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Temperature-dependent screening of neon in an electron gas. Application to pair-potential calculations

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The electronic structure of a neon impurity in jellium as a function of temperature is studied. The self-consistent density profile is calculated within "density-functional formalism." It is shown how the pair interaction between ionized atoms in a neon plasma can be deduced from these calculations.

I. INTRODUCTION

Neon is a material commonly used in laser experiments, either as impurity for diagnostic purposes, or as a substance for filling microballoons in high-compression implosions.[1] The interpretation of such experiments needs reliable numerical data for the electronic properties of a dense neon plasma at various temperatures. Several theoretical models describing the electronic structure of ionized matter may be found in the literature. One of the most popular is the "average-atom" model[2] (AAM), which calculates the average electron density, average occupation numbers, equation of state, etc., each of the various versions having its own degree of accuracy. The basic idea behind the AAM is to isolate an electrically neutral sphere, whose volume is the average-atomic volume, containing a single ion perfectly screened by core and valence electrons. The Thomas-Fermi (TF) statistical model,[3] the most simple AAM, treats the electronic response in the semiclassical approximation, with possible quantum corrections.[4] In the Thomas-Fermi-shell (TFS) models,[5,6] the delocalized electron density is still given by the statistical approximation, but the core electrons are treated as quantum particules. In a recent work, the Dirac equation is solved for free as well as for bound electrons.[7]

The AAM represents the whole plasma as a juxtaposition of identical atomic spheres: the system is viewed as a quasiperiodic arrangement of neutral cells, a picture which is relevant only at low temperatures. In a number of situations, the following description is more appealing: the total electron density in the plasma results from the overlap of the densities attached to single ions. The positions of these ions are given by the pair correlation function which must be calculated for each temperature and density using analytical methods[8] (for instance, the hypernetted chain equation[9]) or computer simulations.[10] In all cases, the pair interaction of two screened ions in the plasma is needed. The pair potential, which depends strongly on the long-range behavior of the electron charge displaced by a *single* ion, cannot be deduced from the AAM.

In this paper, we propose a determination of the pair interaction in an ionized neon plasma, as an application of self-consistent screening calculations. The most simple quantum method for treating that problem is to use the random-phase-approximation (RPA) dielectric constant.[11] But it has been proved in a previous paper that, even in hydrogen, the linear screening of the bare nucleus is inadequate.[12] Solid-state theory has shown that linear screening is relevant only when the concept of pseudopotential[13] is valid, that is when the constraint of orthogonalization to the core electrons cancels the largest part of the potential. In plasma physics, however, it is impossible to define the pseudopotential *a priori:* ionization and ion-core configuration change with temperature and density, and must be deduced from detailed calculations for each value of the plasma parameters. Thus, in temperature-dependent problems, the pseudopotential is practically an output of electronic structure calculations, and not an input as in solid-state physics. Nevertheless, the pseudopotential concept will be useful to deduce the pair interaction from the single-ion calculation.

Our procedure will be the following: We shall use the temperature-dependent density-functional formalism to calculate the self-consistent screening density profile. In Sec. II, we recall the main features and equations of the model, and comment on them in relation with the standard AAM. The results of the single impurity calculation are briefly discussed in Sec. III. A definition of the pseudopotential at finite temperature is proposed and applied to the problem of ion-ion interaction in Sec. IV.

