PHYSICAL REVIEW B VOLUME 59, NUMBER 16 15 APRIL 1999-II

Pseudojellium, ideal metals, and stabilized jellium

Herbert B. Shore*
Department of Physics, San Diego State University, San Diego, California 92182

James H. Rose†
Department of Physics and Astronomy and Ames Laboratory, Iowa State University, Ames, Iowa 50011

(Received 16 October 1998)

Two new electron gas models, introduced in the early 1990s, describe the energetics of metals better than the conventional electron gas, jellium. The first, the ''ideal metal,'' was derived by starting with jellium at a specified density and requiring that no forces act on the positive background when the system is cleaved. The second, ''stabilized jellium,'' was derived by starting with the pseudopotential model of metals, requiring that this model yield equilibrium at the specified average electron density and then averaging the potential seen by the electrons to obtain an equivalent electron gas. Even though these derivations are conceptually quite different, their results, the ideal metal and stabilized jellium models, are very nearly identical. We explain their great similarity by deriving both the ideal metal and stabilized jellium in a unified way from pseudojellium—a stabilized electron gas model derived in the middle 1980s that includes the average electron-ion interaction, while maintaining the uniform ground state and computational simplicity of jellium. This derivation explains the near identity of the ideal metal and stabilized jellium and allows us to understand the small differences between them. [S0163-1829(99)00816-4]

I. INTRODUCTION

The electron gas (jellium) has been one of the most productive models in physics. However, it has many limitations. Perhaps the most obvious is that the positive background is held in place by unphysical external forces. If these external forces were removed, jellium would always collapse to roughly the density of sodium. That is, the jellia that are used to simulate most metals have electrons under high pressure. If the positive background were broken up into pieces of atomic size, such systems would expand in order to lower their average electron density. The root of the problem is that the attraction of the electrons to the ion cores is much stronger in most real metals than can be accounted for by jellium. Pseudojellium,[1] an electron gas model of metals developed during the 1980s, simulates the extra electron-ion interaction while maintaining the uniform ground state and computational simplicity of jellium. Pseudojellium almost, but not quite completely, removes the high electronic pressures found in jellium and consequently improves the description of the ground-state properties of metals. However, the improved physical properties of pseudojellium come at the cost of an additional input parameter for each metal to be modeled—its chemical potential.

In the early 1990s, Perdew, Tran, and Smith[2] and independently the present authors[3,4] developed new models of the electron gas that preserved pseudojellium's improved description of the ground state of metals. Strikingly, these new models do not necessarily require any input beyond the average electron density—*the chemical potential of the metal is not an input*. Rather, these new models determine the chemical potential directly from equilibrium conditions intrinsic to the models themselves. These new models—the ''ideal metal''[3,5] and ''stabilized jellium''[2]—reproduce qualitatively the cohesive energies,[2,4] surface energies,[2,3] and bulk moduli[2,5] of the simple metals. At the same time, they maintain the previous good qualitative agreement with the excited-state properties of the simple metals. Surprisingly, the basic connections between pseudojellium, the ideal metal, and stabilized jellium have not been completely elucidated up to the present time. This is the task we address in this paper.

The common feature of pseudojellium, the ideal metal, and stabilized jellium is that each introduces a new electron potential ν that represents the difference in the binding of electrons in the metal compared to jellium. This step-function potential—defined to be constant everywhere inside the positive background and zero in the vacuum—is the basic new construct that distinguishes the new electron gas models from jellium. The three models determine ν in different ways. Pseudojellium defines the height of the potential step ν_{PJ} to be the difference between the chemical potential of the real metal[6–8] and jellium. That is, the Fermi energy of pseudojellium is shifted by ν_{PJ} so that it will be the same as in the real metal. For the ideal metal the step ν_{IM} is determined by the condition that if the bulk ideal metal is cleaved into two half-spaces, the energy should be stationary for zero separation of the pieces; i.e., no forces should act on the positive background when it is cleaved. In the rest of this paper, we will use the term *ideal* to describe any jelliumlike model with this property: zero force at zero separation. For stabilized jellium the strength of the step-function potential ν_{SJ} is determined by requiring that a simple Ashcroft pseudopotential model of the metal[9] should be in equilibrium at the specified volume per atom. Then ν_{SJ} is the spatially averaged Hartree potential due to the pseudopotential and electrons. We will call a jelliumlike model *stable* if an underlying pseudopotential results in minimum energy at the desired density. We emphasize that the *equilibrium conditions* for the ideal metal and stabilized jellium are established using physically inequivalent models. The ideal metal starts with jellium and the equilibrium condition results in a uniform positive background. Stabilized jellium finds the equilibrium condition for an array of Ashcroft pseudopotentials—with a clearly nonuniform positive background. Nonetheless, the resulting electron gas model for stabilized jellium is essentially identical to the ideal metal model.

Surprisingly, the strengths of the confining potentials for the ideal metal and stabilized jellium, determined in these two quite different ways, are exactly the same, i.e., $\nu_{\mathrm{IM}} = \nu_{\mathrm{SJ}} = \nu_0$, where

$$\nu_0 = -n_0 \frac{\partial e_j}{\partial n}\bigg|_{n_0}. \tag{1}$$

Here, n_0 is the density of the uniform electron gas and e_j is the energy per electron in jellium; i.e., $e_j(n) = t_s(n) + e_{\mathrm{xc}}(n)$, the sum of kinetic and exchange-correlation energies for the uniform electron gas. We note that the potential step ν_{PJ} for pseudojellium is numerically close to ν_0 for most metals.

