

Electric polarizability of small metal particles

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A semiclassical theory of collective excitations based on the Vlasov equation is applied to the study of surface oscillations in small alkali-metal spheres. It is found that, when due allowance is made for the electron "spill-out" and for the exchange-correlation part of the electron-electron interaction, the polarizabilities given by the semiclassical Vlasov theory are similar to those yielded by quantum self-consistent calculations. In particular, the enhancement of the static polarizability and the red shift of the surface-plasmon resonance with respect to the classical values can be reproduced within the present semiclassical approach. Dynamic polarizabilities are evaluated for particles containing from 20 to 2000 sodium atoms.

I. INTRODUCTION

Small particles of alkali metals are being studied both experimentally and theoretically (see Ref. 1 for a recent review of work in this field). Many experimental results can be explained within the jellium model. This model is essentially a mean-field approximation in which the conduction electrons are assumed to move in a potential well of extension comparable to that of the particle.

By using the jellium model both static²⁻⁶ and dynamic⁴⁻⁶ properties of small alkali-metal spheres have been evaluated in a self-consistent approach.

An important result of the self-consistent ground-state calculations is that, if the positive background occupies a sphere of radius R , the conduction electrons extend up to a radius $R + \delta$ (the electron density does not drop abruptly on the surface, however the parameter δ gives a rough measure of the "electron spill-out").

As far as dynamic properties are concerned, calculations have concentrated mostly on the electric dipole polarizability, which is dominated by the surface-plasmon peak. Classically the surface plasmon of a metal sphere is expected to be at the Mie frequency (in Ry)

$$\hbar\omega_M = \frac{2}{(r_s/a_0)^{3/2}}. \quad (1.1)$$

Here r_s is the Wigner-Seitz parameter of the bulk material and a_0 is the Bohr radius. For alkali metals, r_s is related to the radius R by

$$R = r_s N^{1/3}$$

with N the number of atoms in the cluster.

The self-consistent calculations of the dynamic polarizability in Refs. 4-6 give a red shift of the surface plasmon with respect to the value (1.1). This is consistent with the "spill-out" of conduction electrons found in the static calculations since, if the electrons occupy a sphere of radius $R + \delta$, clearly their average density will be smaller than in the bulk material and they will be more

adequately described by a modified Wigner-Seitz parameter r'_s , with

$$R + \delta = r'_s N^{1/3}.$$

Consequently the frequency of the surface plasmon ω'_M for a small sphere is expected to be shifted with respect to the value (1.1):

$$\frac{\omega'_M}{\omega_M} \approx \left[\frac{R}{R + \delta} \right]^{3/2}. \quad (1.2)$$

For sodium clusters, both self-consistent calculations²⁻⁶ and experimental results^{1,7} suggest that the parameter δ should be of the order of 1 or 2 a.u. However, a more detailed comparison between experimental data and the results of self-consistent calculations shows that there are still problems with the exact location of the surface-plasmon peak and with its width.

The approach of Refs. 4-6 requires large-scale numerical calculations, therefore it is not easy to gain from it an intuitive understanding of the most important physical effects which determine the final result. For this reason it is interesting, as pointed out in Ref. 8, to explore the possibility that simpler approaches might reproduce the main physical results of the self-consistent theory. The possibility of using more flexible but sufficiently realistic models might be useful for dealing with some of the problems which are still open in this field.¹

In this paper we employ a simplified approach to study the linear response of small metal particles. This approach is based on the kinetic equation with a self-consistent field, or Vlasov equation. Bertsch has pointed out⁹ that the Pauli principle can be easily incorporated into the classical Vlasov theory, which then becomes semiclassical and can be viewed as intermediate between the quantum theory of Refs. 4-6, and the completely classical hydrodynamic theory. Thus, from this point of view, we can hope to gain an intuitive understanding of the results of more complex quantum calculations and to establish a link between the quantum theory of Refs. 4-6

and more classical approaches, like that of Ref. 10.

The semiclassical theory we want to apply here to (not too small) metal spheres has been developed recently for the study of collective excitations in heavy nuclei.¹¹ This theory gives results very similar to those of quantum random-phase approximation (RPA) calculations, even in nuclei as light as ⁴⁰Ca.¹² In fact, it can be shown that if the quantum numbers involved are large enough, the response function based on the Vlasov equation tends to coincide with the quantum response function.¹³ The same theory has also been applied to the study of photo-absorption in atoms.¹⁴

The explicit evaluation of the response function involves some numerical calculations even within the semiclassical Vlasov theory, however the numerical effort required is much less than in the full quantum theory. For this reason the present theory can be used also for relatively large clusters ($N \gtrsim 500$) for which the numerical burden of the quantum self-consistent approach tends to become unmanageable. Indeed the semiclassical theory is expected to become more and more reliable as N increases.