II. OUTLINE OF THE THEORY

We consider a single impurity atom immersed in an infinite electron gas of density n_0, neutralized by a uniform positive background. The external potential $v(r)$

$$v(r)=-\frac{Z}{r}-\int\frac{1}{|\vec{r}-\vec{r}\,'|}n_0 d\vec{r}$$

polarizes the electron gas. The electron density of the system in thermal equilibrium is $n(r)$. The grand potential $\Omega[n]$, a unique functional of n, is the basic quantity of the density-functional formalism.[14] $\Omega[n]$ is minimum for the exact density corresponding to a given external potential $v(r)$. With the assumption that the exchange-and-correlation free energy can be accurately approximated by a local functional

$$F_{\rm xc}[n]=\int\mathcal{F}_{\rm xc}(n(\vec{r}))d\vec{r}\,, \tag{1}$$

the total electron density is

$$n(r)=n_0+\sum_b f(\epsilon_b)\varphi_b^2+\frac{1}{\pi^2}\int_0^\infty f(\epsilon_k)dk\sum_l(2l+1)[\varphi_{kl}^2-k^2j_l^2(kr)]\,. \tag{2}$$

φ_b is the radial part of a bound eigenfunction, solution of the Schrödinger equation in the effective potential

$$V(r)=-\frac{Z}{r}+\int[n(r')-n_0]\frac{1}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' + V_{\rm xc}(n)-V_{\rm xc}(n_0) \tag{3}$$

which includes the exchange-and-correlation potential

$$V_{\rm xc}(n_0)=\frac{d\mathcal{F}_{xc}(n)}{dn}\,. \tag{4}$$

The eigenvalues ϵ_b correspond to the boundary condition of exponential decay of φ_b at large radii. The occupation number $f(\epsilon_b)$ is given by the Fermi-dirac statistics:

$$f(\epsilon)=\{1+\exp[\beta(\epsilon-\mu)]\}^{-1} \tag{5}$$

(with $\beta^{-1}=k_BT$), the chemical potential μ being fixed by the relation

$$n_0=\frac{\sqrt{2}}{\pi^2}\beta^{-3/2}\int_0^\infty y^{1/2}[1+\exp(y-\beta\mu)]^{-1}dy \tag{6}$$

as for noninteracting free electrons. The summation over the bound states b includes degeneracy on the magnetic quantum number and spin. The contribution of the continuous spectrum to the density is given by the last term in Eq. (2). The wave number k is defined by $\epsilon_k=\frac{1}{2}k^2$ (a.u.), and the discrete sum runs over the angular momenta l. The radial part φ_{kl} of the eigenfunction, integrated in the potential $V(r)$, Eq. (3), is normalized to Bessel functions at infinity. The asympotic value of the density, Eq. (2), is n_0, as a consequence of the total screening of the impurity at large distances.

We make an emphasis on the fact that the local-density approximation for $F_{\rm xc}[n]$ is the only approximation in this model. Once Eq. (1) is accepted, the self-consistent density $n(r)$ is the *exact* density of the impurity problem in the *interacting* electron gas.[14] It has none of the shortcomings of the various AAM (Refs. 4–7); all electrons are treated on the same quantum-mechanical basis, the boundary conditions in the infinite sphere are exactly handled, and the density of states is not arbitrarily fixed (the exact density of states can be deduced from the phase shifts of the wave functions in the continuous spectrum[12]). Finally, the model is perfectly thermodynamically consistent, so that all the properties deduced from $n(r)$ are continuous, as they must be, when a bound state delocalizes into a scattering state.[15] Nevertheless, only average quantities (corresponding to the average over all the possible thermal configurations of the single ion) can be deduced from such calculations. The eigenvalues ϵ, for instance, have no physical meaning and cannot be used straightforward as excitation energies for optical transitions. The correct procedure to deal with optical properties would be to build the relevant Green's functions from the complete basis set of eigenfunctions generated in the self-consistent potential $V(r)$.

We now discuss the exchange-and-correlation functional. The local form in Eq. (1) is recognized as an accurate approximation for simple metals at zero temperature and is used in most band-structure calculations.[16] Nonlocal corrections have been proposed[17] but their effect on $n(r)$ has not been investigated for the moment. The temperature-dependent functional used in the present work reduces to the well-known Wigner formula at $T=0$. For the thermal part of $F_{\rm xc}[n]$, two different approximations, both obtained for a uniform electron gas, are proposed in the literature. One is given by Gupta and Rajagopal, based on the first-order exchange and sum of the ring diagrams.[18] The second is due to Dharma-Wardana and Taylor, including first-order exchange, all second-order graphs, and ring

TABLE I. Variation with temperature of the bound levels ϵ (a.u.) and their occupation number f in neon, at the electron gas density $r_s = 2$ (except for the first column which corresponds to the free atom). The total bound charge Z_b is shown in the last row.

