Classical Model for Jellium

Sandipan Dutta and James Dufty

Department of Physics, University of Florida
Gainesville, FL 32611
(Date textdate)

A simple, practical model for computing the equilibrium thermodynamics and structure of jellium by classical strong coupling methods is proposed. An effective pair potential and coupling constant are introduced, incorporating the ideal gas, low density, and weak coupling quantum limits. The resulting parameter free, analytic model is illustrated by the calculation of the pair correlation function over a wide range of temperatures and densities via strong coupling classical liquid state theory. The results compare favorably with the first finite temperature restricted path integral Monte Carlo simulations reported recently.

PACS numbers:

The limitations of many body theories for strongly coupled quantum systems at finite temperatures have led to attempts to adapt corresponding methods known to be effective for classical systems [1]. Among these are the classical molecular dynamics (MD) simulation method, classical Monte Carlo integration, and liquid state theory [2], modified with effective pair potentials that incorporate essential quantum effects such as diffraction and degeneracy. Early approaches were based on a classical form for the two particle density matrix in coordinate representation to identify the effective pair potential incorporating diffraction effects [3, 4]. Exchange effects were incorporated in a similar way using the pair correlation function for an ideal gas [5, 6]. More recently, effective classical systems have been defined with an effective temperature as well as pair potential [6, 7]. A formalism for construction of a classical system with thermodynamics and structure corresponding to a given quantum system is described in reference [8]. A system of particular interest exhibiting strong Coulomb coupling effects, both classical and quantum, is the electron gas (referred to classically as the one component plasma or quantum mechanically as jellium). In the classical limit its thermodynamics is completely characterized by the Coulomb pair potential and a dimensionless coupling constant \( \Gamma = \beta q^2 / r_0 \). Here \( \beta = 1/k_B T \) is the inverse temperature, \( q \) is the particle charge, and \( r_0 \) is the average distance between particles defined in terms of the density (see below).

The objective here is to provide an effective classical system representing the thermodynamics of the real quantum jellium, using an effective pair potential and an effective coupling constant. Simple analytic expressions are given, based on the more complete but complex results of reference [9]. Application of this model is illustrated using the hypernetted chain (HNC) integral equation of classical liquid state theory to calculate the pair correlation function. Comparison of these calculations with the first finite temperature restricted path integral Monte Carlo (PIMC) simulation results reported recently [10] show good agreement over a wide range of densities and temperatures.

Jellium has a broader current interest than its historical role as a test bed for quantum many body theories. Its thermodynamic properties, particularly the density dependence of the free energy, provide the basis for local density approximations (LDA) in electron density functional theory (DFT) [11]. Fits to zero temperature PIMC simulations have been the basis for virtually all LDA DFT for the past thirty years. Until now there has been no corresponding basis for an LDA at finite temperatures from either theory or simulation. Such conditions of solid densities at temperatures comparable to the Fermi temperature are of central interest to the new studies of "warm, dense, matter" [12].

The system of interest is a collection of \( N \) charges with Coulomb pair interactions \( \phi(r) \) in a uniform neutralizing background, at equilibrium [13]. The thermodynamic variables are the temperature and density, \( T \equiv 1/k_B \beta \) and \( n \). A corresponding effective classical system is considered with pair interactions \( \phi_c(r) \) in a uniform neutralizing background, at equilibrium with temperature and density \( T_c \) and \( n_c \). The correspondence of the classical and quantum systems is established by defining \( \phi_c(r), T_c, n_c \) as functions or functionals of \( \phi(r), T, n \) in such a way as to assure the equivalence of selected equilibrium properties. Three such conditions are chosen [9]. The first two are equivalence of the densities and pair correlation functions

\[
n_c = n, \quad g_c(r, \beta_c, n_c \mid \phi_c) = g(r, \beta, n \mid \phi).
\]

The remaining condition fixing \( T_c \) is replaced by a corresponding condition for an effective coupling constant, as discussed below.

To be useful, the condition equating pair correlation functions must be invertible, \( \phi_c(r) = g_c^{-1}(r, \beta_c, n_c \mid g) \), which entails solution to the classical many-body problem. (This inversion does not need to be unique; see final comments below). In the special case of the ideal gas limit the result is known as the Pauli potential,

\[
\phi_c(r) = \int \frac{4 \pi n_c}{2} \frac{1}{r} \, dr.
\]
denoted \(\phi_c^{(0)}(r)\). Even in this case the inversion cannot be accomplished exactly, but good approximations are known [3, 9]. The relevant dimensionless thermodynamic parameters for the quantum system are the temperature relative to the Fermi temperature \(t = 1/\beta\epsilon_F\) and \(r_s = r_0/a_B\), the mean distance between particles \(r_0\) (defined by \(4\pi r_0^3/3 = 1\)) relative to the Bohr radius \(a_B\). Hence the dimensionless effective potential \(\phi_c^*(x, t, r_s) \equiv \beta_c\phi_c(r, \beta, n | \phi)\) is written in the form
\[
\phi_c^*(x, t, r_s) = \phi_c^{(0)}(x, t) + \Delta^*(x, t, r_s),
\]
where \(x \equiv r/r_0\). It has been recognized that the Pauli potential depends only on \(t\).