The ideal metal, stabilized jellium, or pseudojellium should be preferred to jellium in all applications. These stabilized electron gas models are especially valuable for modeling inhomogeneous metals, since the externally imposed forces that occur in the jellium are then particularly problematic. Important results have been obtained from these models for many properties of inhomogeneous metals. An incomplete list includes the surface energy and work functions of the elemental metals,[10–16] adhesive energies,[17] the structure of the surface excitations of metals, esp. plasmons,[18] Van der Waals forces at surfaces,[19] modeling of fullerines,[20] the behavior of metallic clusters,[21–27] and the energetics of voids in metals.[28,29] The common feature for these calculations is that a step in the potential (of strength ν_0) appears at the interface between the metal and vacuum. Results derived from the ideal metal and stabilized jellium are identical for these inhomogeneous systems. The new electron gas models have also been applied with good results to the calculation of the cohesive energies, chemical potentials, and bulk moduli of homogeneous elemental metals.[30–33] The ideal metal and stabilized jellium will be shown to give the same answers for bulk metals—if electron relaxation is ignored.

Note that the atomic properties of the metal such as valence or cell volume do not appear in the expression for ν_0, Eq. (1). This is not surprising from the point of view of the ideal metal, since no atomic model was introduced in the derivation of ν_{IM}. However, the derivation of stabilized jellium appears to depend essentially on the Ashcroft pseudopotential and it is far from obvious why neither of its parameters (the valence or the ion core radius, r_c) appears in the expression for ν_{SJ}.

We will attempt to elucidate the connection between all three of the new electron gas models. To this end, we will deal with a series of questions. First, why is ν_0 the same in stabilized jellium and the ideal metal, or equivalently, why are both models not only *stable* but also ideal? We will see that, in fact, the condition $\nu_{\mathrm{SJ}} = \nu_0$ depends on replacing the polyhedral Wigner-Seitz cell by an equivalent sphere and thus ignoring cell-cell interactions in the pseudopotential calculation. Second, what is the role of the pseudopotential? Third, can the ideal metal be cast as a pseudopotential theory? Finally, to what degree are the ideal metal and stabilized jellium identical? We will derive both the ideal metal and stabilized jellium from pseudojellium. This allows us to explain the great similarity of the two approaches, as well as their apparent differences.

The structure of this paper is as follows. In Sec. II, we first introduce the pseudojellium model. Next, we show how the ideal metal is a particular realization of pseudojellium whose chemical potential is determined by the condition that *no forces* act on the positive background when the electron gas is cleaved. Finally, we show that stabilized jellium is a different realization of the pseudojellium model, where the chemical potential is derived from Ashcroft pseudopotential perturbation theory. In Sec. III, we generalize the stabilized jellium model by calculating the step potential ν or the shift in the chemical potential due to a pseudopotential, including lattice effects and electrostatic cell-cell interactions. We find results that are *independent of the form of the pseudopotential* for a very wide class of pseudopotentials—there is nothing special about the use of the Ashcroft pseudopotential. We then examine the consequences of the spherical cell approximation and show that the ideal metal can be derived from a limiting case of this same class of pseudopotentials. This connection makes clear why the two models give identical results for physical quantities such as the bulk modulus when calculated to first order. We show that the energy as a function of volume, the equation of state, the bulk modulus, and the chemical potential are all given by simple universal formulas in this approach. We then discuss the changes introduced into the pseudopotential description of the two models by going beyond the spherical cell approximation. Finally, the paper concludes with a brief discussion and summary.

II. PSEUDOJELLIUM, IDEAL METAL, AND STABILIZED JELLIUM

We commence this section with a brief discussion of pseudojellium and the problem in the physics of metals that it solves. We point out the key role that the concept of the chemical potential plays in the formulation of the pseudojellium model. Finally, we show how the ideal metal and stabilized jellium can be derived simply from pseudojellium by introducing different ways of estimating the chemical potential.

Pseudojellium corrects for jellium's misestimate of the metal's electron-ion interaction in the simplest possible way. Namely, while retaining the features of jellium, it adds an attractive (repulsive) potential that is a constant ν_{PJ} inside the positive background and zero outside—as shown in Fig. 1. This additional potential increases (decreases) the electron's binding to pseudojellium and provides an improved simulation of the actual electron-ion interaction found in metals. The strength of the additional potential ν_{PJ} is determined from the difference in the chemical potentials of jellium and the actual metal. The strength ν_{PJ} is chosen so that pseudojellium has the same chemical potential as the metal

$$\nu_{\mathrm{PJ}} \equiv \mu_m - \mu_j. \tag{2}$$

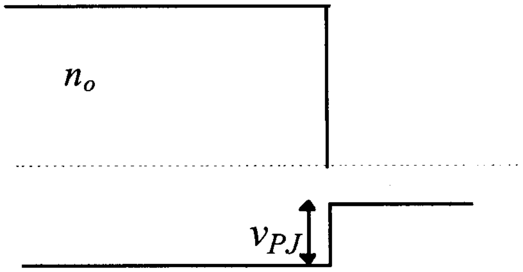

FIG. 1. The additional confining potential that appears in pseudojellium, the ideal metal, and stabilized jellium is pictured. The potential has strength ν_{PJ} inside the background and zero outside.

Consequently, the Fermi energy of pseudojellium would be identical with that of the actual metal if we could determine the chemical potentials of jellium and the metal exactly. In practice, the chemical potentials of the metals were taken from the compilation of Weinert and Watson.[8]

The ideal metal is a pseudojellium model but with a different prescription for obtaining ν_0. The strength of the step-function potential is chosen so that there is no net force on the positive background for infinitesimal separation. The strength ν_0 is given by Eq. (1), as can be shown by evaluating the energy change exactly, upon initial separation of the two half-spaces using first-order perturbation theory. The value of ν_0 does not depend on the shape of the cleavage surface, which may be arbitrary—one can divide the ideal metal up however one likes. Details of the derivation of Eq. (1) for the ideal metal can be found in Refs. 3 and 4.

