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Parametrized equation of state for electron liquids in the Singwi-Tosi-Land-Sjölander approximation

Shigenori Tanaka and Shinichi Mitake
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Setsuo Ichimaru
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
and Institute for Theoretical Physics, University of California,
Santa Barbara, California 93106

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We calculate the interaction and excess free energies of the electron system at finite temperatures on the basis of the Singwi-Tosi-Land-Sjölander approximation [Phys. Rev. **176**, 589 (1968)]. The results are parametrized in the form of analytic formulas, which adequately describe the equation of state for homogeneous, paramagnetic electron liquids over a wide range of the density and temperature parameters.

The electron liquid is a one-component plasma (OCP) of the electrons embedded in a uniform neutralizing background of positive charges. The system is characterized basically by two dimensionless parameters,

$$\Gamma = e^2/ak_BT, \quad \theta = k_BT/E_F \ , \tag{1}$$

where $a=(3/4\pi n)^{1/3}$ and $E_F=\hbar^2(3\pi^2 n)^{2/3}/2m$ for the electrons with mass m, number density n, and temperature T. The parameter Γ refers to the Coulomb coupling constant for the classical OCP,[1] and θ is the Fermi-degeneracy parameter. The usual r_s parameter for a degenerate electron liquid is then expressed as

$$r_s = ame^2/\hbar^2 = \Gamma\theta/2\alpha^2 \ , \tag{2}$$

where $\alpha=(4/9\pi)^{1/3}$. The r_s parameter measures the strength of Coulomb coupling in such a degenerate electron system.[1]

In the limit of complete Fermi degeneracy ($\theta \rightarrow 0$), the ground-state energy of the electron liquid has been accurately calculated through the Green's-function Monte Carlo (GFMC) method by Ceperley and Alder[2] for several values of r_s up to 100. Vosko, Wilk, and Nusair[3] then derived an interpolation formula for those data through a Padé-approximant technique. In the classical limit ($\theta \rightarrow \infty$), extensive Monte Carlo (MC) studies have been performed[4,5] and accurate formulas for the internal and free energies are available over the domain $1 \leq \Gamma \leq 170$ for the OCP in the fluid state.

In many of the actual plasmas, however, the state of the electrons is found to be in neither of those limiting cases. Examples include the stellar interiors, the heavy planets such as Jupiter, those plasmas in the projected inertial-confinement fusion experiments, and the liquid metals. A theoretical study of such an electron system offers a complex problem, because it now involves two parameters Γ and θ, describing an interplay between the strong Coulomb-coupling effect and the degrees of Fermi degeneracy. For the analysis of thermodynamic properties of dense plasmas it is essential to have a reliable equation of state for the electron system covering a wide range of density and temperature parameters.

We are motivated to derive such an equation of state in view of another theoretical utility as well. Recently, quantum MC simulations of fermion systems have been undertaken to include the finite-temperature effects.[6] In such a simulation one is faced with difficulties inherent in a fermion system, associated with possible negativities in the weight functions; a method of quantum simulation with proven accuracy is yet to be established in those cases. We thus consider that an equation of state derived independently by purely analytic means will provide a useful guideline for a construction of such a simulation procedure.

In this Brief Report we wish to report the results of a theoretical study for such an equation of state on the basis of the Singwi-Tosi-Land-Sjölander (STLS) approximation.[1,7] For practical utilities, the calculated results are parametrized in the form of analytic formulas for the interaction and excess free energies, which are applicable over a wide range of parameters as long as the electrons are in a paramagnetic fluid state.

There exist a number of theoretical schemes, such as the convolution approximation[1,8] and the hypernetted-chain (HNC)[1,9] schemes, that command better overall accuracies than the STLS scheme in describing the correlation properties in the OCP. Nevertheless, we adopt the STLS scheme, because it offers the best compromise between simplicity and accuracy. As Eq. (4) below illustrates, the local-field correction (LFC) describing the strong-coupling effects beyond the random-phase approximation[10] (RPA) is expressed in terms of the integration over a single variable in the STLS scheme. Such a simplicity is valuable particularly when iterative solutions to the resulting integral equations are to be obtained over numerous combinations of Γ and θ. As for the accuracy of the STLS scheme, we recall that it has predicted the values of the correlation energy close to those obtained in the GFMC method[2] for the degenerate electron liquids (see Table I for comparison). This accuracy results from the fact that the STLS scheme takes a correct account of the long-range part of the repulsive Coulomb hole in the correlation functions. In the classical limit, where the problem involves only a single parameter Γ, we shall use the solutions to the HNC equations for the OCP equation of state, which are known[1] to be superior to the STLS scheme.