Two exact limits for \(\Delta^*(x, t, r_s)\) are important for the discussion here. The first is the weak coupling limit
\[
\phi_c^*(x, t, r_s) \rightarrow -c_c(x, t, r_s),
\]
where \(c_c(x, t, r_s)\) is the direct correlation function. It is related to the pair correlation function \(g_c(x, t, r_s)\) by the exact Ornstein-Zernicke equation [2]. Using the correspondence conditions [1], the Ornstein-Zernicke equation defines the direct correlation function in terms of the quantum pair correlation function
\[
c_c(x) = g(x) - 1 - \frac{3}{4\pi} \int d\mathbf{x}'|\mathbf{x} - \mathbf{x}'| g(x') - 1 |. \tag{4}
\]
A sufficient condition for weak coupling is large \(x\), for which the behavior of \(c_c(x, t, r_s)\) is determined from the perfect screening sum rule for \(g(x, t, r_s)\) [18], giving
\[
\Delta^*(x, t, r_s) \rightarrow \Gamma_c(t, r_s) x^{-1}. \tag{5}
\]
This is the same form as for the classical one component plasma, except with the classical Coulomb coupling constant \(\Gamma = \beta q^2 / r_0 = 4(2/3\pi)^{1/3} r_s/3t\) replaced by the effective coupling constant
\[
\Gamma_c(t, r_s) = \frac{2}{\beta \hbar \omega_p \coth(\beta \hbar \omega_p / 2)} \Gamma. \tag{6}
\]
Here \(\omega_p = (4\pi nq^2/m)^{1/2}\) is the plasma frequency (or, equivalently, \(\beta \hbar \omega_p = 4(2\sqrt{3}\pi^{-2})^{1/3} r_s^{1/2}/3t\)). At low temperatures and fixed density \(\Gamma_c(0, r_s)\) becomes divergent whereas the effective coupling constant remains finite \(\Gamma_c(0, r_s) \approx 1.155 r_s^{1/2}\). At high temperatures \(\Gamma_c(t, r_s) \rightarrow \Gamma \approx 0.543 t r_s / t\).

The second exact limit is that for low density and weak coupling. The condition of low density means that \(g(x, t, r_s)\) is determined by the two electron Slater sum. The weak coupling \(\Delta^*(x, t, r_s)\) in that case is known as the Kelbg potential [3, 4, 14]
\[
\Delta^*(x, t, r_s) \rightarrow \Gamma x^{-1} \left(1 - \exp(-ax^2)\right) + \sqrt{\pi} a x \text{erfc}(ax), \tag{7}
\]
where \(a = (r_s/\Gamma)^{1/2}\). This weak coupling result at low density can be improved by imposing the exact behavior of the two particle Slater sum at \(x = 0\), to include some strong coupling effects [3, 4, 15, 16]. The modified form is
\[
\Delta_K^*(x, \Gamma, r_s) = \frac{\Gamma}{x} \left(1 - \exp((ax)^2) + \sqrt{\pi} \frac{ax \text{erfc}(\gamma ax)}{\gamma} \right), \tag{8}
\]
with
\[
\gamma(\Gamma r_s) = -\frac{\pi \Gamma r_s^{1/2}}{\ln S(\Gamma r_s)} \tag{9}
\]
where \(S(\Gamma r_s)\) is the two electron relative coordinate Slater sum at \(x = 0\)
\[
S(\Gamma r_s) = -4(\pi \Gamma r_s)^{1/2} \int_0^\infty dy e^{-y^2} \frac{y}{1 - e^{\pi y}}. \tag{10}
\]

The proposal here is to further extend this Kelbg form to apply broadly across a wide range of values \(t, r_s\) by imposing the exact asymptotic limit [5]. This is accomplished by replacing \(\Gamma\) with the effective coupling constant \(\Gamma_c\) given by [6]. The approximate effective pair potential is thus
\[
\phi_c^*(x, t, r_s) \approx \phi_c^{(0)}(x, t) + \Delta_K^*(x, \Gamma_c, r_s). \tag{11}
\]
Since \(\Delta_K^*(x, \Gamma_c, r_s)\) is an analytic, parameter free form this potential is suitable for practical applications in classical many-body theory, classical Monte Carlo calculations, and molecular dynamics simulations.