The ideal metal is characterized completely by a single parameter, the equilibrium electron density, n_0. It is often useful to elaborate a more detailed model, based on the ideal metal, which takes account of the atomic character of real metals. For example, the cohesive energy and bulk modulus depend on the size of the atoms, and thus a model that incorporates the volume per atom (or equivalently the valence, $Z \equiv \Omega_0 n_0$) is required to model them.[4] This more elaborate model is defined as follows. First, choose a ghost lattice of points that correspond to the nuclei in the real uniform bulk metal. Second, divide the uniform positive background into space-filling rigid pieces with each piece filling one Wigner-Seitz cell of the ghost lattice (since the ideal metal can be cleaved in any arbitrary way, it can, in particular, be split into Wigner-Seitz cells). Third, let the confining potential be proportional to the positive background density. For the undeformed metal the density is n_0 and the potential is ν_0. If the metal is deformed, different Wigner-Seitz cells will overlap or be separated by the deformation. At any point where the cells overlap, the positive background density and the confining potential are taken to be the sum of the background densities and potentials of the individual overlapping cells at that point. At a point where the Wigner-Seitz cells separate, the density of positive charge and the confining potential are identically zero in the interstitial region. This extended version of the ideal metal is characterized by the volume of the equilibrium Wigner-Seitz cell, Ω_0, in addition to n_0.

As in jellium, the electrostatic energy of the undeformed ideal metal due to the uniform positive background and the electrons is zero, since the net charge density is everywhere zero. This implies that the positive charge *within a single Wigner-Seitz cell* is allowed to interact with itself. One could imagine subtracting off this intracell self repulsion of the positive background, but this is *not* done in defining the ideal metal, which, like jellium, includes the intracell self-interaction energy. As discussed in Sec. III B, one can include or not include this term as one chooses; the values of physical quantities calculated from the model, which depend only on energy *differences*, are independent of the choice.

Stabilized jellium[2] is perhaps more nearly a realization of pseudojellium than is the ideal metal. Namely, the total energy and chemical potential are computed from a simple model of the metal and the values so obtained are then assigned to a uniform electron gas model. In this computation, the quantities are calculated for a system of electrons in the potential of a regular lattice of Ashcroft pseudopotentials. The calculation is greatly simplified by ignoring band-structure effects, i.e., by constraining the electron density to remain uniform and by evaluating electrostatic potentials and energies in a spherical cell approximation. The parameters of the pseudopotential are chosen to have (i) the proper valence and (ii) the correct cell volume at equilibrium. These two quantities, Z and Ω_0, then characterize the model. The shift in chemical potential with respect to that of jellium is the average potential seen by the electrons—the average of the pseudopotential plus the electrostatic potential of the electron cloud. As stressed earlier, the strength of the confining potential determined in this way is ν_0—the same as was found for the ideal metal. Thus, we have the remarkable result that requiring the simple pseudopotential model of the metal to be *stable* at density n_0 implies that the resulting electron gas model is also *ideal*. In Sec. III A we will show that this second condition depends on the spherical cell approximation and the consequent lack of ion-ion interactions. Stability does not imply ideality if the electrostatic energy and potential are calculated using the actual polyhedral Wigner-Seitz cells. We note that for stabilized jellium the interaction of the electrons with the ionic cores is described by a potential, rather than by a positive background charge density as in the ideal metal. A consequence is that there is no intracell self-interaction energy for stabilized jellium, unlike the ideal metal. As stated earlier, this distinction between stabilized jellium and the ideal metal is inconsequential.

III. IDEAL METAL AND STABILIZED JELLIUM FROM PSEUDOPOTENTIAL THEORY

In this section the step-function potential, for both stabilized jellium and the ideal metal, will be obtained from first-order pseudopotential perturbation theory (i.e., the electron density remains uniform and thus band-structure effects are ignored). By treating the difference between stabilized jellium and the ideal metal as primarily a difference in the choice of pseudopotential, the connection between the two will be clarified. Briefly, one adjusts the pseudopotential so that the calculated energy is a minimum for the specified uniform electron density, n_0. Next, one calculates the chemical potential using this pseudopotential. Then this chemical potential is inserted into pseudojellium to yield either stabilized jellium or the ideal metal, depending on the choice of the pseudopotential.

In Sec. III A we carry out the above program for a general class of pseudopotentials on a cubic lattice. In Sec. III B we replace the polyhedral Wigner-Seitz cell of the actual lattice with a sphere. We show that, in this approximation, the Ashcroft pseudopotential and the pseudopotential appropriate to the ideal metal yield identically the same equilibrium chemical potentials, energies, and bulk moduli. In Sec. III C we examine the differences between the two models that arise if one goes beyond the spherical cell approximation to include the full symmetry of the lattice.

A. The electron gas and first-order pseudopotential perturbation theory

We will obtain the condition for stability and the resulting chemical potential for a large class of pseudopotentials arrayed on a cubic lattice. These pseudopotentials, $w(\mathbf{r})$, are defined to be spherically symmetric and have the form $-Z/r$ outside some ''ion-core'' radius that is less than or equal to the radius of the sphere that inscribes the unit cell. Here Z denotes the valence, i.e., the number of electrons per unit cell. Furthermore, these pseudopotentials are chosen to minimize the energy for the chosen equilibrium density n_0 when the energy is calculated in first-order pseudopotential perturbation theory (keeping the electron density uniform). The calculations in this section are conceptually similar to that of Perdew *et al.*,[2] and where possible we use similar notation.