	Atom $T=0.0$		$T=0.5T_F$		$T=T_F$		$T=2T_F$		$T=4T_F$	
	ϵ	f	ϵ	f	ϵ	f	ϵ	f	ϵ	f
1s	−30.280	1.0000	−30.113	1.0000	−30.571	1.0000	−31.747	1.0000	−34.071	0.99999
2s	−1.3132	1.0000	−1.1897	0.99871	−1.4974	0.96198	−2.2716	0.77492	−3.7854	0.43158
2p	−0.48971	1.0000	−0.36395	0.95552	−0.66511	0.80584	−1.4544	0.58632	−3.0457	0.33692
3s							−0.05267	0.23622	−0.49678	0.11293
3p									−0.31834	0.10358
3d									−0.08205	0.09226
4s									−0.03286	0.09005
4p									−0.00733	0.08892
Z_b		10.000		9.7305		8.7590		7.5402		7.3682

graphs.[19] The results may be rather different at low temperatures but seem to be in reasonable agreement for T higher than the Fermi temperature. In the calculations reported in this paper, we have used the first of these approximations which was implanted in our routines before we became aware of the second one. The accuracy of such approximations is still an open question.

For given values of the atomic number, temperature T and electron density n_0, Eqs. (2)–(4) are solved self-consistently. The practical difficulties of such a calculation are the following:

(a) There is the possible existence of very shallow bound states (particularly at high temperatures) which may appear and disappear from an iteration to the following one, leading to numerical oscillations and instabilities.

(b) There exists a large number of wave-vector sampling points at high temperatures; the maximum value k_m of the wave vector to be treated in the continuum is approximately such that $\mu+7kT=\frac{1}{2}k_m^2$, which increases with T (although μ decreases).

(c) The large value of the maximum angular momentum l_m needed for convergence [cf. Eq. (2)] when the screening length of the impurity is large.

So there are cases where the calculation may be difficult. Fortunately these cases, in general, correspond to high temperatures where the physics of the problem is simple and where "asymptotic" models (like Debye-Hückel or Thomas-Fermi) may be relevant. We don't reproduce here the formulas giving the thermodynamic quantities (total energy, entropy, etc.) which can be found in Ref. 12.

III. SINGLE NEON IMPURITY CALCULATION

We report the results of calculations for an impurity of neon embedded in an electron gas $r_s=2$ a.u. [$n_0=3/(4\pi r_s^3)$, so that $n_0=2.012\times10^{23}$ cm^{-3}]. The temperature is varied from $T=0.5T_F$ to $T=4T_F$, where T_F is the Fermi energy ($T_F=12.53$ eV). This range is physically interesting since it covers the transition from degenerate to nondegenerate electrons.

In Table I are shown the discrete eigenvalues of the spectrum. Let us recall that they have no simple physical significance within the temperature-dependent density-functional formalism. They are mathematical quantities occurring in the construction of the electron density, but are not one-electron energies. Comparing the eigenvalues for the lowest temperature at $r_s=2$ to those of the free atom at $T=0$, one sees that ϵ rises as a consequence of the electron gas environment. Then, when the temperature is increased at fixed electron density n_0, the eigenvalues lower because the impurity nucleus is less and less screened by the bound charge which is more and more delocalized. This is a well-known effect. As the potential becomes deeper when T increases, new bound levels are found: The $3s$ level appears at $T=2T_F$ and then the $3p$, $3d$, $4s$, and $4p$ at $T=4T_F$. These new levels accommodate 2.26 additional electrons which compensate the decrease of the population of the deep levels; this mechanism explains the quasistationarity of the total number of bound electrons Z_b between $2T_F$ and $4T_F$. This splitting into bound and free electrons is somewhat arbitrary since there is no discontinuity in the behavior of the density when an eigenvalue crosses the zero energy.[15]