To illustrate the utility of this model potential the pair correlation function \(g(x, t, r_s)\) for jellium is calculated here using the classical liquid state HNC integral equation [2]. The first step is a determination of \(\phi_c^{(0)}(x, t)\) for the ideal Fermi gas. Since the pair correlation function \(g^{(0)}(x, t, r_s)\) is known exactly, the HNC equations can be inverted to determine \(\phi_c^{(0)}(x, t)\). These equations are solved numerically using the method of Ng [19]. Next, with \(\phi_c^{(0)}(x, t)\) known the pair correlation function for jellium can be determined from the HNC equations using [17].

Very recently restricted path integral Monte Carlo (PIMC) simulations have been reported for the pair correlation function spanning conditions ranging from extreme quantum to semi-classical. These results provide important benchmarks for existing quantum many-body methods, as well as the approach proposed here. Consider first the relatively high temperature \(t = 8\). Figure (1a) shows good agreement with PIMC for all densities, \(1 \leq r_s \leq 40\). Figure (1b) shows the same comparison for \(t = 1\). Again the agreement is good, except at the extreme condition \(r_s = 40\). In this case a strong correlation peak has formed that is badly under estimated by the theory, although its location is adequately described.
Generally, it is found for $t \leq 1$ the theory is quite good for $1 \leq r_s \leq 10$. This is illustrated in Figures (2a) and (2b) at $t = 0.5$ and 0.0625 (the latter is essentially the same as $t = 0$, as confirmed by a comparison with diffusion Monte Carlo simulations at $t = 0$ [20]). Some trends are evident even from this limited data. For example, the temperature dependence for $t \leq 0.5$ is quite weak for $r_s > 1$. However, for $r_s = 1$ a significant temperature dependence is seen for $0.5 \leq t \leq 8$. In summary, the model potential [11] provides a practical form for the analysis of jellium when quantum methods under conditions that are difficult to access by existing quantum methods (e.g., $r_s > 1$ and $t < 10$).

The thermodynamic properties of jellium can be calculated from the pair correlation function. For example, the pressure can be obtained from a coupling constant integration. Let $p(t, r_s, q)$ be the exact quantum pressure and $g(r, t, r_s, q)$ the exact quantum pair correlation function where now the dependence on the charge $q$ has been made explicit. Then

$$p(t, r_s, q) = p(t, r_s, 0) + 8\pi \int_0^q dy \int_0^\infty drdr' \phi(r_0) \left[ g(r, t, r_s, y) - 1 \right].$$

Here $\phi(r)$ is the Coulomb pair potential. Therefore, approximating $g(r, t, r_s, y)$ by the corresponding classical result obtained using the model potential [11] determines the pressure for arbitrary $t, r_s$. A more direct approach would be classical Monte Carlo integration of the Gibbs distribution for the free energy

$$F = -\beta^{-1} \ln \int d\textbf{x}_1...d\textbf{x}_N e^{-\sum_{ij} \phi_0(x_{ij}) + \Delta_K(x_{ij}, \Gamma, r_s)},$$

with $x_{ij} = |\textbf{x}_i - \textbf{x}_j|$. As noted in the introduction, the idea of an effective classical pair potential with an effective classical temperature was already introduced more than ten years ago by Perrot and Dharma-wardana [6]. Instead of the Kelbg potential they chose the Deutsch potential [17], originally introduced as a simpler representation of the Kelbg potential. The PDW effective classical potential is similar to [11], but with $\Delta_K(x, \Gamma, r_s)$ replaced by

$$\Delta_{PDW}(x, \Gamma_{PDW}, r_s) \equiv \Gamma_{PDW} x^{-1} (1 - \exp(-bx))$$

Here, $b = (\pi r_s/\Gamma_{PDW})^{1/2}$ and the effective coupling constant is

$$\Gamma_{PDW} = \left[ 1 + \left( \frac{T_0}{T} \right)^2 \right]^{-1/2} \Gamma$$

This follows from their phenomenological form for the classical temperature interpolating between the real temperature $T$ and a finite value $T_0$ at $T = 0$. The single parameter $T_0/T$ is determined by fitting the classical correlation energy calculated with this potential to the quantum exchange/correlation energy determined from PIMC at $T=0$. It is given as an explicit fitting function of $r_s$ in reference [6]. Although the dependence of $\Gamma_{PDW}$ on $r_s$ is quite different from that derived here, and the shape of the resulting effective pair potential can be quite different, nevertheless the HNC pair correlation function calculated from the PDW potential has a similar accuracy to that reported here. This indicates that an effective pair potential has no inherent physical interpretation, but rather is a non-unique tool for generating physical properties of interest through classical many-body methods. Here that potential has been constructed by imposing three exact constraints: the ideal gas limit,
low density limit, and large distance limit. Consequently no fitting parameters are required. The result provides theoretical support for the ideas of reference [6] and provides insight into the relevant physical mechanisms. For example, the exact screening sum rule that determines the form of $\Gamma_c$ here appears to incorporate quantum effects as significant as those of $\Gamma_{PDW}$ imposed by empirical $T = 0$ exchange/correlation energy data.