We start by calculating the equilibrium energy of a uniform space of an elemental metal, where the metal is divided into polyhedral Wigner-Seitz unit cells of volume Ω on a regular lattice. The volume will also be specified in terms of the ''Wigner-Seitz radius'' R (equilibrium radius R_0) of a sphere with equal volume, i.e., $\Omega = 4\pi R^3/3$. The total energy—assuming a uniform electron density n—of a system with N unit cells of volume Ω, each containing Z electrons, is given by

$$E=\sum_i \int d^3\mathbf{r}\, n w(\mathbf{r}-\mathbf{R}_i)+U_{ee}+U_{ii}+NZe_j(n). \quad (3)$$

Here $w(\mathbf{r}-\mathbf{R}_i)$ is the pseudopotential of the ion at lattice site $\mathbf{R}_i$, the sum is over all sites, while e_j is the energy per electron of jellium. The ion-ion interaction energy U_{ii} is the same as the interaction of point charges at the lattice sites since we have assumed that the spherically symmetric ion cores do not overlap. That is,

$$U_{ii}=\frac{1}{2}\sum_{i\neq j}\frac{Z^2}{|\mathbf{R}_i-\mathbf{R}_j|}. \quad (4)$$

Similarly, the electron-electron Coulomb energy is

$$U_{ee}=\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{nn}{|\mathbf{r}-\mathbf{r}'|}. \quad (5)$$

These terms are individually divergent, but their sum is finite and well defined. If we add and subtract the potential of a point charge at the center of each cell, Eq. (3) becomes

$$E=\sum_i \int d^3\mathbf{r}\, n\left[w(\mathbf{r}-\mathbf{R}_i)+\frac{Z}{|\mathbf{r}-\mathbf{R}_i|}\right]+NZe_j(n)$$
$$+\left\{U_{ee}+U_{ii}-\sum_i \int d^3\mathbf{r}\, n\frac{Z}{|\mathbf{r}-\mathbf{R}_i|}\right\}. \quad (6)$$

The terms inside the curly brackets represent the electrostatic energy U_M of the Wigner solid, i.e., the energy of a lattice of point charges immersed in a compensating uniform background. We define the term in square brackets by the shifted pseudopotential $\tilde{w}(\mathbf{r})=w(\mathbf{r})+Z/r$, which has no Coulomb tail and is identically zero outside the ion-core radius. Equation (6) is rewritten

$$E=N\int_\Omega d^3\mathbf{r}\, n\tilde{w}(r)+NZe_j(n)+U_M, \quad (7)$$

where the integral is now over one unit cell.

The Wigner solid's contribution, $e_M=U_M/NZ$, to the energy per electron has been extensively studied[34,35] and can be expressed conveniently as

$$e_M=-\frac{9}{10}\frac{Z}{R}\alpha_L. \quad (8)$$

If the unit cell is approximated by a sphere—resulting in a compensating uniform density ball of electrons with a point charge at the center—one finds $\alpha_L=1$. For the cubic lattices sc, bcc, and fcc, the values of α_L are, respectively, 0.9778, 0.9955, and 0.9954.

The energy per electron follows directly from Eq. (6) and is given by

$$e=e_j+\overline{w_R}+e_M. \quad (9)$$

Here, the bar denotes the volume average, i.e.,

$$\overline{w_R}=\Omega^{-1}\int_\Omega d^3\mathbf{r}\,\tilde{w}(r). \quad (10)$$

Equation (9) corresponds to Eq. (4) of Perdew *et al.*,[2] but calculated for a general pseudopotential and without the spherical cell approximation.

The pseudopotential is to be defined so that the energy is a minimum for $n=n_0$, i.e., $\partial e/\partial\Omega=0$. The derivative is easily calculated using the identities $\partial\overline{w_R}/\partial\Omega=-\overline{w_R}/\Omega$, $\partial e_j/\partial\Omega=-(n/\Omega)\partial e_j/\partial n$, $\partial R^{-1}/\partial\Omega=-(3R\Omega)^{-1}$. The first of these follows from the fact that the integral in Eq. (10) is independent of cell volume—assuming no overlap of ion cores. Hence, for the energy to be a minimum at $n=n_0$, it is necessary that the pseudopotential satisfy the constraint

$$\overline{w_R}=\frac{3}{10}\frac{Z}{R_0}\alpha_L-n_0\left.\frac{\partial e_j}{\partial n}\right|_{n_0}, \quad (11)$$

which follows from Eqs. (8)–(10). That is, any pseudopotential whose volume average is given by Eq. (11), and that is otherwise in the class defined above, yields a metal with the predefined equilibrium density. We will henceforth refer to Eq. (11) as the equilibrium condition.

The chemical potential, μ, is the change in electron energy with respect to electron number at constant volume, i.e.,

$\mu = \partial(ne)/\partial n|_{\Omega=\Omega_0}$. Here, ne is the energy density, which can be obtained from Eq. (6) by dividing E by the total volume $N\Omega$. This can be written

$$\frac{E}{N\Omega} = ne_j(n) + \frac{1}{N\Omega}\int d^3\mathbf{r}\, n \sum_i \tilde{w}(\mathbf{r}-\mathbf{R}_i) + \frac{1}{N\Omega}U_M . \tag{12}$$

Differentiating with respect to n while holding Ω constant gives

$$\mu = \mu_j + \frac{1}{N\Omega}\int d^3\mathbf{r}\,\delta\nu(\mathbf{r}), \tag{13}$$

where

$$\delta\nu(\mathbf{r}) = \sum_i \tilde{w}(\mathbf{r}-\mathbf{R}_i) - \sum_i \frac{Z}{|\mathbf{r}-\mathbf{R}_i|} + \int d^3\mathbf{r}\frac{n}{|\mathbf{r}-\mathbf{r}'|}. \tag{14}$$

We recognize $\delta\nu(\mathbf{r})$ as the potential seen by the electrons. Thus, $\mu-\mu_j$ is the average electron potential:

$$\mu - \mu_j = \overline{w}_R + \nu_M , \tag{15}$$

where ν_M is the average potential of the Wigner solid.

