A Letters Journal Exploring the Frontiers of Physics

June 2013

EPL, **102** (2013) 67005
doi: 10.1209/0295-5075/102/67005

www.epljournal.org

Uniform electron gas at warm, dense matter conditions

Sandipan Dutta and James Dufty

Department of Physics, University of Florida - Gainesville, FL 32611, USA

received 7 April 2013; accepted in final form 4 June 2013
published online 4 July 2013

PACS 71.10.Ca – Electron gas, Fermi gas
PACS 05.70.-a – Thermodynamics
PACS 67.10.Fj – Quantum statistical theory

Abstract – A simple, practical model for computing the equilibrium thermodynamics and structure of the uniform electron gas (jellium) by classical strong-coupling methods is proposed. Conditions addressed are those of interest for recent studies of warm dense matter: solid densities and temperatures from zero to plasma states. 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 via strong-coupling classical liquid state theory. The results compare favorably with the first finite-temperature restricted path integral Monte Carlo simulations reported recently.

Introduction. – The prototypical test bed for strong Coulomb coupling effects in materials sciences and plasma physics, both classical and quantum, is the uniform 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). In spite of its intense attention over the past fifty years at zero and high temperatures, the intermediate domain of solid densities and temperatures comparable to the Fermi temperature has remained beyond the limits of both theory and simulation. Renewed interest in this domain has been prompted by recent studies of "warm, dense matter". These include terrestrial experiments and extra-terrestrial observations of exoplanets [1]. The present standard for the theoretical study of this domain is *ab initio* molecular dynamics driven by the Kohn-Sham calculations using the finite-temperature extension [2] of standard density functional theory (DFT) [3]. Examples include refs. [4–8] and references therein. Almost always such simulations use ground-state approximate exchange-correlation functionals [9]. Full exploitation of finite-temperature DFT for warm, dense matter conditions, however, requires knowledge of the thermodynamic properties of uniform jellium to formulate appropriate finite-temperature functionals, at least at the level of the local density approximation (or preserving that limit) [10,11]. In response to these new developments, the first path integral Monte Carlo simulations for these conditions have now been reported [12]. The objective here is to report a corresponding practical theoretical description and demonstrate its substantial agreement with the new simulations.

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 [13]. Among these are the classical molecular-dynamics (MD) simulation method, classical Monte Carlo integration, and liquid state theory [14], modified with effective 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 [15]. For additional references see [16,17]. Exchange effects were incorporated in a similar way using the pair correlation function for an ideal gas [10,18]. More recently, such classical systems have been defined with an effective temperature as well as pair potential [10,19]. A formalism for construction of a classical system with thermodynamics and structure corresponding to a given quantum system is described in ref. [20].

Here, an effective classical system representing the thermodynamics of jellium is provided, using an effective pair potential and an effective coupling constant. Simple analytic expressions are given, based on the more complete but complex results of ref. [21]. 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 [12] show good agreement over a wide range of densities and temperatures relevant for warm, dense matter.

Effective classical system. – The system of interest is a collection of N charges with Coulomb pair interactions $\phi(r)$ in a uniform neutralizing background, at equilibrium [22]. 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 [20]. The first two are equivalence of the densities and pair correlation functions

$$n_c = n, \qquad g_c(r, \beta_c, n_c \,|\, \phi_c) = g(r, \beta, n \,|\, \phi). \tag{1}$$

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

To be useful, the condition equating pair correlation functions must be invertible, $\phi_c\left(r\right) = g_c^{-1}(r, \beta_c, n_c \,|\, g)$, 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, arising from the Pauli exchange principle, denoted by $\phi_c^{(0)}\left(r\right)$. Even in this case the inversion cannot be accomplished exactly, but good approximations are known [18,20]. 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 $4\pi n r_0^3/3 = 1$) 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

$$\phi_c^*(x, t, r_s) = \phi_c^{(0)*}(x, t) + \Delta^*\left(x, t, r_s\right), \tag{2}$$

where $x \equiv r/r_0$. It has been recognized that the Pauli potential depends only on t.

