of thermodynamic behavior. A dynamical multistability behavior is seen at low energies in microcanonical Monte Carlo simulations, suggesting that flat-histogram methods are in fact superior alternatives to traditional simulation in complex systems.

**I. INTRODUCTION**

The thermodynamics of charged particles has remained a challenging subject, mainly due to the long-range nature of the interaction which breaks some assumptions of classical statistical mechanics. While exact results are common for the two-dimensional Coulomb potential [1, 2], the situation in three dimensions for the unscreened Coulomb potential is not as clear, even using computer simulation.

One interesting phenomenon in long-range interacting systems is the origin of non-Maxwellian velocity distributions, not only in plasmas but in model systems such as the Hamiltonian mean-field (HMF) model [3, 4]. In such long-range systems different mechanisms have been proposed to explain these distributions, such as Tsallis’ nonextensive statistical mechanics [5, 6], superstatistics [7], among others. For an isolated system, the velocity distribution of its components is governed by properties of the interaction potential, more precisely by its configurational density of states (CDOS), as for instance shown by J. R. Ray [8] in small systems. Therefore, it makes sense to gain some understanding of the behavior of this CDOS for long-range potentials.

In the field of condensed matter physics, on the other hand, the computation of the CDOS for systems with complex interactions (such as proteins) using Monte Carlo methods in generalized ensembles has recently emerged as a promising alternative [9, 10] to molecular dynamics simulations. Nevertheless, we are not aware of a calculation of the CDOS for pure Coulomb systems in the literature.

In this work, we focus on the thermodynamics of a model system, where charged particles interacting via the unscreened Coulomb potential are confined inside a spherical region. We present a computation of the CDOS using the Wang-Landau algorithm [11], and from this we determine its equilibrium thermodynamic properties in the canonical and microcanonical ensembles.

This article is organized as follows. Section II defines the interaction energy and the choice of natural units. Sections III and IV review the microcanonical formalism in terms of the configurational degrees of freedom, and the implementation of Monte Carlo methods, while Section V presents the main results. Finally we close with some concluding remarks in Section VI.

**II. DESCRIPTION OF THE MODEL**

We will consider a group of $N = N_+ + N_-$ charged particles in three dimensions. The $N$ particles are divided exactly into two equal groups of $N_+ = N_− = N/2$ with charge $q_+ = e$ and $q_- = −e$, respectively, in order to have exact neutrality. In this system, the Hamiltonian is

$$H(r_1, \ldots, r_N, p_1, \ldots, p_N) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \Phi(r_1, \ldots, r_N),$$

(1)

where $\Phi$ is the electrostatic potential energy, given by

$$\Phi(r_1, \ldots, r_N) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \frac{q_i q_j}{4 \pi \epsilon_0 |r_j - r_i|},$$

(2)

which can be expressed in natural units by defining a natural length unit $r_0$. We can write

$$\Phi(r_1, \ldots, r_N) = \frac{\phi_0}{2} \sum_{i=1}^{N} \sum_{j \neq i} \frac{\sigma_i \sigma_j}{|r_j - r_i|},$$

(3)

with $\sigma_i = \pm 1$ and $r_{ij}$ in units of $r_0$, the model now resembling a long-range Ising-type interaction but with mobile “spins”.

The unit of energy corresponds to

$$\phi_0 := \frac{e^2}{4 \pi \epsilon_0 r_0},$$

(4)

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arXiv:2004.11189v1 [cond-mat.stat-mech] 23 Apr 2020
TABLE I: Parameters in physical units for the choice of $r_0$ equal to the Bohr radius.

| Description          | Symbol | Reference value |
|----------------------|--------|-----------------|
| Length unit          | $r_0$  | 0.529 Å         |
| Energy unit          | $\phi_0 = e^2/(4\pi\epsilon_0 r_0)$ | 27.211 eV |
| Temperature unit     | $T_0 = \phi_0/k_B$ | 315774 K |
| Number of particles  | $N$    | 210             |
| Confining radius     | $R$    | 146 Å           |
| Particle density     | $n = N/(\pi^2 R^3)$ | $8.05 \times 10^{24}$ m$^{-3}$ |
| Debye length at $T = T_0$ | $\lambda_D$ | 137.1 Å |

At this point, we will introduce two modifications to the model. First, in order to “soften” the interaction at very short distances, we have corrected the interparticle distance as

$$|r_j - r_i| \rightarrow \max(|r_j - r_i|, r_0),$$

which avoids the singular behavior at $r_{ij}=0$, making the potential energy bounded. As shown originally by Fisher and Ruelle [12], this truncation of the Coulomb potential is one mechanism able to restore stability. Second, because our aim is to describe an isolated, finite-size system, the particles are confined inside a sphere of radius $R$, so that $|r_i| < R$.