The quantity ν_M must be calculated with some care. The two right-hand terms of Eq. (14), representing, respectively, the electron potential due to the point charges and that due to the other electrons, are individually divergent. The sum of these two terms is finite, but the value depends on the way in which the terms are combined, or equivalently, on the boundary conditions at the surface of the crystal. If there is a dipole layer at the surface, this will shift the potential in the interior, so the potential at point **r** does not necessarily depend only on charges in the vicinity of **r**. There has been considerable controversy in the literature as to whether it is even possible to define a unique ''average electron potential'' in a crystal.[36–38] The value of ν_M is well defined, and there is no contribution from the surface, if we require that all cells, including those at the surface, have the same uniform electron density as those in the interior. For cubic lattices with the point charge at the center of the cell, the Wigner-Seitz cell has no net charge, dipole moment, or quadrupole moment. In this case ν_M should be close to the spherical cell value $-3Z/10R$; the average potential in a cell will be primarily due to the charges within that cell, with small corrections from neighboring cells. The average ν_M is given by the Callaway-Glasser formula[39,40] for the average potential of a Wigner solid:

$$\nu_M = -\frac{2\pi Z}{3\Omega^2}\int_\Omega r^2 d^3\mathbf{r} = -\frac{3}{10}\frac{Z}{R}\beta_L . \tag{16}$$

In the spherical cell approximation $\beta_L = 1$. For the cubic lattices, the integral over the cell volume can be evaluated exactly,[41] yielding

$$\beta_L = \left(\frac{4\pi}{3}\right)^{2/3}\frac{5}{12} = 1.0827 \quad \text{for sc}, \tag{17a}$$

$$\beta_L = \left(\frac{\pi}{3}\right)^{2/3}\frac{95}{96} = 1.0205 \quad \text{for bcc}, \tag{17b}$$

$$\beta_L = \left(\frac{2\pi}{3}\right)^{2/3}\frac{5}{8} = 1.0231 \quad \text{for fcc}. \tag{17c}$$

The correction to the average potential due to the lattice is at least 2%—much greater than the corresponding correction to the energy.

For pseudojellium, the strength of the confining potential is defined to be the difference between the actual chemical potential of the metal and the chemical potential of jellium. With the chemical potential from Eq. (15), we obtain a confining potential $\tilde{\nu}_0$:

$$\tilde{\nu}_0 \equiv \mu - \mu_j = \overline{w}_R - \frac{3}{10}\frac{Z}{R}\beta_L . \tag{18}$$

Inserting $\overline{w}_R$ from Eq. (11), we have

$$\tilde{\nu}_0 = -n\left.\frac{\partial e_j}{\partial n}\right|_{n_0} + \frac{3}{10}\frac{Z}{R_0}(\alpha_L - \beta_L). \tag{19}$$

Thus $\tilde{\nu}_0$ differs from the famous formula for ν_0 in Eq. (1) as a result of including lattice effects. This result for $\tilde{\nu}_0$ depends only on the lattice type and does not depend on the specific form of the pseudopotential, as long as the pseudopotential belongs to the class specified at the beginning of this section. However, $\tilde{\nu}_0 = \nu_0$ if the unit cell is replaced by a sphere, which has the effect of setting $\alpha_L = \beta_L = 1$. Thus, an implementation of pseudojellium using a pseudopotential belonging to the specified class, such as the Ashcroft pseudopotential, is *stable*, but not exactly *ideal*. The difference $\tilde{\nu}_0 - \nu_0$ can be estimated from the magnitude of the second term of Eq. (19), by replacing Z/R by $Z^{2/3}/r_s$. For aluminum, with $Z=3$ and $r_s \approx 2$, the correction is about -0.2 eV. It would be somewhat more for the transition metals (and Be) and somewhat less for the other simple metals.

B. Spherical cell approximation

The comparison of the ideal metal and stabilized jellium can be simplified and other useful results can be obtained if we approximate the Wigner-Seitz cell by a sphere of equal volume, which sets $\alpha_L = \beta_L = 1$. First, we note that the equilibrium condition of Eq. (11) refers to the average of the *shifted* pseudopotential $\tilde{w}(\mathbf{r})$. Since the average of Z/r over a sphere is just $3Z/2R_0$, we can rewrite the equilibrium condition in terms of the average $\overline{w}$ of the unshifted $w(\mathbf{r})$:

$$\overline{w} = \nu_0 - \frac{6}{5}\frac{Z}{R_0}. \tag{20}$$

The Ashcroft pseudopotential with the core radius r_c given by Eq. (26) of Ref. 2 satisfies this condition.

The ideal metal can be described by a pseudopotential:

$$w_{\mathrm{IM}}(\mathbf{r}) \equiv \nu_{\mathrm{IM}}\Theta(\mathbf{r}) - n_0\int_{\Omega_0} d^3\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{21}$$

Here, $\Theta(\mathbf{r})$ is defined to be 1 if **r** lies within the unit cell centered at the origin and zero otherwise. The second term on the right-hand side corresponds to the electrostatic potential due to a positive charge Z uniformly distributed on a sphere of volume Ω_0, while the first term is just the confining potential step ν_{IM}. Outside of the sphere w_{IM} falls off as $-Z/r$, so that (within the spherical cell approximation) w_{IM} can be regarded as belonging to the class of pseudopotentials of Sec. III A. The volume average of the ideal metal pseudopotential is $\overline{w}_{\mathrm{IM}}=\nu_{\mathrm{IM}}-6Z/5R_0$. It follows from Eq. (20) that $\nu_{\mathrm{IM}}=\nu_0$. Thus, both stabilized jellium and the ideal metal can be derived from different pseudopotentials. However, because both pseudopotentials satisfy the same equilibrium condition, these models have exactly the same strength for the confining potential ν_0.