In Fig. 1, we show the displaced electron density $n(r)-n_0$ as a function of r. At $T=0.5T_F$, the curve exhibits a bump around $r=3$ a.u. This bump is due to the continuous spectrum contribution to $n(r)-n_0$: The free electrons are mainly $3s$ and $3p$ in character and have a maximum of density at this place. The bump disappears at higher temperatures because the free electrons are distributed more uniformly in more angular momenta and in a wider range of energies. For $T>T_F$, the density spreads out very regularly. Friedel oscillations have been observed at $T=0.5T_F$ only, the first node of $n(r)-n_0$ occurring at $r=10.75$ a.u. The delocalization of the density when T is increased is illustrated in Table II: The density at the nucleus $n(r)-n_0$ decreases and, conversely, the characteristic radii R_0 (the displaced charge inside the sphere of radius R_0 is $0.594Z$; in the Debye-Hückel theory, R_0 is twice the inverse of the screening constant) and R_1 [such that $n(R_1)-n_0=\frac{1}{2}n_0$] increase continuously. Finally, the total internal energy and entropy of the impurity (as defined in Ref. 2) are given in Table III.

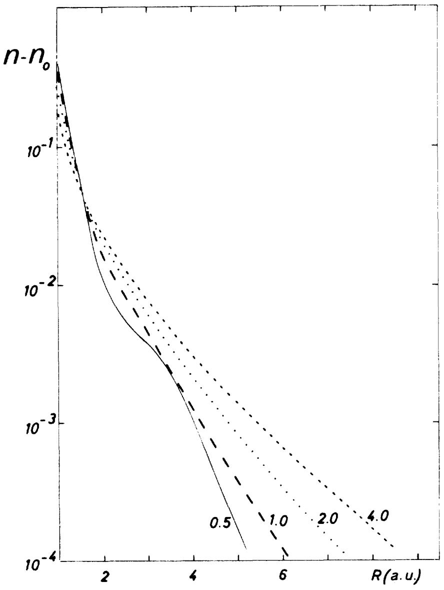

FIG. 1. Modification with temperature of the screening density profile of a neon impurity in the jellium at $r_s=2$. The curves correspond to the temperatures 0.5, 1.0, 2.0, and 4.0 in units of T_F.

TABLE II. Modification with temperature of the displaced electron density around Ne, at $r_s=2$. $n(0)-n_0$ is the displaced density at the nucleus. R_0 is the radius of the sphere containing a displaced charge $Q=0.594Z$. The radius R_1 is such that $n(R_1)-n_0=\frac{1}{2}n_0$. Units of measurement are in a.u.

T/T_F	$n(0)-n_0$	R_0	R_1
0.5	591.6	0.835	1.891
1.0	592.3	0.867	2.069
2.0	590.9	1.003	2.259
4.0	583.1	1.843	2.350

IV. TEMPERATURE-DEPENDENT ION-ION INTERACTION

The previous sections have dealt with the self-consistent determination of the electron charge displaced by a single Ne atom in an electron gas. It is well known from the solid-state theory that the pair interaction between two ions in a simple metal at $T=0$ is related to the valence density outside the ion core.[13] The main assumption is that the density

TABLE III. Energy and entropy of the neon impurity (a.u.) for various temperatures.

