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Interpretation of an Exactly Solvable Two-Component Plasma

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The interpretation of the exact calculation of the partition function and correlations of a two-component plasma obtained earlier is considered. The system has species of charge ratio 1 : 2 which are constrained to lie on a circle and interact via the two-dimensional Coulomb potential. By studying the exact results we gain an understanding of why the excess thermodynamic quantities of the two component system can be well approximated by the sum of the appropriate excess thermodynamic quantities of the one-component systems.

KEY WORDS: Exactly solvable; two-component plasma; mixing; degenerate states.

1. INTRODUCTION

In a paper hereafter referred to as I(1) the partition function and two-particle correlation functions of a two-component classical Coulomb system (plasma) were evaluated at a special value of the coupling constant. The system consists of particles of charges $+q$ and $+2q$ constrained to lie on a circle and interact via the two-dimensional Coulomb potential. Charge neutrality is obtained by the presence of a uniform background charge density. The analogous system interacting in a three-dimensional domain via the three-dimensional Coulomb potential is a model of a H^+–He^{2+} mixture immersed in a neutralizing background of degenerate electrons. This model is directly relevant to the description of fully ionized matter characteristic of white dwarf stars or the interior of Jupiter.(2,3)

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In I we restricted our attention to the technical details of the derivation and verification of the sum rules satisfied by the correlation functions, which are of general applicability to Coulomb systems. Here we use the expressions obtained in I for the partition function to evaluate the free energy per particle in the thermodynamic limit. This allows us to calculate the excess free energy of mixing, which is a quantity of considerable importance when discussing astrophysical phenomena such as demixing of the two-component system into separate one-component phases.(3,4) We thus provide an exact result on which the accuracy of approximate methods of calculating this quantity can be tested. In particular we can test the linear interpolation method, which is known to be remarkably accurate, in which the free energy of the two-component system is equated to the sum of the free energies of the two separate one-component systems.

Further information about the system is obtained by examining the large separation asymptotic expansions of the truncated two-particle correlations and also by plotting these functions to reveal their short-distance behavior. This gives us some insight into the behavior of two-component plasmas in general, and allows an explanation of the accuracy of the linear interpolation method as an approximation to the free energy.

2. THE EXCESS FREE ENERGY

In I we considered a system of aN particles of charge $+q$ and bN particles of charge $+2q$, labeled $\theta_1, \theta_2, \ldots, \theta_{aN}$ and $\theta_{aN+1}, \theta_{aN+2}, \ldots, \theta_{(a+b)N}$, respectively, interacting on the circle of radius R via the two-dimensional Coulomb potential

$$V(\theta_j, \theta_k) = -q_k \log\left(\frac{R}{L}\right)|e^{i\theta_j} - e^{i\theta_k}| \tag{2.1}$$

Here L is an arbitrary length scale which we take equal to 1. In the presence of a neutralizing background charge density

$$q\frac{(a+2b)N}{2\pi R} \equiv qQ \tag{2.2}$$

the Hamiltonian for such a system, which consists of terms corresponding to the particle–particle, particle–background, and background–background interactions (the last two terms yielding only constants) is given by

$$H = q^2 N(2b + a/2)\log R - q^2 \sum_{1 \leqslant j < k \leqslant (a+b)N} \log|e^{i\theta_j} - e^{i\theta_k}|^{q_j q_k} \tag{2.3}$$

In (2.3) $q_j = 1$ for $1 \leqslant j \leqslant aN$ and $q_j = 2$ for $aN + 1 \leqslant j \leqslant (a+b)N$.