Two exact limits for $\Delta^*\left(x, t, r_s\right)$ are important for the discussion here. The first is the weak-coupling limit

$$\phi_c^*(x, t, r_s) \to -c_c(x, t, r_s), \tag{3}$$

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 [14]. Using the correspondence conditions (1) the Ornstein-Zernicke equation defines the direct correlation function in terms of the quantum pair correlation function

$$c_c(x) = g(x) - 1 - \frac{3}{4\pi}\int \mathrm{d}\mathbf{x}' c_c(|\mathbf{x} - \mathbf{x}'|)\left[g(x') - 1\right]. \tag{4}$$

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 $g(x, t, r_s)$ [23]

$$\int \mathrm{d}\mathbf{x} x^2\left(g(x) - 1\right) = -\frac{8\pi}{3\Gamma}\frac{\beta\hbar\omega_p}{2}\coth\left(\frac{\beta\hbar\omega_p}{2}\right). \tag{5}$$

Here $\omega_p = \left(4\pi n q^2/m\right)^{1/2}$ is the plasma frequency (or, equivalently, $\beta\hbar\omega_p = 4\left(2\sqrt{3}\pi^{-2}\right)^{1/3} r_s^{1/2}/3t$). This gives for the large-x behavior

$$\Delta^*\left(x, t, r_s\right) \to \Gamma_c\left(t, r_s\right) x^{-1}. \tag{6}$$

This is the same form as for the classical one-component plasma, except with the classical Coulomb coupling constant $\Gamma = \beta q^2/r_0 = 4\left(2/3\pi^2\right)^{1/3} r_s/3t$ replaced by the effective coupling constant

$$\Gamma_c\left(t, r_s\right) = \frac{2}{\beta\hbar\omega_p \coth\left(\beta\hbar\omega_p/2\right)}\Gamma. \tag{7}$$

At low temperatures and fixed density Γ becomes divergent whereas the effective coupling constant remains finite $\Gamma_c\left(0, r_s\right) \simeq 1.155\, r_s^{1/2}$. At high temperatures $\Gamma_c\left(t, r_s\right) \to \Gamma \simeq 0.543 r_s/t$.

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 $\Delta^*\left(x, t, r_s\right)$ in that case is known as the Kelbg potential [15–17]

$$\Delta^*\left(x, t, r_s\right) \to \Gamma x^{-1}\Big(1 - \exp(-(ax)^2) + \sqrt{\pi}(ax)\mathrm{erfc}(ax)\Big), \tag{8}$$

where $a = \left(r_s/\Gamma\right)^{1/2}$ and $\mathrm{erfc}(x)$ is the complementary error function. 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 due to contributions from nonlinear dependence of the Slater sum on the Coulomb potential [16,17,24,25]. The modified form is

$$\Delta_K^*\left(x, \Gamma, r_s\right) \equiv \frac{\Gamma}{x}\left(1 - \exp(-(ax)^2) + \sqrt{\pi}\frac{ax}{\gamma}\mathrm{erfc}(\gamma ax)\right)$$

with

$$\gamma\left(\Gamma r_s\right) = -\frac{\left(\pi\Gamma r_s\right)^{1/2}}{\ln S(\Gamma r_s)} \tag{9}$$

where $S(\Gamma r_s)$ is the two electron relative coordinate Slater sum at $x = 0$

$$S(\Gamma r_s) = -4\left(\pi\Gamma r_s\right)^{1/2}\int_0^\infty \mathrm{d}y e^{-y^2}\frac{y}{1 - e^{\pi(\Gamma r_s)^{1/2}/y}}. \tag{10}$$

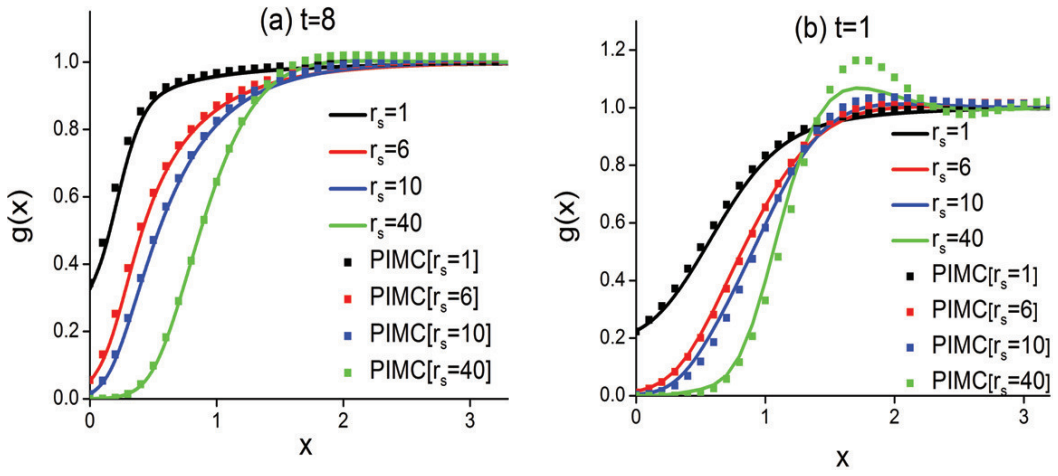

Fig. 1: (Colour on-line) Pair correlation function $g(x)$ at (a) $t=8$ and (b) $t=1$ for $r_s=1,6,10,40$. Also shown are the results of PIMC.