We caution that the above argument relies heavily on the spherical cell approximation. In Eq. (21), which defines the ideal metal pseudopotential, the positive charge density extends beyond the boundary of the inscribing sphere. Hence these pseudopotentials would violate the condition that the cores should not overlap if they were arrayed on a cubic lattice. In the next section we will nevertheless show that the relation $\nu_{\mathrm{IM}}=\nu_0$ is exact, and can be obtained from a pseudopotential model for the ideal metal.

Remaining within the spherical cell approximation and first-order perturbation theory, we obtain several useful results that apply equally to both the ideal metal and stabilized jellium. The equilibrium energy per electron follows from Eq. (9) and Eq. (11),

$$e(n_0)=e_j(n_0)+\nu_0-\frac{3Z}{5R_0}. \tag{22}$$

This result corresponds to Eq. (31) of Perdew *et al.*[2] and represents the energy per electron of stabilized jellium. For the ideal metal, we add to this the positive energy per electron $+3Z/5R_0$ due to self-interaction of the positive background, which cancels the corresponding negative term in Eq. (22). Thus, the energy per electron of the ideal metal is

$$e_{\mathrm{IM}}=e_j(n_0)+\nu_0. \tag{23}$$

It is important to note that the self-interaction energy of the positive background is a constant independent of cell size. Since only energy differences enter in the calculation of physical quantities, the ideal metal and stabilized jellium are equivalent when used to model bulk metals to first order; the only difference is one of bookkeeping. For example the energy per electron to assemble the system from separated electrons and pseudopotentials is given by Eq. (22) in both models.

The equilibrium bulk modulus is obtained by evaluating the second derivative of the total energy, Eq. (9), with respect to Ω, using the rules following Eq. (10) to simplify, and then eliminating $\overline{\omega}_R$ using Eq. (11). We find

$$B\equiv\Omega\frac{\partial^2(Ze)}{\partial\Omega^2}=n_0^3\frac{\partial^2 e_j}{\partial n^2}+n_0\frac{Z}{5R_0}. \tag{24}$$

No details of the pseudopotential appear in the formulas for either the equilibrium energy or the bulk modulus—thanks to the equilibrium condition. The values for the bulk moduli calculated using the ideal metal and reported in Ref. 4 differ from the values calculated using stabilized jellium and reported in Ref. 2. This apparently led to some speculation that the ideal metal and stabilized jellium differed essentially when used to evaluate bulk properties of the elemental metals. Actually, this is not the case. The differences in the reported bulk moduli come about because the results in Ref. 2 were calculated to first order in the pseudopotential, as in Eq. (24), while those in Ref. 4 were calculated to second order, i.e., electron relaxation was accounted for. We repeated the calculations of Ref. 4 keeping the electron density uniform, and found values for B that were very nearly those of the universal predictions of Eq. (24). There were some small differences that arose because our calculations used the actual Wigner-Seitz cells appropriate to the lattice rather than approximating them by spheres.

We also obtain general results for the ground-state energy per electron for densities away from equilibrium, and the equation of state—as long as the pseudopotentials are in the general class defined above, there is no ion-core overlap and all quantities are evaluated in first-order pseudopotential perturbation theory. The energy per electron is given by

$$e(n)=\frac{3}{10}\frac{Z}{R_0}\frac{n}{n_0}-\frac{9}{10}\frac{Z}{R}+\nu_0\frac{n}{n_0}+e_j(n). \tag{25}$$

The equation of state (pressure p versus volume) follows immediately from Eq. (25):

$$p=n^2\left[\frac{3}{10}Z\left(\frac{1}{n_0R_0}-\frac{1}{nR}\right)+\frac{\nu_0}{n_0}+\frac{\partial e_j}{\partial n}\right]. \tag{26}$$

Here, R denotes the volume and radius of the compressed/expanded Wigner-Seitz sphere. Equations (25) and (26) evaluate, respectively, to the equilibrium energy and to zero when n is set equal to the equilibrium density, i.e., n, $R\rightarrow n_0,R_0$. It should be remembered that all quantities have only been evaluated to first order in perturbation theory (i.e., the uniform electron density was not allowed to respond to the pseudoionic cores). Hence, it is unlikely that these formulas will be very useful for metals other than the alkalis. These expressions are equivalent to Eqs. (31) and (33) of Ref. 2. However, in the present formulation the energy and equation of state are manifestly dependent only on the jellium $e_j(n)$ and its derivatives; there is no apparent dependence on properties of the pseudopotential.

C. Beyond the spherical cell approximation

The equality $\nu_{\mathrm{IM}}=\nu_0$ and Eq. (23) for the ideal metal energy per electron are *exact* for a general cubic lattice. This is somewhat surprising since the numerical factors multiplying Z/R_0 in the formulas of Sec. III B are approximations valid only in the spherical cell approximation. Similarly, from Eq. (19), we see that $\nu_{\mathrm{SJ}}=\tilde{\nu}_0$ is only approximately equal to ν_0 for a general cubic lattice. Furthermore, we cannot use the method of Sec. III A to show the exact nature of the results for the ideal metal, since the pseudopotential corresponding to the polyhedral cell of the ideal metal does not have a pure $-Z/r$ tail outside of nonoverlapping cores and thus does not fit into the class of spherically symmetric pseudopotentials used in Secs. III A and III B. Instead we will use the method of Refs. 3–5 to obtain the desired exact results.

What considerations are important for constructing a pseudopotential suitable for the ideal metal on a lattice? First and foremost, we want to have an electron gas that is uniform and in equilibrium at a specified density n_0. We start by assuming that a pseudopotential can be constructed from a pseudocharge via Coulomb's law. Next, we imagine arranging the pseudoions on each site of some particular regular lattice that has an interatomic spacing corresponding to the density n_0. Since an electron gas has a uniform positive background, we require that the sum of the pseudocharges should be the uniform positive background. Consequently, to arrive at our goal, we must choose a different pseudopotential for each different lattice symmetry. We emphasize that the pseudopotential given below is the basic object in the theory of the ideal metal. The pseudocharge is only a particularly vivid and useful way of describing the pseudopotential.