T/T_F	ΔE	$T\Delta S$
0.0 (free atom)	-128.00	0.0
0.5 ($r_s=2$)	-126.76	0.28
1.0 ($r_s=2$)	-125.30	2.49
2.0 ($r_s=2$)	-120.14	11.62
4.0 ($r_s=2$)	-100.98	41.28

is accurately obtained to first-order in the pseudopotential w. Outside the core, w is equal to the bare ion potential $-Z^*/r$, Z^* being the number of valence electrons. Inside the core, w is much smaller because the orthogonality constraint acts on the valence electrons as a repulsive potential. For a metal at $T=0$, it is often possible to choose w *a priori* since Z^* is known. The Fourier transform of the pseudovalence density is, in linear response,

$$n_v(q)=\mathcal{X}(q)w(q)\ ,$$

where $\mathcal{X}(q)$ is the susceptibility of the interacting electron gas at $T=0$. It has been shown that the pair interaction is improved if the following procedure is applied[20]: The "exact" (to all orders in the potential) valence density is first calculated, using, at $T=0$, a method equivalent to that described in Sec. II for finite temperatures. The pseudopotential is then chosen in such a manner that the linear response of the electron gas outside the core is just the exact density.

We shall develop similar ideas for Ne at finite temperatures. First, we note that, at low temperatures, two atoms with complete shells interact only through van der Waals forces. An ion-ion interaction due to "metallic" bonding can occur only at temperatures high enough to produce appreciable ionization. Let us assume that this is the case. Dharam-wardana suggested to define the pseudopotential, in reciprocal space, by[21]

$$w(q,T)=\frac{n_f(q,T)}{\mathcal{X}(q,T)}\ , \tag{7}$$

where $n_f(q,T)$ is the Fourier transform of the free-spectrum contribution to the density $n(r)$ defined in Eq. (2). Such a definition gives rise to some difficulties. First, when shallow bound states do exist (see Table I, $T=4T_F$), there is no clear distinction between the contributions of negative or positive eigenvalues close to the threshold; the definition is somewhat arbitrary and the variation of Z^* with temperature will be discontinuous. Second, the quick oscillations of n_f near the nucleus generate much too large a pseudopotential with an incorrect behavior at large q. We propose the alternative definition for a pseudodensity $\bar{n}$ to use in Eq. (7) instead of n_f:

$$\bar{n}(r)=\begin{cases}\lambda n_0, & \text{if } n(r)-n_0>\lambda n_0\\ n(r)-n_0, & \text{otherwise}\ .\end{cases} \tag{8}$$

λ must be strictly lower than one since $\bar{n}(r)$ must be consistent with linear response of the electron gas at density n_0. In Ref. 20, for instance, the value of the valence density at the core radius ranges between $0.65n_0$ in Li and $1.03n_0$ in Al. We shall see later that, in our example, the Ne-Ne interaction is not sensitive to the value of λ in the range $0.5<\lambda<0.66$. With $\lambda=0.5$ at $T=4T_F$, $\bar{n}(r)$ is constant in the region $r<R_1=2.35$ a.u. But R_1 cannot be considered as a *core* radius since the bound states still contribute for 70% to $n(R_1)-n_0$. The total charge corresponding to $n(r)$ is taken as the valence Z^*. At $T=4T_F$, $Z^*=3.75$ with $\lambda=\frac{1}{2}$, and $Z^*=3.98$ with $\lambda=\frac{2}{3}$. These numbers differ significantly from $Z-Z_b=2.63$ found in Table I. The potential w defined in Eq. (7), with $\bar{n}$ instead of n_f, is compared to the bare potential $v(q)=-4\pi Z^*/q^2$ in Fig. 2. The ratio $g(q)=w(q)/v(q)$ is well behaved and, except for a small maximum near $q=0$, not very different from the standard local form

$$g(q)=D\frac{\sin qR_c}{qR_c}+(1-D)\cos qR_c\ ,$$

with $D=1.3$ and $R_c=2.7$ a.u. The routine used to calculate $\mathcal{X}(q,T)$ has been written by Pélissier[22]; the exchange-and-correlation effects are included by means of the local field factor[23]

$$\mathcal{X}(q)=dV_{\text{xc}}(n_0)/dn_0$$

The correct numerical values found for $w(q)$ suggest that our approximation is correct at $T=4T_F$. When temperature is decreased, the pseudopotential is still correct at $T=2T_F$; but $g(q)$ becomes much larger than one at lower temperatures so that the method is inapplicable, as expected, when ionization is too low.