This research has been supported by NSF/DOE Partnership in Basic Plasma Science and Engineering award DE-FG02-07ER54946 and by US DOE Grant de-SC0002139.

FIG. 2: Pair correlation function $g(r^*)$ at (a) $t = 0.5$ and (b) $t = 0.0625$ for $r_s = 1, 6, 10$. Also shown are the results of PIMC.

[1] C. Jones and M. Murillo, High Energy Density Physics 3, 379 (2007); F. Graziani et al, High Energy Density Physics 8, 105 (2012).
[2] J-P Hansen and I. MacDonald, Theory of Simple Liquids, (Academic Press, San Diego, CA, 1990).
[3] For references see W. Ebeling, A. Filinov, M. Bonitz, V. Filinov, and T. Pohl, J. Phys. A 39, 4309 (2006).
[4] A. Filinov, V. Golubnychiy, M. Bonitz, W. Ebeling, and J. Dufty, Phys. Rev. E 70, 046411 (2004).
[5] G.E. Uhlenbeck, L. Groppe, Phys. Rev. 41 (1932) 79; F. Lado, J. Chem. Phys. 47, 5369 (1967); J. W. Dufty, S. Dutta, M. Bonitz, and A. Filinov, Int. J. Quant. Chem. 109, 3082 (2009).
[6] F. Perrot and M. W. C. Dharma-wardana, Phys. Rev. B 62, 16536 (2000); M. W. C. Dharma-wardana, Int. J. Quant. Chem. 112, 53 (2012).
[7] J. W. Dufty and S. Dutta, Contrib. Plasma Phys. 52, 100 (2012).
[8] J. W. Dufty and S. Dutta, "Classical Representation of a Quantum System at Equilibrium: Theory", Phys. Rev. E (to appear).
[9] S. Dutta and J. W. Dufty, "Classical Representation of a Quantum System at Equilibrium: Application", Phys. Rev. E (to appear).
[10] E. Brown, B. Clark, J. DuBois, D. Ceperley, Path Integral Monte Carlo Simulation of the Warm-Dense Homogeneous Electron Gas, cond mat arXiv:1211.6130, 2012.
[11] Density Functional Theory: An Advanced Course, E. Engel and R.M. Dreizler (Springer, Heidelberg, 2011).
[12] V.V. Karasiev, T. Sjostrom, D. Chakraborty, J.W. Dufty, F.E. Harris, K. Runge, and S.B. Trickey, "Innovations in Finite-Temperature Density Functionals", chapter in Computational Challenges in Warm Dense Matter, F. Graziani et al. eds., Springer Verlag, (to appear); Basic Research Needs for High Energy Density Laboratory Physics (Report of the Workshop on Research Needs, Nov. 2009). U.S. Department of Energy, Office of Science and National Nuclear Security Administration (2010); see Chapter 6 and references therein.
[13] D. Kremp, M. Schlages, W. Kraeft, Quantum Statistics of Nonideal Plasmas, (Springer-Verlag, Berlin, 2005); G. Giuliani and G. Vignale, Quantum Theory of the Electron Liquid, (Cambridge U. Press, Cambridge, 2005).
[14] G. Kelbg, Ann. Phys. 12, 219 (1963).
[15] M.-M. Gombert and H. Minoo, Contrib. Plasma Phys. 29, 355 (1989).
[16] H. Wagenknecht, W. Ebeling, and A. Förster, Contrib. Plasma Phys. 41, 15 (2001).
[17] C. Deutsch, Phys. Lett. A 60, 317 (1977); H. Minoo, M. Gombert, and C. Deutsch, Phys. Rev. A 23, 924 (1981).
[18] D. Pines and Ph. Nozieres, The Theory of Quantum Liquids, (Benjamin, NY, 1966); D. Brydges and Ph. Martin, J. Stat. Phys. 96, 1163 (1999).
[19] K-C Ng, J. Chem. Phys. 61, 2680 (1974).
[20] G. Ortiz and P. Ballone, Phys. Rev. B 50, 1391 (1994).