Introducing the dimensionless coupling constant

$$\Gamma \equiv q^2/kT = q^2\beta \tag{2.4}$$

it follows immediately from (2.3) that in the finite system the excess free energy per particle, to be denoted $\phi^{(\mathrm{ex})}$, is given by

$$\beta\phi^{(\mathrm{ex})}(\Gamma, Q, aN, bN) = -\left[\frac{(2b+a/2)\Gamma}{a+b}\log 2\pi Q + f(\Gamma, aN, bN)\right] \tag{2.5}$$

where the function f is defined as

$$f(\Gamma, aN, bN) = \left[\frac{(2b+a/2)\Gamma}{a+b} - 1\right]\log(a+2b)N - \log 2\pi$$
$$+ \frac{1}{(a+b)N}\log I(\Gamma, aN, bN) \tag{2.6}$$

and

$$I(\Gamma, aN, bN) = \prod_{l=1}^{(a+b)N}\int_0^{2\pi} d\theta_l \prod_{1 \leqslant j < k \leqslant (a+b)N} |e^{i\theta_j} - e^{i\theta_k}|^{\Gamma q_j q_k} \tag{2.7}$$

By a generalization of an integration procedure due to Dyson and Mehta[(5)] we proved

$$I(1, aN, bN) = \frac{(aN)!(bN)![N(b+a/2)]!}{[N(2b+a)]!}(16\pi)^{aN/2+bN}$$
$$\times \sum_c \prod_{l=1}^{bN}\left[c(l) - \frac{1}{2}\right]^2 \tag{2.8}$$

where the sum is over all combinations of $\{1, 2, \ldots, N(b+a/2)\}$ taken bN at a time. Furthermore, by using a local limit theorem we showed

$$\sum_c \prod_{l=1}^{bN}\left[c(l) - \frac{1}{2}\right]^2 \sim \frac{|\Gamma(i\alpha + N(b+a/2) + 1/2)|^2 \cosh \pi\alpha}{\pi\alpha^{Na}(2\pi\sigma^2)^{1/2}} \tag{2.9}$$

[the Γ in (2.9) denotes the γ function], where if ν is the unique positive solution of the equation

$$\frac{a}{a+2b} = \frac{\operatorname{artan}\nu}{\nu} \tag{2.10}$$

then

$$\alpha = \frac{(b+a/2)N}{\nu} \quad \text{and} \quad \sigma^2 = \frac{(b+a/2)N}{2}\left(\frac{\operatorname{artan}\nu}{\nu} - \frac{1}{1+\nu^2}\right)$$

Using Stirling's formula for the γ function in (2.9) we can obtain the thermodynamic limit of the free energy. However, we first note both $\phi^{(\mathrm{ex})}$ and f, which depended on both aN and bN in the finite system, are now dependent on the concentrations

$$x_1 = \frac{a}{a+b}, \qquad x_2 = \frac{b}{a+b} \tag{2.11}$$

x_1 denoting the concentration of the $+q$ charges and x_2 the concentration of $+2q$ charges. Since $x_1 + x_2 = 1$, in the thermodynamic limit we can write $\phi^{(\mathrm{ex})}$ and f as $\phi^{(\mathrm{ex})}(\Gamma, Q, x_1)$ and $f(\Gamma, x_1)$. With this notation, we have in the thermodynamic limit

$$f(\Gamma = 1, x_1) = \frac{x_1}{2}\log\frac{2x_1^2(\nu^2+1)}{\pi(x_1+2x_2)^2} + x_2\log\frac{x_2(1+1/\nu^2)}{x_1+2x_2} - \frac{x_1}{2} - 2x_2 \tag{2.12}$$

3. THE EXCESS FREE ENERGY OF MIXING

In a finite system the excess free energy of mixing ΔF is defined as[3]

$$\Delta F^{(\mathrm{ex})} = F^{(\mathrm{ex})}(\Gamma, Q', aN, bN) - F^{(\mathrm{ex})}(\Gamma, Q', aN, 0) - F^{(\mathrm{ex})}(\Gamma, Q', 0, bN) \tag{3.1}$$

This quantity is introduced as an indicator of the demixing of the two charge species. Thus the background charge density Q', being a fixed quantity, must keep the same value in the two separate one-component phases as that in the two-component phase, as indicated in (3.1). Denoting the excess free energy of mixing per particle by $\Delta\phi^{(\mathrm{ex})}$, we have from (3.1)

$$\beta\Delta\phi^{(\mathrm{ex})} = \beta\big[\phi^{(\mathrm{ex})}(\Gamma, Q', x_1) - x_1\phi^{(\mathrm{ex})}(\Gamma, Q', x_1 = 1) - x_2\phi^{(\mathrm{ex})}(\Gamma, Q', x_1 = 0)\big] \tag{3.2}$$