The basis STLS set of equations for the static structure

TABLE I. Negative correlation energies (mRy) of electron liquids at $T=0$. GFMC refers to the results in Ref. 2; STLS, in Ref. 7; and Eq. (15), the present parametrization.

r_s	GFMC	STLS	Eq. (15)
1	119	124	125.6
2	90.2	92	91.99
5	56.3	56	56.42
10	37.22	36	36.34
20	23.00	22	22.05
50	11.40		10.54
100	6.379		5.762

factor $S(x)$ is

$$S(x)=\tfrac{3}{2}\theta\sum_{l=-\infty}^{\infty}\left\{\frac{\Phi(x,l)}{1+(2\Gamma\theta/\pi\alpha x^2)[1-G(x)]\Phi(x,l)}\right\}, \tag{3}$$

$$G(x)=-\tfrac{3}{4}\int_0^\infty dy\, y^2[S(y)-1]\left\{1+\frac{x^2-y^2}{2xy}\ln\left|\frac{x+y}{x-y}\right|\right\}. \tag{4}$$

Here x and l are normalized wave-number and imaginary-frequency variables,

$$\Phi(x,l)=\frac{1}{2x}\int_0^\infty dy\frac{y}{\exp[(y^2/\theta)-\mu]+1}\times\ln\left|\frac{(2\pi l\theta)^2+(x^2+2xy)^2}{(2\pi l\theta)^2+(x^2-2xy)^2}\right| \tag{5}$$

is the dimensionless free-electron polarizability, and the chemical potential μ (in units of k_BT) is to be determined through the normalization

$$\tfrac{3}{2}\theta^{3/2}\int_0^\infty dz\frac{z^{1/2}}{\exp(z-\mu)+1}=1\ . \tag{6}$$

Equation (3) represents the fluctuation-dissipation theorem applied to the density-density response function; Eq. (4) is the STLS expression for the LFC. The interaction energy E_{int} and the excess free energy F_{ex} are then calculated as

$$\frac{E_{\text{int}}}{Nk_BT}=\frac{\Gamma}{\pi\alpha}\int_0^\infty dx[S(x)-1]\ , \tag{7}$$

$$\frac{F_{\text{ex}}}{Nk_BT}=\int_0^\Gamma\frac{d\Gamma}{\Gamma}\left(\frac{E_{\text{int}}}{Nk_BT}\right)_\theta\ , \tag{8}$$

where N is the total number of the electrons; in the coupling-constant integration of Eq. (8), θ is kept constant.

To ensure accuracy of the numerical solution we find it useful to rewrite Eq. (3) in the form,

$$S(x)=S_{\text{HF}}(x)-\frac{3\Gamma\theta^2}{\pi\alpha x^2}[1-G(x)]\left\{\frac{2}{9\theta^2}\left[\operatorname{csch}^2\left(\frac{x^2}{2\theta}\right)+\frac{2\theta}{x^2}\coth\left(\frac{x^2}{2\theta}\right)\right]+\sum_{l=-\infty}^{\infty}P(x,l)\right\}\ . \tag{9}$$

Here

$$S_{\text{HF}}(x)=1-\frac{3\theta}{4x}\int_0^\infty dy\frac{y}{\exp[(y^2/\theta)-\mu]+1}\ln\left|\frac{1+\exp[\mu-(y-x)^2/\theta]}{1+\exp[\mu-(y+x)^2/\theta]}\right| \tag{10}$$

is the structure factor in the Hartree-Fock approximation,

$$P(x,l)=\frac{[\Phi(x,l)]^2-[A(x,l)]^2\{1+(2\Gamma\theta/\pi\alpha x^2)[1-G(x)]\Phi(x,l)\}}{1+(2\Gamma\theta/\pi\alpha x^2)[1-G(x)]\Phi(x,l)}\ , \tag{11}$$

and $A(x,l)=(\frac{4}{3})x^2/[(2\pi l\theta)^2+x^4]$. We then note that the function $P(x,l)$ decays as quickly as x^{-6} or l^{-6} for large x or l.