In the following we use $N=210$ particles and a confining radius $R = 276$ $r_0$. For reference, the values of some parameters of interest in plasma physics are given in Table I for the choice of $r_0$ equal to the Bohr radius, $r_0=0.529$ Å. In this case, the system is denser than magnetic confinement plasmas but less dense than inertial fusion plasmas [13].

### III. MICROCANONICAL THERMODYNAMICS

For a system with Hamiltonian given by Eq. 1 because the form of the kinetic energy is universal, the CDOS becomes the key quantity for the thermodynamics in steady states. We will consider a steady state described by the ensemble function $\rho(E)$, such that

$$P(R, P|S) = \rho(H(R, P)), \quad (5)$$

where $R = (r_1, \ldots, r_N)$ and $P = (p_1, \ldots, p_N)$.

In such an ensemble, the expectation of any function $g(H)$ of the energy can be computed as

$$\left< g \right>_S = \int dR dP \ g(H(R, P)) \ P(R, P|S)$$

$$= \int dR dP \ g(K(P) + \Phi(R)) \rho(K(P) + \Phi(R))$$

$$= \int d\phi \ . \ K \ . \ \Omega_K(K) \ D(\phi) \ . \ g(K + \phi) \rho(K + \phi), \quad (6)$$

where we have introduced $\Omega_K(K)$, the density of states of the classical ideal gas,

$$\Omega_K(K) := \int dp_1 \ldots dp_N \ . \ \delta \left( \sum_{i=1}^{N} \frac{p_i^2}{2m} - K \right)$$

$$= \Omega_0 K^{2N-1}, \quad (7)$$

and $D(\phi)$, the configurational density of states, defined in our case by the multidimensional integral

$$D(\phi) := \int_{S(R)} dr_1 \ldots dr_N \ . \ \delta(\phi - \Phi(r_1, \ldots, r_N)), \quad (8)$$

where $\int_{S(R)}$ denotes integration over the region $|r_i| < R$ for $i = 1, \ldots, N$.

Taken as an isolated system, the appropriate description is the microcanonical ensemble,

$$P(R, P|E) = \frac{\delta(E - K(P) - \Phi(R))}{\Omega(E)} \ . \ \Omega(E) \ . \ (9)$$

where the configurational distribution is obtained by integration over the momenta,

$$P(R|E) = \frac{1}{\eta(E)} \ . \ [E - \Phi(R)]^{2N-1}, \quad (11)$$

where $[x]_+ = x$ for $x >= 0$, zero otherwise. The normalization constant $\eta(E)$ is given by

$$\eta(E) = \int d\phi \ D(\phi) \ . \ [E - \phi]^{2N-1}. \quad (12)$$

Using the CDOS it is possible to write the microcanonical probability density of $\phi$ as

$$P(\phi|E) = \frac{1}{\eta(E)} \ . \ [E - \phi]^{2N-1} \ . \ D(\phi). \quad (13)$$

The entropy $S(E)$ can also be expressed [14] in terms of $\eta(E)$ in Eq. [12]

$$S(E) = S_0 + k_B \ln \eta(E). \quad (14)$$

By differentiation with respect to $E$, it follows that

$$\frac{\partial}{\partial E} \ln \eta(E) = \beta(E) = \langle \frac{3N-2}{2(E-\phi)} \rangle_E. \quad (15)$$
which gives us the kinetic estimator of the inverse temperature,

$$\beta_K(\phi) := \frac{3N - 2}{2(E - \phi)},$$  \hspace{1cm} (16)

such that $$\langle \beta_K \rangle_E = \beta(E)$$. In a similar way as the microcanonical inverse temperature $$\beta(E)$$ is defined in terms of the full density of states $$\Omega(E)$$, it is possible to define an inverse temperature from the CDOS, namely the configurational inverse temperature, as

$$\beta_D(\phi) := \frac{\partial}{\partial \phi} \ln \mathcal{D}(\phi),$$  \hspace{1cm} (17)

for which it holds that $$\langle \beta_D \rangle_E = \langle \beta_K \rangle_E = \beta(E)$$. This can be seen from the conjugate variables theorem applied to the potential energy distribution in Eq. 13,

$$\langle \frac{\partial \omega}{\partial \phi} \rangle_E = -\langle \omega(\phi) \frac{\partial}{\partial \phi} \ln P(\phi|E) \rangle_E = \langle \omega(\phi) (\beta_K(\phi) - \beta_D(\phi)) \rangle_E,$$  \hspace{1cm} (18)

for $$\omega = \omega(\phi)$$ an arbitrary, differentiable function of $$\phi$$. For the choice $$\omega(\phi) = 1$$, we have

$$\langle \beta_K \rangle_E = \langle \beta_D \rangle_E.$$  \hspace{1cm} (19)