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 (6). This is accomplished by replacing Γ with the effective coupling constant Γ_c given by (7). The approximate effective pair potential is thus

$$\phi_c^*(x,t,r_s) \simeq \phi_c^{(0)*}(x,t) + \Delta_K^*(x,\Gamma_c,r_s)\,. \qquad (11)$$

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.

Pair correlation function. – 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 [14]. 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 [26]. Next, with $\phi_c^{(0)*}(x,t)$ known the pair correlation function for jellium can be determined from the HNC equations using (11).

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 [12]. 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 1(a) shows good agreement with PIMC for all densities, $1 \leqslant r_s \leqslant 40$. Figure 1(b) 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 underestimated by the theory, although its location is adequately described. The origin of this discrepancy is not clear at present. It could be a failure of the HNC implementation of this potential, or it could be a failure of the potential to contain sufficient information about quantum strong coupling.

Generally, it is found for $t \leqslant 1$ the theory is quite good for $1 \leqslant r_s \leqslant 10$. This is illustrated in fig. 2(a) and (b) 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 $t=0$ [27]). Some trends are evident even from this limited data. For example, the temperature dependence for $t \leqslant 0.5$ is quite weak for $r_s > 1$. However, for $r_s=1$ a significant temperature dependence is seen for $0.5 \leqslant t \leqslant 8$. In summary, the model potential (11) provides a practical form for the analysis of jellium using classical 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

$$p(t,r_s,q) = p(t,r_s,0) + 8\pi \int_0^q \mathrm{d}y\, y \times \int_0^\infty \mathrm{d}r r^2 \phi(r) \left(g(r,t,r_s,y) - 1\right). \qquad (12)$$

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

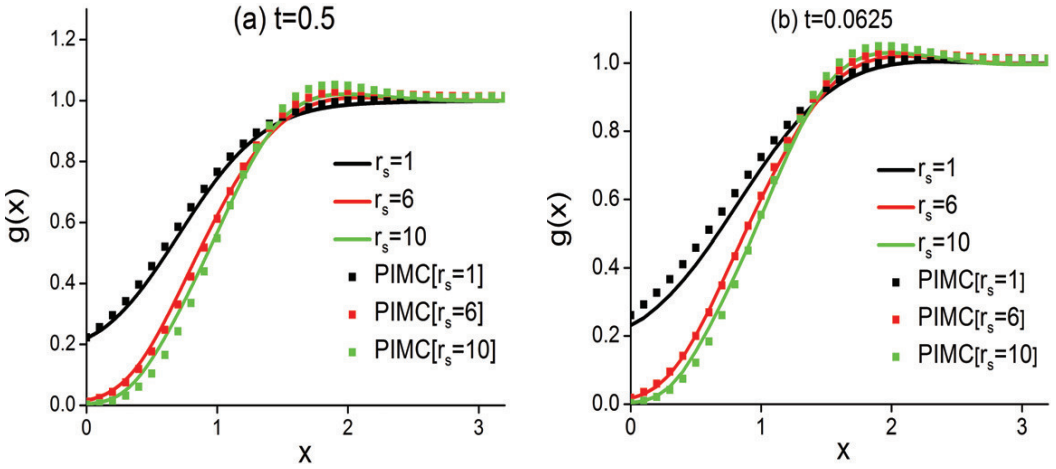

Fig. 2: (Colour on-line) Pair correlation function $g(x)$ at (a) $t=0.5$ and (b) $t=0.0625$ for $r_s=1,6,10$. Also shown are the results of PIMC.

would be classical Monte Carlo integration of the Gibbs distribution for the free energy

$$F=-\beta^{-1}\ln r_0^N\int \mathrm{d}\mathbf{x}_1\ldots\mathrm{d}\mathbf{x}_N\exp\left(-\Phi^*\right), \tag{13}$$

$$\Phi^*=\frac{1}{2}\sum_{ij}\left(\phi_c^{(0)*}(x_{ij},t)+\Delta_K^*\left(x_{ij},\Gamma_c,r_s\right)\right) \tag{14}$$

with $x_{ij}=|\mathbf{x}_i-\mathbf{x}_j|$.