The generalization to nonzero temperatures of the ion-ion interaction formula,[20] within second-

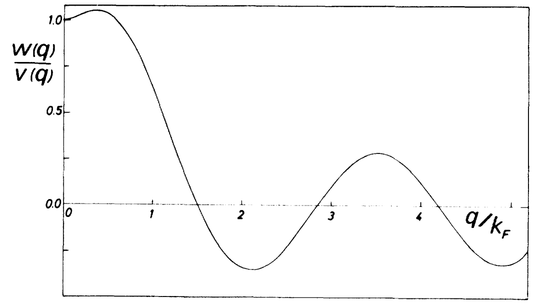

FIG. 2. Ratio of the effective pseudopotential $w(q)$ to the bare Coulomb interaction $-4\pi Z^*/q^2$ for neon at $r_s=2$ and $T=4T_F$.

order perturbation theory, is straightforward:

$$\phi(R)=\frac{Z^{*2}}{R}+\frac{1}{2\pi^2 R}\times\int_0^\infty q\,dq\,\bar{n}(q,T)w(q,T)\sin qR\ . \quad (9)$$

R is the distance between the two nuclei. According to the conclusions of Ref. 20, it is legitimate to assume that a large amount of the nonlinear effects (beyond second-order perturbation theory) are included in ϕ through $\bar{n}(q,T)$ which is nonlinear in essence. We should mention at this point that an even better approximation could be obtained using the displaced density of an atom with minimum scattering (i.e., the screening density of an auxiliary impurity neutralized by a hole of charge Z^* in the positive background; such an impurity, at $T=0$, gives rise to a zero Friedel sum). The pair potential ϕ is shown in Fig. 3; it is expected to be correct for $R>2R_1$, approximately 5 a.u. The two curves shown for $T=4T_F$ correspond to the values $\lambda=0.5$ and 0.66 [cf. Eq. (8)]; the variation of ϕ, a quantity generally very sensitive to pseudopotential modifications, can be considered as relatively small. The bonding is important at $T=4T_F$, but disappears at $T=2T_F$.

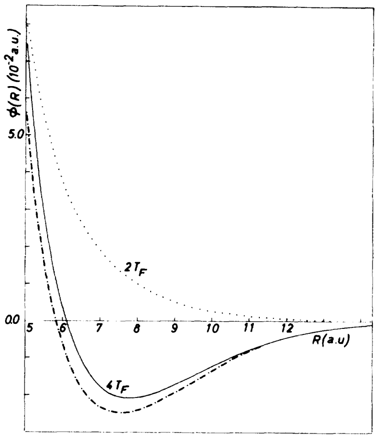

FIG. 3. Ion-ion interaction in neon at $r_s=2$. Two curves are shown for the temperature $T=4T_F$; the solid line corresponds to $\lambda=\frac{1}{2}$ [cf. Eq. (8)] and the dot-dashed line to $\lambda=\frac{2}{3}$. At $T=2T_F$, the pair potential has been calculated with $\lambda=\frac{1}{2}$.

V. CONCLUSION

We have presented the extension to a more complicated system of the model previously used for the temperature-dependent screening of a proton.[12] The self-consistent electronic structure of a neon impurity in an electron gas has been calculated as a function of temperature, at a given density of the jellium. The accurate evaluation of the spectrum, electron density profile and thermodynamic quantities, which is shown to be possible in these calculations, might be useful for laser diagnostics. The pair potential generated using the calculated density profiles could be the input for Monte Carlo or molecular-dynamics calculations leading to new properties, for instance, the ion-pair distribution function

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