We have solved Eqs. (4) and (9) for $S(x)$ and $G(x)$ by numerical iteration with the aid of the fast-converging extrapolation procedure due to Ng.[11] Since the most pressing area to look for new information is in the domain of intermediate Fermi degeneracy $\theta\simeq 1$, we have chosen 70 combinations of the density and temperature parameters, in the range of $0.001\leq\Gamma\leq 300$ and $\theta=0.1, 1,$ and 5. The y integration in Eq. (4) was carried out up to 216; the l summation in Eq. (9) was performed up to $|l|=1000$ for $\theta=1$ and to $|l|=300$ for $\theta=0.1$ and 5. The convergence criterion which we have adopted is

$$\left[\int_0^\infty dx\,|G_{\text{out}}(x)-G_{\text{in}}(x)|^2\right]^{1/2}<10^{-4}\Gamma\ , \tag{12}$$

where $G_{\text{in}}(x)$ and $G_{\text{out}}(x)$ are the input and output values of the LFC at a given step of the iteration. All the 70 cases studied satisfy $\Gamma\theta\leq 40$; for $\Gamma\theta>40$ we found that the iteration did not converge at any θ. Some of the computed values of the interaction energy for $\theta=1$ are listed in Table II, together with the corresponding RPA values which are obtained by setting $G(x)=0$ in Eqs. (9) and (11).

We derive an analytic expression for the interaction energy parametrizing the values obtained for the 70 cases mentioned above and satisfying the STLS and HNC boundary

TABLE II. Values of $-E_{\text{int}}/Nk_BT$ calculated in the STLS and RPA schemes at $\theta=1$. (9 out of the total 23 cases calculated are shown here.)

Γ	r_s	STLS	RPA
0.01	1.842×10^{-2}	2.320×10^{-3}	2.327×10^{-3}
0.1	0.1842	3.389×10^{-2}	3.456×10^{-2}
0.5	0.9208	0.2390	0.2560
1.0	1.842	0.5488	0.6138
2.0	3.683	1.234	1.469
5.0	9.208	3.454	4.616
10.0	18.42	7.298	10.90
20.0	36.83	15.12	
40.0	73.66	30.93	

conditions at $\theta \rightarrow 0$ and $\theta \rightarrow \infty$, respectively.[12] The result is

$$-\frac{1}{\Gamma}\frac{E_{\text{int}}}{Nk_BT}=\frac{a(\theta)+b(\theta)\Gamma^{1/2}+c(\theta)\Gamma}{1+d(\theta)\Gamma^{1/2}+e(\theta)\Gamma}\ , \tag{13}$$

where

$$a(\theta)=\frac{1}{\pi\alpha}\frac{0.75+3.043\,63\theta^2-0.092\,270\theta^3+1.703\,50\theta^4}{1+8.310\,51\theta^2+5.110\,5\theta^4}\tanh\left(\frac{1}{\theta}\right)\ , \tag{14a}$$

$$b(\theta)=\theta^{1/2}\frac{0.323\,119+0.005\,348\theta^{1/2}+3.490\,43\theta^{3/2}}{1+0.000\,836\theta+4.030\,40\theta^2}\ , \tag{14b}$$

$$c(\theta)=\theta\frac{0.514\,517+0.436\,502\theta+0.711\,644\theta^2}{1+1.860\,96\theta^2+0.538\,374\theta^3}\ , \tag{14c}$$

$$d(\theta)=\theta^{1/2}\frac{0.549\,860+0.565\,967\theta^{1/2}-1.158\,90\theta+1.356\,63\theta^{3/2}}{1-0.651\,931\theta+\theta^2}\ , \tag{14d}$$

$$e(\theta)=\theta\frac{0.636\,274+0.487\,840\theta+1.615\,92\theta^2}{1+2.367\,97\theta^2+1.090\,10\theta^3}\ . \tag{14e}$$

Those formulas reproduce the computed values of E_{int} for all the 70 cases with relative errors less than 0.6%. In the classical limit, they agree with the HNC values computed by Springer, Pokrant, and Stevens, Jr.[13] for $0.05 \leq \Gamma \leq 10$ with digressions of less than 0.4%. Finally, in the limit of strong Fermi degeneracy, Eqs. (13) and (14) agree with the values of E_{int} computed by STLS themselves[7] for the eight cases ranging $1 \leq r_s \leq 20$ within relative errors of 0.1%.

Several remarks are in order concerning Eqs. (13) and (14): (i) E_{int}/Nk_BT given by Eq. (13) takes a form proportional to Γ both in the weak-coupling limit ($\Gamma \ll 1$) and in the strong-coupling limit ($\Gamma \gg 1$). The former is the Hartree-Fock exchange energy; the latter is a Madelung-like contribution. (ii) The form of the Hartree-Fock term, Eq. (14a), is exactly the same as that derived originally by Perrot and Dharma-wardana.[14] (iii) In the classical limit, $a(\theta)$ vanishes; in the weak-coupling limit, the Debye-Hückel value $-\sqrt{3}\Gamma^{3/2}/2$ then becomes the leading contribution to E_{int}/Nk_BT. (iv) In the classical, strong-coupling limit, E_{int}/Nk_BT approaches $-0.891\,713\Gamma$. This value differs slightly from $-0.897\,744\Gamma$ in the MC fitting[5] or $-0.900\,470\Gamma$ in the HNC fitting.[15] Correspondingly, the forms of the Γ dependence in the rest of the terms are different. (v) The functions $b(\theta)$, $c(\theta)$, $d(\theta)$, and $e(\theta)$ increase monotonically as functions of θ. At $\theta = 0$, they all vanish in such a way that Eq. (13) becomes a function of $r_s^{1/2}$.