Discussion. – 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 [10]. Instead of the Kelbg potential they chose the Deutsch potential [28], originally introduced as a simpler representation of the Kelbg potential. The PDW effective classical potential is similar to (11), but with $\Delta_K^*\left(x,\Gamma_c,r_s\right)$ replaced by

$$\Delta_{PDW}^*\left(x,\Gamma_{PDW},r_s\right)\equiv\Gamma_{PDW}x^{-1}\left(1-\exp(-bx)\right). \tag{15}$$

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

$$\Gamma_{PDW}=\left(1+\left(\frac{T_0}{T}\right)^2\right)^{-1/2}\Gamma. \tag{16}$$

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 ref. [10]. Although the dependence of Γ_{PDW} on t,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 ref. [10] and provides insight into the relevant physical mechanisms. For example, the exact screening sum rule that determines the form of Γ_c here appears to incorporate quantum effects as significant as those of Γ_{PDW} imposed by empirical $T=0$ exchange/correlation energy data.

The Kelbg functional form used here is the exact weak-coupling form determined from the two particle pair correlation function. It is modified here first by a factor γ chosen to preserve the exact two-particle pair correlation function at $x=0$. Independently, it is possible to show that the Kelbg potential satisfies the cusp condition [29] relating the two-particle pair correlation function to its derivative at $x=0$. An improvement over the present procedure would be to determine the parameter a in (8) self-consistently to satisfy the cusp condition for the actual pair correlation function, rather than only its two particle limit. In this way, the small- and large-x limits for the potential would be "pinned" by three exact conditions.

As noted above, the analysis of the uniform electron gas at finite temperatures is particularly important for applications of density functional theory to problems of warm, dense matter. The density dependence of the free energy can be fit at each temperature of interest. A corresponding local free energy can then be defined by replacing the uniform density by a chosen local density. In this way a local density functional (LDA) for the

exchange/correlation free-energy density is determined. In practice, more general functionals including the effects of density gradients are required —generalized gradient approximations (GGA). While their construction is phenomenological an important constraint is that they should have an accurate uniform limit. Hence a finite-temperature LDA is the first step in the construction of finite-temperature GGA. The work of [10,11] is a first step in this direction. This practice has been in use for thirty years as the basis for zero-temperature DFT. The new PIMC and its extension by the method proposed here and that of PDW provide the means for construction of a reliable, benchmarked local density functional at finite temperature. A detailed comparison of free energies from various theories and simulation will be reported elsewhere.

The use of a modified Kelbg potential for the uniform electron gas can be extended to more realistic systems. Of particular interest are charge neutral electron-ion systems. Presently, for strong-coupling quantum conditions these are described by a classical molecular-dynamics (MD) simulation of the ions, using a DFT calculation for the electron density at each time step. This computationally intensive approach can be complemented by an extension of the classical effective potential/coupling constant method described here to two-component systems. The construction of the potentials (electron-electron, electron-ion, ion-ion) can be accomplished in the same way. The corresponding Kelbg forms for the two particle density matrices, and their parametrization to give correct values at $x = 0$ are known [17]. Determination of the three effective coupling constants is more complex since the corresponding perfect screening sum rule [30] provides only one constraint among them all. However, additional constraints are available such as the compressibility sum rule and the cusp conditions [29]. With the effective potentials determined, the two-component HNC equations can be solved efficiently for all pair correlations and thermodynamics. Furthermore, the HNC approximation can be avoided by direct classical Monte Carlo evaluation of the free energy. These approaches are under investigation. There are recent finite-temperature PIMC simulations for this case now (carbon and water) [31], to benchmark such analysis as is done in the case of jellium here.

* * *

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.

REFERENCES

[1] Karasiev V. V., Sjostrom T., Chakraborty D., Dufty J. W., Harris F. E., Runge K. and Trickey S. B., *Innovations in Finite-Temperature Density Functionals,* Chapter in *Computational Challenges in Warm Dense Matter*, edited by Graziani F. *et al.* (Springer Verlag) in print; *Basic Research Needs for High Energy Density Laboratory Physics* (Report of the Workshop on Research Needs, November 2009), U.S. Department of Energy, Office of Science and National Nuclear Security Administration, 2010, see Chapt. 6 and references therein.

[2] Mermin N., *Phys. Rev.*, **137** (1965) A1441.

[3] Engel E. and Dreizler R. M., *Density Functional Theory: An Advanced Course* (Springer, Heidelberg) 2011.