Hence from (2.5) and (2.12) we have at $\Gamma = 1$

$$\beta\Delta\phi^{(\mathrm{ex})} = -\left[\frac{x_1}{2}\log\frac{x_1^2(1+\nu^2)}{(2-x_1)^2} + x_2\log\frac{2x_2(1+1/\nu^2)}{1+x_2}\right] \tag{3.3}$$

Table I.

x_1	ν	$f(1,x_1)$	$\beta\Delta\phi^{(\mathrm{ex})}$	P
0.2	13.47025	− 2.35813	0.00862	.37%
0.3	8.21473	− 2.11494	0.01200	.57%
0.4	5.57299	− 1.92080	0.01460	.76%
0.5	3.97258	− 1.72572	0.01625	.94%
0.6	2.88719	− 1.52947	0.01674	1.09%
0.7	2.08754	− 1.33181	0.01581	1.19%
0.8	1.45110	− 1.13234	0.01308	1.15%

In Table I we give values of ν, $f(1,x_1)$, $\Delta\phi^{(\mathrm{ex})}$, $P \equiv |\beta\Delta\phi^{(\mathrm{ex})}/f(1,x_1)| \times 100\%$, for various values of the concentration x_1.

4. THE CORRELATION FUNCTIONS

If we denote the five integrals

$$I_1 = \int_0^1 dt \frac{\sin \pi y Q t}{t(t^2 + 1/\nu^2)}, \qquad I_2 = \int_0^1 dt \frac{\cos \pi y Q t}{t^1 + 1/\nu^2}$$

$$I_3 = \int_0^1 dt \frac{t \sin \pi y Q t}{t^2 + 1/\nu^2}, \qquad I_4 = \int_0^1 dt \frac{t^2 \cos \pi y Q t}{t^2 + 1/\nu^2}$$

$$I_5 = \int_0^1 dt \frac{t^3 \sin \pi y Q t}{t^2 + 1/\nu^2}$$

then the double integral representations given in I for the correlation functions can be written in terms of these functions. We thus have for the truncated two-particle correlations

$$\rho^T_{+1,+1}(y) = -\frac{Q^2}{\nu^4}\left(I_1 I_3 + I_2^2\right) + \frac{\pi}{2\nu^2} I_3 \tag{4.1a}$$

$$\rho^T_{+1,+2}(y) = -\frac{Q^2}{2\nu^2}\left(I_2 I_4 + I_3^2\right) \tag{4.1b}$$

$$\rho^T_{+2,+2}(y) = -\frac{Q^2}{4}\left(I_3 I_5 + I_4^2\right) \tag{4.1c}$$

where y denotes the particle separation.

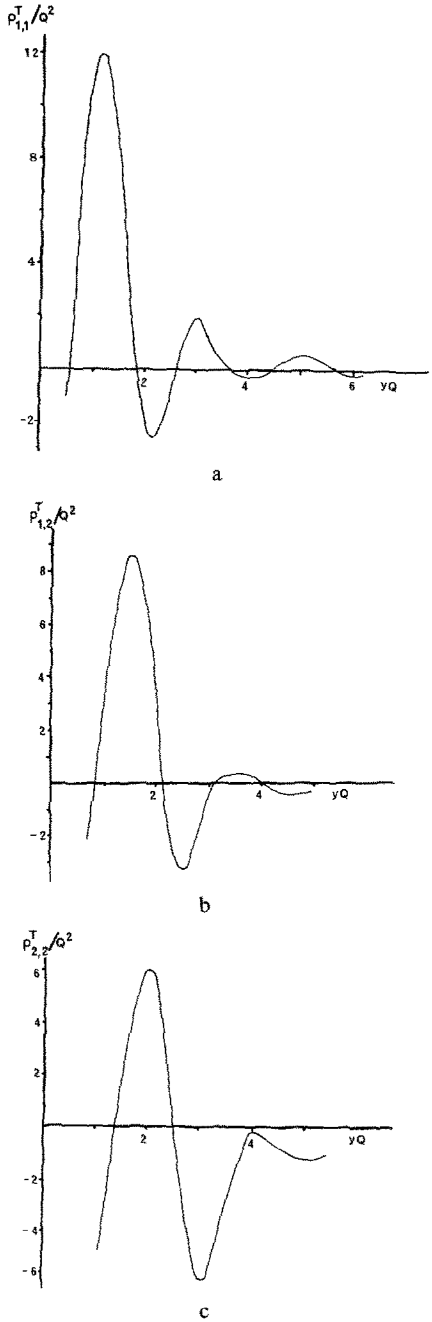

Fig. 1. The scale on the vertical axis has been multiplied by 1,000.