The pseudocharge ρ_{ps} will be constructed from two pieces. First, the requirement of a uniform equilibrium state with background density n_0 implies that one piece should be

$$\rho_{\mathrm{ps}}^1(\mathbf{r}) = n_0 \Theta(\mathbf{r}). \tag{27}$$

We remark that ρ_{ps}^1 is the pseudocharge that would be appropriate for jellium. The second part of the pseudocharge ρ_{ps}^2 should (i) exactly cancel for the uniform equilibrium state and (ii) generate a potential that is a constant ν_{IM} inside the unit cell and zero outside. A δ-function charge dipole at the surface of $\Theta(\mathbf{r})$ satisfies these conditions, i.e., the dipole generates the appropriate step function change in the potential, while the overlapping dipoles from two adjacent cells that just touch will exactly cancel. The dipole moment is determined by the condition that the potential has strength ν_{IM} inside the unit cell.

The pseudopotential for the ideal metal, $w_{\mathrm{IM}}(\mathbf{r})$, is generated from ρ_{ps} via

$$w_{\mathrm{IM}}(\mathbf{r}) \equiv \int d^3\mathbf{r}' \frac{\rho_{\mathrm{ps}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{28}$$

The integral is formally over all space. However, it need only be evaluated over the unit cell since the pseudocharge is identically zero elsewhere. Using $\rho_{\mathrm{ps}} = \rho_{\mathrm{ps}}^2 + \rho_{\mathrm{ps}}^1$ we obtain Eq. (21) for the ideal metal pseudopotential, except that $\Theta(\mathbf{r})$ and Ω_0 now refer to the polyhedral cell rather than the spherical cell.

For jellium the uniform positive background is regarded as a real charge which can interact with itself as well as with the electrons. In contrast, for the pseudopotential theory of metals, one assumes there is no self-interaction of the pseudocharge within a cell, and neglects interactions due to the overlap of the pseudopotential cores of neighboring cells. Since, the ideal metal is an electron gas model, we will also include the self-interaction of the uniform positive background, i.e., we allow ρ_{ps}^1 to interact with itself. Consequently, after calculating the equilibrium energy due to w_{IM} using pseudopotential theory, we add the self-energy of the positive background. Our construction of the ideal metal treats the pseudocharge ρ_{ps}^2 that generates the dipole barrier differently. Its self-interaction energy and the energy of interaction when two different dipole barriers coincide are neglected.

With this model of the ideal metal it can be shown that the potential ν_{IM} is given by Eq. (1) and that the equilibrium energy per electron is given by Eq. (23). The argument is an exact analog of the derivation in Refs. 3–5 for cleaving the solid into two half-spaces. The infinite bulk metal consists of a lattice of Wigner-Seitz cells with the ideal metal pseudopotential—the step potential ν_{IM} inside the cell plus the electrostatic potential arising from the cell's positive background. In equilibrium the cells touch, the electron and background charges cancel everywhere, and therefore the electrons see a constant potential ν_{IM} everywhere. The energy per electron is therefore $e = e_j + \nu_{\mathrm{IM}}$. The stability condition requires that $\partial e/\partial n = 0$ at the equilibrium density n_0. The electrostatic energy is exactly zero in equilibrium, and increases as $(n-n_0)^2$ if the lattice is expanded or compressed. It therefore does not contribute to the first derivative with respect to expansion of the lattice. The number of electrons in a cell does not change if the cell volume changes, i.e., $Z = n_0\Omega_0 = n\Omega$, but the number that occurs in the potential ν_{IM} is $n\Omega_0$. To first order in $n-n_0$ the energy per cell is therefore $Ze = \Omega_0[n_0 e_j(n) + n\nu_{\mathrm{IM}}]$. Setting the derivative equal to zero immediately gives $\nu_{\mathrm{IM}} = \nu_0$. Thus we have shown that a pseudojellium model based on $w_{\mathrm{IM}}(\mathbf{r})$ is both *stable* and *ideal*.

IV. DISCUSSION AND SUMMARY

The derivation of the equilibrium energy and the equilibrium condition for the ideal metal using a cubic lattice is exact—in the sense that the derivation depends neither on the approximation of a spherical Wigner-Seitz cell nor on the constraint that the density is *a priori* uniform. The ideal metal pseudopotential is constructed to yield a total electron potential that is a constant, independent of position at equilibrium. The self-consistent solution of the Schrödinger equation then yields a uniform electron density. That is, the uniformity of the density is not an externally imposed constraint. If the lattice is expanded or contracted, the total electron potential and thus the electron density of the ideal metal will no longer be uniform. The change in energy will be proportional to $(\Omega-\Omega_0)^2$ as will the change in the electrostatic contribution, and thus neither will influence the equilibrium condition. However, quantities such as the bulk modulus depend on energy derivatives beyond the first. Consequently ''exact'' calculations of the bulk modulus for the ideal metal differ slightly from the result in Eq. (24) due to lattice effects, and by a much larger amount if computed to second order in the pseudopotential,[4] thus including electron relaxation to the ion cores.

In this paper, we have shown that stabilized jellium and the ideal metal can both be interpreted as pseudopotential theories. Each approach has advantages and disadvantages. The Ashcroft pseudopotential used in the derivation of stabilized jellium more closely resembles the potential of the actual ion core in a real metal, but the derivation of the major result Eq. (1) requires the spherical cell and uniform electron density approximations. The ideal metal pseudopotential is not physically realistic, in that the ion core extends over the entire cell, but Eq. (1) is then an exact consequence of the ideality condition.