[4] Horner D., Lambert F., Kress J. and Collins L., *Phys. Rev. B*, **80** (2009) 024305.

[5] Recoules V., Lambert F., Decoster A., Canaud B. and Clerouin J., *Phys. Rev. Lett.*, **102** (2009) 075002.

[6] Vinko S., Gregori G., Desjarlais M., Nagler B., Whitcher T., Lee R., Audebert P. and Wark J., *High Energy Density Phys.*, **5** (2009) 124.

[7] Wunsch K., Vorberger J. and Gericke D., *Phys. Rev. E*, **79** (2009) 010201(R).

[8] Clerouin J., Starrett C., Faussurier G., Blancard C., Noiret P. and Renaudin P., *Phys. Rev. E*, **82** (2010) 046402.

[9] Perdew J. and Zunger A., *Phys. Rev. B*, **23** (1981) 5048; Perdew J. and Wang Y., *Phys. Rev. B*, **45** (1992) 13244; Perdew J., Burke K. and Ernzerhof M., *Phys. Rev. Lett.*, **77** (1996) 3865; **78** (1997) 1396(E).

[10] Perrot F. and Dharma-wardana M. W. C., *Phys. Rev. B*, **62** (2000) 16536; Dharma-wardana M. W. C., *Int. J. Quantum Chem.*, **112** (2012) 53.

[11] Karasiev V., Sjostrom T. and Trickey S., *Phys. Rev. B*, **86** (2012) 115101.

[12] Brown E., Clark B., DuBois J. and Ceperley D., *Phys. Rev. Lett*, **110** (2013) 146405.

[13] Jones C. and Murillo M., *High Energy Density Phys.*, **3** (2007) 379; Graziani F. *et al.*, *High Energy Density Phys.*, **8** (2012) 105.

[14] Hansen J.-P. and MacDonald I., *Theory of Simple Liquids* (Academic Press, San Diego, Cal.) 1990.

[15] Morita T., *Prog. Theor. Phys.*, **20** (1958) 829; **23** (1960) 829; Kelbg G., *Ann. Phys. (N.Y.)*, **12** (1963) 219; Dunn T. and Broyles A., *Phys. Rev.*, **157** (1967) 1.

[16] Ebeling W., Filinov A., Bonitz M., Filinov V. and Pohl T., *J. Phys. A*, **39** (2006) 4309.

[17] Filinov A., Golubnychiy V., Bonitz M., Ebeling W. and Dufty J., *Phys. Rev. E*, **70** (2004) 046411.

[18] Uhlenbeck G. E. and Gropper L., *Phys. Rev.*, **41** (1932) 79; Lado F., *J. Chem. Phys.*, **47** (1967) 5369; Dufty J. W., Dutta S., Bonitz M. and Filinov A., *Int. J. Quantum Chem.*, **109** (2009) 3082.

[19] Dufty J. W. and Dutta S., *Contrib. Plasma Phys.*, **52** (2012) 100.

[20] Dufty J. W. and Dutta S., *Phys. Rev. E*, **87** (2013) 032101.

[21] Dutta S. and Dufty J. W., *Phys. Rev. E*, **87** (2013) 032102.

[22] Kremp D., Schlanges M. and Kraeft W., *Quantum Statistics of Nonideal Plasmas* (Springer-Verlag, Berlin) 2005; Giuliani G. and Vignale G., *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge) 2005.

[23] Pines D. and Nozieres Ph., *The Theory of Quantum Liquids* (Benjamin, New York) 1966; Martin Ph., *Rev. Mod. Phys.*, **60** (1988) 1075.
[24] Gombert M.-M. and Minoo H., *Contrib. Plasma Phys.*, **29** (1989) 355.
[25] Wagenknecht H., Ebeling W. and Förster A., *Contrib. Plasma Phys.*, **41** (2001) 15.
[26] Ng K.-C., *J. Chem. Phys.*, **61** (1974) 2680.
[27] Ortiz G. and Ballone P., *Phys. Rev. B*, **50** (1994) 1391.
[28] Deutsch C., *Phys. Lett. A*, **60** (1977) 317; Minoo H., Gombert M. and Deutsch M., *Phys. Rev. A*, **23** (1981) 924.
[29] Kimball J., *Phys. Rev. A*, **7** (1973) 1648; Rajagopal A., Kimball J. and Banerjee M., *Phys. Rev. B*, **18** (1978) 2339.
[30] Samaj L., *J. Stat. Phys.*, **137** (2009) 1.
[31] Driver K. and Millitzer B., *Phys. Rev. Lett.*, **108** (2012) 115502.