We use these representations to obtain the large y asymptotic expansions to order $1/y^4$, valid for nonzero concentrations x_1 and x_2:

$$\rho^T_{+1,+1}(y) \sim -\frac{Q^2}{(1+\nu^2)^2}\left\{\frac{1}{(\pi y Q)^2} - \frac{\cos^2 \pi y Q}{(\pi y Q)^4} + \frac{1}{(\pi y Q)^4}\left[-1 + \frac{4\nu^2}{1+\nu^2} - \frac{12\nu^4}{(1+\nu^2)^2}\right]\right\} \tag{4.2a}$$

$$\rho^T_{+1,+2}(y) \sim -\frac{Q^2\nu^2}{2(1+\nu^2)^2}\left\{\frac{1}{(\pi y Q)^2} - \frac{\cos^2 \pi y Q}{(\pi y Q)^4} + \frac{1}{(\pi y Q)^4}\left[-1 + \frac{8\nu^2}{1+\nu^2} - \frac{12\nu^4}{(1+\nu^2)^2}\right]\right\} \tag{4.2b}$$

$$\rho^T_{+2,+2}(y) \sim -\frac{Q^2\nu^4}{4(1+\nu^2)^2}\left\{\frac{1}{(\pi y Q)^2} - \frac{\cos^2 \pi y Q}{(\pi y Q)^4} + \frac{1}{(\pi y Q)^4}\left[-1 + \frac{12\nu^2}{1+\nu^2} - \frac{12\nu^4}{(1+\nu^2)^2}\right]\right\} \tag{4.2c}$$

In Figs. 1a, 1b, and 1c we give plots of $\rho^T_{+1,+1}/Q^2$, $\rho^T_{+1,+2}/Q^2$, and $\rho^T_{+2,+2}/Q^2$, respectively, as functions of yQ for the concentration $x_1 = 0.5$.

5. DISCUSSION

We demonstrated in I that the truncated charge–charge correlation, defined as

$$C_2^T(y) = \rho^T_{+1,+1}(y) + 4\rho^T_{+1,+2}(y) + 4\rho^T_{+2,+2}(y) \tag{5.1}$$

satisfies Jancovici's sum rule$^{(6,7)}$

$$C_2^T(y) \sim -\frac{kT}{\pi^2 y^2} \qquad \text{as} \quad y \to \infty \tag{5.2}$$

Although $C_2^T(y)$ is a linear sum of the $\rho_{(2)}^T(y)$, and thus the asymptotic form (5.2) does not imply the decay of the truncated two-particle correlations will also be of order $1/y^2$, we see from (4.2) that in fact the $\rho_{(2)}^T$ do decay as $O(1/y^2)$. Indeed it is reasonable to conjecture from (5.2) that the decay of the $\rho_{(2)}^T$ will always be at least as slow as $O(1/y^2)$, so from Jancovici's physical argument,(6) the origin of this term can be regarded as being well understood.

We note the asymptotic expansions (4.2) all contain an oscillatory term of period $1/Q$ at order $1/y^4$. Such a term was first noted by Dyson(8) in the asymptotic expansion of the truncated two-particle correlation of the same system as considered here but with $x_2 = 0$. He found an oscillatory term of period $1/\rho$, ρ being the particle density. The appearance of the oscillatory term was interpreted as being indicative of an incipient crystalline structure of period $1/\rho$, and indeed it can easily be proved that this is the ground state of the one-component system. Thus if Dyson's interpretation is to be consistent with our results, we must interpret the oscillatory term seen here as being indicative of an incipient crystalline structure of period $1/Q$.