One of the questions we had at the start of this investigation was, can one construct a better uniform electron gas model, which would simulate the properties of real metals more closely, by using a different local pseudopotential? For example, is there some local pseudopotential (within the class defined in this paper) that would allow one to choose the equilibrium density and chemical potential independently? Our conclusion is that this is not possible. The volume average of the pseudopotential over the cell is the only adjustable parameter of the pseudopotential that enters in our calculations, and once the desired density n_0 is chosen, the value of this average is fixed by the equilibrium condition Eq. (11).

In Sec. III B we obtained simple analytic formulas for the bulk modulus, energy versus density, and the equation of state. We regard these results as useful improvements over uncorrected jellium; for example, the pressure does go to zero at the equilibrium density. However, because these results are valid only to *first order* in pseudopotential perturbation theory, they cannot be expected to provide realistic estimates of these quantities, except possibly for the alkali metals.

In summary, we have shown that pseudojellium provides a framework for deriving the ideal metal and stabilized jellium on the same footing. We have learned why the two models are so similar and why they provide exactly the same answer to physical questions in two cases: for inhomogeneous metals and for uniform bulk metals calculated to first order in the underlying pseudopotential. We have found interesting first-order formulas for the energy, the chemical potential, the bulk modulus, and the equation of state of the homogeneous bulk metal that are independent of the details of the underlying pseudopotentials.

ACKNOWLEDGMENTS

Ames Laboratory is operated by the U.S. DOE by Iowa State University under Contract No. W-7405-ENG-82. This work was supported, in part, by the Director, Office of Basic Energy Sciences.

---

*Electronic address: hshore@quantum.sdsu.edu
†Electronic address: jhrose@iastate.edu

[1] C. A. Utreras-Díaz and H. B. Shore, Phys. Rev. Lett. **53**, 2335 (1984).

[2] J. P. Perdew, H. Q. Tran, and E. D. Smith, Phys. Rev. B **42**, 11 627 (1990).

[3] H. B. Shore and J. H. Rose, Phys. Rev. Lett. **66**, 2519 (1991).

[4] J. H. Rose and H. B. Shore, Phys. Rev. B **43**, 11 605 (1991).

[5] H. B. Shore and J. H. Rose, Phys. Rev. Lett. **67**, 3045 (1991).

[6] V. Heine and C. H. Hodges, J. Phys. C **5**, 225 (1972).

[7] C. H. Hodges, J. Phys. F **4**, 1961 (1974).

[8] M. Weinert and R. E. Watson, Phys. Rev. B **29**, 3001 (1984).

[9] N. W. Ashcroft, Phys. Lett. **23**, 48 (1966).

[10] T. L. Ainsworth and E. Krotscheck, Phys. Rev. B **45**, 8779 (1992).

[11] C. Fiolhais and J. P. Perdew, Phys. Rev. B **45**, 6207 (1992).

[12] A. Kiejna, Phys. Rev. B **47**, 7361 (1993).

[13] A. Solomatin and V. Sahni, Phys. Rev. B **56**, 3655 (1997).

[14] A. Kiejna and P. Ziesche, Phys. Rev. B **56**, 1095 (1997).

[15] A. Liebsch, Phys. Rev. B **55**, 13 263 (1997).

[16] P. García-González, J. E. Alvarellos, and E. Chacón, Phys. Rev. B **57**, 4857 (1998).

[17] A. Kiejna, J. Phys.: Condens. Matter **10**, 6621 (1998).

[18] H. Ishida and A. Liebsch, Phys. Rev. B **54**, 14 127 (1996).

[19] E. Hult, Y. Andersson, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. Lett. **77**, 2029 (1996).

[20] C. Yannouleas and U. Landman, Chem. Phys. Lett. **217**, 175 (1994).

[21] C. A. Utreras-Díaz and H. B. Shore, Phys. Rev. B **40**, 10 345 (1989).

[22] M. Brajczewska, C. Fiolhais, and J. P. Perdew, Int. J. Quantum Chem., Symp. **27**, 249 (1993).

[23] A. Vieira, C. Fiolhais, M. Brajczewska, and J. P. Perdew, Int. J. Quantum Chem., Symp. **30**, 1537 (1996).

[24] B. Montag, P. G. Reinhard, and J. Meyer, Z. Phys. D **32**, 125 (1994).

[25] H. Koizumi and Y. Fukumoto, Int. J. Quantum Chem., Symp. **30**, 1701 (1996).

[26] H. Koizumi and S. Sugano, Phys. Rev. A **51**, R886 (1995).

[27] M. Seidl, J. P. Perdew, M. Brajczewska, and C. Fiolhais, J. Chem. Phys. **108**, 8182 (1998).

[28] J. P. Perdew, P. Ziesche, and C. Fiolhais, Phys. Rev. B **47**, 16 460 (1993).

[29] P. Ziesche, J. P. Perdew, and C. Fiolhais, Phys. Rev. B **49**, 7916 (1994).

[30] J. H. Rose and H. B. Shore, Phys. Rev. B **48**, 18 254 (1993).

[31] J. H. Rose and H. B. Shore, Phys. Rev. B **49**, 11 588 (1994).

[32] K. F. Wojciechowski, Phys. Rev. B **53**, 961 (1996).

[33] K. F. Wojciechowski, Physica B **229**, 55 (1996).

[34] K. Fuchs, Proc. R. Soc. London, Ser. A **151**, 585 (1935).

[35] C. A. Sholl, Proc. Phys. Soc. London **92**, 434 (1967).

[36] J. Ihm and M. L. Cohen, Phys. Rev. B **21**, 3754 (1980).

[37] L. Kleinman, Phys. Rev. B **24**, 7412 (1981).

[38] G. L. Hall, Phys. Rev. B **24**, 7415 (1981).

[39] J. Callaway and M. L. Glasser, Phys. Rev. **112**, 73 (1958).

[40] J. Callaway, *Energy Band Theory* (Academic, New York, 1964), p. 65.

[41] G. L. Hall, Phys. Rev. B **19**, 3921 (1979).