IV. COMPUTATIONAL METHODS

For the calculation of the density of states, in this case $$\mathcal{D}(\phi)$$, several methods exist. One of the most widely known is the Wang-Landau procedure, in which a random walk is performed in configuration space through the Metropolis algorithm, with acceptance probability given by

$$p_{\text{acc}}(\mathbf{R} \rightarrow \mathbf{R}') = \min \left(1, \frac{\mathcal{D}(\Phi(\mathbf{R}))}{\mathcal{D}(\Phi(\mathbf{R}'))} \frac{3N-1}{2} \right).$$

This achieves a flat distribution of energies as the Markov Chain dynamics converges to the generalized ensemble

$$\rho(\phi) \propto \frac{1}{\mathcal{D}(\phi)}.$$

Because the value of $$\mathcal{D}(\phi)$$ is not known a priori, the procedure starts with an initial guess (usually uniform) and updates it for every visited energy $$\phi$$ using the rule

$$\mathcal{D}(\phi_i) \rightarrow \mathcal{D}(\phi_i) \cdot f,$$

where $$f$$ is a factor which is decreased according to some predefined schedule, usually by the rule $$f_{i+1} = \sqrt{f_i}$$ so it converges to 1.

Microcanonical simulations in the ensemble defined by Eq. 14 can be performed via Monte Carlo Metropolis as proposed by J. R. Ray, in which the acceptance probability becomes

$$p_{\text{acc}}(\mathbf{R} \rightarrow \mathbf{R}') = \min \left(1, \frac{E - \Phi(\mathbf{R}')}{E - \Phi(\mathbf{R})} \frac{3N-1}{2} \right),$$

instead of the usual

$$p_{\text{acc}}(\mathbf{R} \rightarrow \mathbf{R}') = \min (1, \exp(-\beta \Delta \phi)),$$  \hspace{1cm} (21)

employed in canonical Metropolis simulation. Note that, for $$|\Delta \phi| \ll E - \Phi$$ where $$\Delta \phi = \Phi(\mathbf{R}') - \Phi(\mathbf{R})$$, we can provide the following convenient approximation,

$$\left[ \frac{E - \Phi(\mathbf{R}')}{E - \Phi(\mathbf{R})} \right]^{\frac{3N-1}{2}} = \left[ 1 - \frac{\Delta \phi}{E - \Phi(\mathbf{R})} \right]^{\frac{3N-1}{2}} \approx \exp(-\beta K \Phi(\mathbf{R})) \Delta \phi).$$  \hspace{1cm} (22)

This means that, for small proposed displacements, microcanonical Metropolis sampling can be treated as a canonical Metropolis sampling with variable inverse temperature, given by $$\beta_K$$ in Eq. 16. In the case of vanishing potential energy fluctuations, the microcanonical ensemble predictions coincide with the canonical predictions at $$\beta = \beta(E)$$. 

![FIG. 1: Logarithm of the configurational density of states $$\mathcal{D}(\phi)$$ for a Coulomb system confined to a sphere, for energies $$\Phi$$ between -535 $$\phi_0$$ and 950 $$\phi_0$$, as computed by the Wang-Landau algorithm. The dashed line indicates $$\phi=0$$, value above which the curvature changes.](image-url)
V. RESULTS

For the system of $N$ particles interacting via $\Phi$ in Eq. (3) inside a sphere of radius $R$, the logarithm of the CDOS calculated using the Wang-Landau algorithm is shown in Fig. 1. It can be seen that the CDOS is asymmetrical, having an inflection point exactly at $\phi=0$ which divides two regions with different curvature. These regions can be described by the simple empirical model,

$$\ln D(\phi) = \begin{cases} 
  a + A(\phi + b)^\alpha, & \text{if } \phi < 0, \\
  a + A \cdot b^\alpha - B\phi^\alpha, & \text{if } \phi \geq 0,
\end{cases} \tag{23}$$

with parameters $a=-596.0357$, $b=626.8341$, $A=44.9553$, $B=5.3482$ and $\alpha=0.5731$.