To gain some insight into why this is so, consider the short-distance behavior of the correlations as revealed by Fig. 1. Take special note of the maximum probability peaks at approximately a distance $1/Q$ in the $\rho^T_{+1,+1}$ plot, $3/2Q$ in the $\rho^T_{+1,+2}$ plot and $2/Q$ in the $\rho^T_{+2,+2}$ plot, the exact location of the peaks being distances 6%, 3%, and 2% greater, respectively. Writing $r_{\alpha\delta}$ for the spacing between a particle of charge αq and a particle of charge δq, we thus have as a good approximation at $\Gamma = 1$,

$$r_{11}, r_{12}, r_{22} = Q^{-1}, 3Q^{-1}/2, 2Q^{-1} \tag{5.3}$$

respectively, and would expect (5.3) to remain a good approximation in the ground state. More importantly though, the short-range behavior of the correlations indicate there is little or no preferred sequential ordering of the $+q$ and $+2q$ charges. The two species of charges have thus mixed.

The reason for the appearance of an oscillatory term can now be understood as a consequence of the mixing. At large distances a fixed test charge cannot distinguish a $+2q$ charge from two $+q$ charges at positions $1/2Q$ either side of the position of the $+2q$ charge. The test charge thus "sees" the incipient crystalline structure of the corresponding one-component system which has lattice spacing $1/Q$.

It is interesting to note that the one-dimensional system with the linear potential satisfies (5.3) exactly in the ground state, with each different sequential ordering having the same ground state energy. Consider the interval $[-L, L]$ of the real line. If we take as the pair potential

$$\phi(x_i, x_j) = -q_j|x_i - x_j| \tag{5.4}$$

and consider aN particles of charge $+q$ labeled $x_1, x_2, \ldots, x_{aN}$ and bN particles of charge $+2q$ labeled $x_{aN+1}, \ldots, x_{(a+b)N}$ immersed in a neutralizing background of charge density

$$qQ = q(aN + 2bN)/2L \tag{5.5}$$

it is easy to show the Hamiltonian for the system, disregarding constant terms, can be written

$$H = \sum_{k=1}^{aN} qQ\left(x_k - \frac{w_k}{2Q}\right)^2 + 2\sum_{k=aN+1}^{(a+b)N} qQ\left(x_k - \frac{w_k}{2Q}\right)^2 \tag{5.6}$$

where

$$w_k = \sum_l q_l - \sum_r q_r \tag{5.7}$$

In (5.7) the first sum is over all charges to the left of q_k and the second sum is over all charges to the right of q_k. This formula holds for any given sequential ordering. Thus the ground state occurs at $y_k = w_k/2Q$, and since $w_{k+1} = w_k + q_k + q_{k+1}$, we have $x_{k+1} = x_k + (q_k + q_{k+1})/2Q$, so the ground state spacing is given by (5.3).

Of course the linear potential is unique among the Coulomb potentials, for a one-dimensional charge $+\alpha q$ at the center of a strip of uniform neutralizing background of length α/Q produces a strictly vanishing potential outside the strip. This is not the case with the logarithmic potential, for which the analogous neutral cell has a qaudrupole moment. This means we have no prior reason to suppose different sequential orderings of the $+2q$ and $+q$ charges interacting via the logarithmic potential will have exactly the same ground state energy, nor would we expect (5.3) to exactly represent the ground state spacings.

However, we have seen at $\Gamma = 1$, in the thermodynamic limit, (5.3) is a good approximation to the most probable charge spacing. By considering the magnitude of the excess free energy of mixing we can also use our exact result to test whether the majority of different sequential orderings have nearly the same energies at $\Gamma = 1$. This will be done below, where we conclude that this is in fact the case. We thus have the features of the ground state of the linear potential Coulomb system with a uniform background persisting as a good approximation in the logarithmic case.

Indeed, supposing the features of the ground state of the linear potential system are those of the logarithmic potential to a good approximation, we have the states of the system at $\Gamma = 1$ dominated by the stationary points of the potential.