The excess free energy is then obtained by performing the Γ integration as prescribed in Eq. (8);

$$\begin{aligned}-\frac{F_{\text{ex}}}{Nk_BT}={}&\frac{c}{e}\Gamma+\frac{2}{e}\left(b-\frac{cd}{e}\right)\Gamma^{1/2}+\frac{1}{e}\left[\left(a-\frac{c}{e}\right)-\frac{d}{e}\left(b-\frac{cd}{e}\right)\right]\ln|e\Gamma+d\Gamma^{1/2}+1|\\&-\frac{2}{e(4e-d^2)^{1/2}}\left[d\left(a-\frac{c}{e}\right)+\left(2-\frac{d^2}{e}\right)\left(b-\frac{cd}{e}\right)\right]\left[\tan^{-1}\left(\frac{2e\Gamma^{1/2}+d}{(4e-d^2)^{1/2}}\right)-\tan^{-1}\left(\frac{d}{(4e-d^2)^{1/2}}\right)\right]\ .\end{aligned} \tag{15}$$

The condition that $4e-d^2>0$ is satisfied for any θ. Although we have parametrized E_{int}/Nk_BT quite accurately in Eq. (13), we presume that the parametrization errors in Eq. (15) may have increased on the order of 1%, because of the coupling-constant integration involved. This feature is seen in the comparison between Eq. (15) and the STLS correlation energy listed in Table I.

Taking account of the errors inherent in the STLS approximation, we expect that the equation of state derived from the parametrized expression Eq. (15) may remain close to the true value within a maximum error of 5%, say, over the entire density and temperature domain, where the electrons are in a paramagnetic fluid state. We remark in this connection that Eq. (15) cannot be used for the analysis of transition between the fluid and crystalline states (Wigner crystallization), because an accurate determination of such a transition condition would call for an extremely accurate evaluation of the free energies both in the fluid and crystalline states.[1,2,5] For many other practical purposes, however, Eq. (15) should give an adequate description of the equation of state for homogeneous, paramagnetic electron liquids.

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[1] S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982).

[2] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[3] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[4] S. G. Brush, H. L. Sahlin, and E. Teller, J. Chem. Phys. **45**, 2102 (1966); J. P. Hansen, Phys. Rev. A **8**, 3096 (1973).

[5] W. L. Slattery, G. D. Doolen, and H. E. DeWitt, Phys. Rev. A **21**, 2087 (1980); **26**, 2255 (1982).

[6] See e.g., M. Imada and M. Takahashi, J. Phys. Soc. Jpn. **53**, 3770 (1984), and references therein.

[7] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. **176**, 589 (1968).

[8] S. Ichimaru, Phys. Rev. A **2**, 494 (1970).

[9] J. M. J. van Leeuwen, J. Groeneveld, and J. De Boer, Physica **25**, 792 (1959); T. Morita, Prog. Theor. Phys. **23**, 829 (1960).

[10] See e.g., A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[11] K. C. Ng, J. Chem. Phys. **61**, 2680 (1974).

[12] This procedure is different from, and superior to, the method followed recently by W. Richert and W. Ebeling, Phys. Status Solidi (b) **121**, 633 (1984), in their treatment of a similar problem. These authors undertook a Padé-approximant fitting by using only the information obtained from the GFMC values at $\theta = 0$ and an expansion of Debye-Hückel type with quantum corrections, applicable, therefore, in the domain $\theta >> 1$ and $\Gamma << 1$; no reliable information was included at $\theta \simeq 1$ or for $\Gamma \gtrsim 1$ at $\theta >> 1$.

[13] J. F. Springer, M. A. Pokrant, and F. A. Stevens, Jr., J. Chem. Phys. **58**, 4863 (1973).

[14] F. Perrot and M. W. C. Dharma-wardana, Phys. Rev. A **30**, 2619 (1984).

[15] H. E. DeWitt, Phys. Rev. A **14**, 1290 (1976); this value, however, appears to be superseded by -0.8996Γ, in a recent study of the HNC solutions [H. E. DeWitt (private communication)].