The configurational inverse temperature $\beta_D$, defined in Eq. (17) is shown in Fig. 1. A discontinuity at $\phi=0$ can be seen, reflecting the change in curvature of the CDOS. Because $\beta_D < 0$ for $\phi > 0$, no macroscopic state in the microcanonical ensemble is compatible with strictly positive potential energies, as this would imply

$$\langle \beta_D \rangle_E = \langle \beta_K \rangle_E < 0,$$

which is incompatible with the definition of

$$\beta_K(\phi) = \frac{3N}{2(E-\phi)} > 0.$$

Consequence of this is the fact that the potential energies tend to “pile up” towards $\phi = 0$ for high enough total energies, as can be seen in the lower panel of Fig. 5 for energies up to $E=3000 \phi_0$. In other words, despite the fact that microscopic states with $\phi$ above $900 \phi_0$ do exist, as shown by the CDOS in Fig. 1 they are not accessible in microcanonical conditions.

A. Thermodynamical properties

Using the microcanonical Monte Carlo method defined by the acceptance probability in Eq. (20), we have computed the caloric curve $T(E)$ by collecting the average

$$\frac{1}{k_B T(E)} = \frac{3N - 2}{2(E - \Phi)}$$

and compared with the predictions of Eqs. (15) and (13) with the CDOS in Fig. 1. This caloric curve is shown in Fig. 3 together with independent canonical Monte Carlo simulations, using the acceptance probability in Eq. (21) instead.

Complete equivalence between both ensembles is seen, despite the fact that a transition seems to occur between two branches with nearly constant specific heat, around $T^*=0.5 T_0$, the temperature corresponding to $E=0$. The continuous behavior of the caloric curve is verified in the microcanonical entropy $S(E) = k_B \ln \eta(E)$, shown in Fig. 4. The entropy is monotonically increasing with $E$ without any “backbending”, thus despite the discontinuity of the configurational inverse temperature there is no evidence in this system of a first-order phase transition, as commonly occurs in long-range interacting [18] and small systems [19].
FIG. 4: Total entropy for a Coulomb system confined to a sphere, for energies $E$ between $-535 \phi_0$ and $950 \phi_0$.

In order to assess the accuracy of the CDOS computed using the Wang-Landau algorithm beyond averages, we computed the microcanonical potential energy distributions according to Eq. 13 for several total energies, and compared them with empirical histograms collected from microcanonical Monte Carlo simulation. These results are shown in Fig. 5. We can see that, in all cases, the CDOS is capable of describing correctly the shape of the potential energy fluctuations, at least above $E=-200 \phi_0$. In the lower branch of the caloric curve, however, an interesting phenomenon of dynamical multistability is observed in the microcanonical Monte Carlo simulation, as shown for $E=-450 \phi_0$ in Fig. 6. In this case, even when the simulation starts from the most probable potential energy, given by the condition

$$\frac{\partial}{\partial \phi} \ln P(\phi|E)|_{\phi=\phi^*} = 0,$$

that is,

$$\beta_K(\phi^*) = \beta_D(\phi^*),$$

(24)

which has solution $\phi^*=-534.231 \phi_0$ for $E=-450 \phi_0$ (shown as the black dashed line in Fig. 6) the system transits between several macroscopic states, with considerable lifetimes. This effect resembles the behavior of glasses [20] and proteins [21], which commonly have a complex potential energy landscape that makes direct sampling difficult. The dynamical multistability phenomenon reduces the efficiency of microcanonical sampling for low energies, as we have to wait much longer times for the system to explore the different macroscopic states with the correct frequency, thus requiring extremely long simulations to collect reliable statistics.

VI. CONCLUDING REMARKS

We have computed thermodynamic properties of a system of unscreened charged particles confined into a spherical region by using one of the well-established flat-histogram methods, the Wang-Landau algorithm. Our system, while conceptually simple, is still challenging from the point of view of computational statistical mechanics, as we have shown in direct microcanonical Metropolis sampling. We have determined the thermodynamics of the system, in particular we report the configurational density of states, the full thermodynamic entropy, the caloric curve and the microcanonical potential energy distributions.
The shape of the configurational inverse temperature easily explains a concentration of the potential energy distribution mass around $\Phi = 0$ at high total energies, which makes most states with $\Phi > 0$ inaccessible from the microcanonical ensemble. On the other hand, the presence of a dynamical multistability phenomenon complicates the direct microcanonical sampling at low energies, highlighting the usefulness of the generalized-ensemble approaches to computational statistical mechanics.

**Acknowledgements**

The authors gratefully acknowledge funding from Anillo ACT-172101 grant.

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