Now consider the excess free energy of mixing. From Table I we see at $\Gamma = 1$ that $\beta\Delta\phi^{(\mathrm{ex})}$ is positive. We know from plots of the correlation functions that the two-component plasma does mix, but in view of $\beta\Delta\phi^{(\mathrm{ex})}$

being positive we might enquire into the thermodynamic reasons for this. The free energy of mixing per particle is the sum total of $\Delta\phi^{(\mathrm{ex})}$ and $\Delta\phi^{(\mathrm{id})}$ where $\Delta\phi^{(\mathrm{id})}$ is the entropy of mixing per particle of the ideal gas. We note, in view of the comment after (3.1), the relative volume occupied by charge species is determined by the charge density, which must be the same in all systems. Thus the $+q$ charges must occupy a portion $x_1/(x_1+2x_2)$ of the volume and the $+2q$ charges a portion $2x_2/(x_1+2x_2)$, so $\Delta\phi^{(\mathrm{id})}$ is given by

$$\Delta\phi^{(\mathrm{id})} = \phi^{(\mathrm{id})}\left(\rho = \frac{(a+b)N}{2\pi R}\right) - \phi^{(\mathrm{id})}\left[\rho = \left(\frac{2x_2+x_1}{x_1}\right)\frac{aN}{2\pi R}\right] - \phi^{(\mathrm{id})}\left[\rho = \left(\frac{2x_2+x_1}{2x_2}\right)\frac{bN}{2\pi R}\right] \tag{5.8}$$

Here the first term on the right of (5.8) denotes the free energy of a two-component ideal gas of aN particles of species 1 and bN particles of species 2, the other terms on the right denoting the free energy of the one-component ideal gas. Evaluating the right-hand side of (5.8) we have

$$\beta\Delta\phi^{(\mathrm{id})} = -\left[\log(2-x_1) - (1-x_1\log 2)\right] + x_1\log x_1 + x_2\log x_2 \tag{5.9}$$

Computation of (5.9) shows $\beta\Delta\phi^{(\mathrm{id})}$ to be negative and some 30 times the magnitude of $\beta\Delta\phi^{(\mathrm{ex})}$. Thus the total free energy of mixing per particle is negative, so the system does mix.

As commented above, the conjecture of the majority of different sequential orderings having approximately the same energy has consequence with regard to the excess free energy of mixing. Suppose the conjecture to be true. Then we conclude the entropy gained by re-ordering can be well approximated by the entropy of mixing of the ideal gas. Subtracting out this portion we need only consider the free energy of any one of the ordered states. In particular we can consider the state in which the $+q$ and $+2q$ charges are separate, occupying a portion $x_1/(2x_2+x_1)$ and $2x_2/(2x_2+x_1)$ of the volume, respectively. Thus we would expect

$$\phi(\Gamma, Q', x_1) \cong \Delta\phi^{(\mathrm{id})} + \phi(\Gamma, Q', x_1 = 1) + \phi(\Gamma, Q', x_1 = 0) \tag{5.10}$$

But $\Delta\phi^{(\mathrm{id})}$ is given by (5.8) so we can write (5.10) as

$$\phi^{(\mathrm{ex})}(\Gamma, Q', x_1) \cong \phi^{(\mathrm{ex})}(\Gamma, Q', x_1 = 1) + \phi^{(\mathrm{ex})}(\Gamma, Q', x_1 = 0) \tag{5.11}$$

Recalling the definition (3.2) this is equivalent to saying

$$\beta\Delta\phi^{(\mathrm{ex})} \cong 0 \tag{5.12}$$

and indeed from Table I we see at $\Gamma = 1$ that $0 \leqslant \beta\Delta\phi^{(\mathrm{ex})} < 0.017$, which is in qualitative agreement with (5.12).

Equation (5.12) is well known from approximate studies of two-component systems with a rigid neutralizing background in the case of the three-dimensional Coulomb potential within a three-dimensional domain.(3) By the converse of the argument leading to (5.12) we would expect this to be an indication that all states of the system are almost identical up to re-ordering. Explicitly, if the charge ratio was $\alpha:\delta$, by analogy with the exactly solved model, we would expect as a good approximation the average volume occupied by the charges to be in the ratio $\alpha:\delta$, with different states merely being different sequential orderings, each having nearly the same energy.

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