Here we do not attempt a fully self-consistent calculation based on the Vlasov equation. Rather we assume that the electrons in a small metal particle behave like an interacting Fermi gas confined to a sphere of radius $R + \delta$. Through the parameter δ we account empirically for the electron spill-out found in the self-consistent calculations. Also, we use the quantum results obtained by Ekardt⁴ for sodium spheres containing up to 198 atoms as a reference, which enables us to fix the value of parameters involved. Then we use the model for larger clusters containing up to 2000 atoms.

II. FORMALISM

Following Ref. 11, in order to determine the linear response of a finite many-body system within the Vlasov theory, we need to solve the integral equation

$$D(\mathbf{r}, \mathbf{r}', \omega) = D^0(\mathbf{r}, \mathbf{r}', \omega) + \int d\mathbf{x} \int d\mathbf{y} D^0(\mathbf{r}, \mathbf{x}, \omega) u(\mathbf{x}, \mathbf{y}) D(\mathbf{y}, \mathbf{r}', \omega). \quad (2.1)$$

This equation is the classical equivalent of the integral equation satisfied by the particle-hole Green's function in the RPA (see, e.g., Ref. 15, p. 558). The function $D(\mathbf{r}, \mathbf{r}', \omega)$ is the semiclassical analogue of the susceptibility $\chi(\mathbf{r}, \mathbf{r}', \omega)$ of Ref. 4. Similarly $D^0(\mathbf{r}, \mathbf{r}', \omega)$ corresponds to the single-particle susceptibility $\chi^0(\mathbf{r}, \mathbf{r}', \omega)$.

In the local-density approximation of Ref. 4 the interaction two electrons is assumed to be the sum of a

$$D_L^0(q, q', \omega) = \frac{16}{\hbar^3} \sum_{n=-\infty}^{+\infty} \sum_{N=-L}^L \left[\frac{4\pi}{2L+1} |Y_{LN}(\pi/2, \pi/2)|^2 \int_0^{\bar{\lambda}} d\lambda \lambda [n\pi + N \arccos(\lambda/\bar{\lambda})] \frac{Q_{nN}^{(L)}(\lambda, q) Q_{nN}^{(L)}(\lambda, q')}{\omega - \omega_{nN}(\lambda) + i\eta} \right]. \quad (2.8)$$

In this equation λ is the angular momentum of electrons which are moving with the Fermi velocity v_F (in the Vlasov theory only electrons on the Fermi surface can contribute to the excitation process¹¹); the quantity $\bar{\lambda}$ is

direct part plus a zero-range exchange-correlation part

$$u(\mathbf{x}, \mathbf{y}) = \frac{e^2}{|\mathbf{x} - \mathbf{y}|} - 4\pi e^2 r_{xc}^2 \delta(\mathbf{x} - \mathbf{y}). \quad (2.2)$$

In agreement with Ref. 4, we take¹⁶

$$r_{xc}^2 = \frac{1}{18} \left[1.222 + 0.759 \frac{r_s}{r_s + 11.4a_0} \right] r_s^2. \quad (2.3)$$

Within our approximation of a uniform equilibrium electron density, the interaction (2.2) is a function of the coordinate difference $(\mathbf{x} - \mathbf{y})$. In this case Eq. (2.1), for the dynamic polarizability, is most conveniently solved in momentum space. By taking the Fourier transform of (2.1) and expanding in partial waves, we have

$$D_L(q, q', \omega) = D_L^0(q, q', \omega) + \frac{1}{(2\pi)^3} \int_0^\infty dk k^2 D_L^0(q, k, \omega) \bar{u}(k) \times D_L(k, q', \omega), \quad (2.4)$$

where L gives the multiplicity of the external field.

The interaction in momentum space

$$\bar{u}(k) = 4\pi \frac{e^2}{k^2} [1 - G(k)] \quad (2.5)$$

contains a local-field correction $G(k)$, which, in our case, is given by

$$G(k) = r_{xc}^2 k^2. \quad (2.6)$$

This form of the local-field correction, which is associated with a zero-range exchange-correlation potential in coordinate space, is not realistic for large k (see, e.g., Refs. 17 and 18). Also, when combined with the semiclassical approximation, expression (2.6) gives rise to a diverging integral in the perturbative expansion of (2.4). For this reason we shall assume the following more reasonable behavior for $G(k)$:

$$G(k) = \frac{k^2}{k^2 + 1/r_{xc}^2}. \quad (2.7)$$

Clearly, for $k \ll 1/r_{xc}$, Eq. (2.7) reproduces the value of (2.6).

Although in the Vlasov theory the basic integral equation to be solved is essentially the same as in the quantum case; the advantage of using this semiclassical theory lies in the fact that the function D^0 is simpler to evaluate than its quantum counterpart χ^0 . For a gas of zero-temperature electrons confined within a square-well potential of radius $R' = R + \delta$ we have, by taking the Fourier transform of the quantity in Eq. (5.22) of Ref. 11,

the maximum possible angular momentum, which in our case is clearly given by

$$\bar{\lambda} = m v_F R',$$

with m the electron mass.

The frequencies of normal modes, which appear in the denominator of (2.8), can be easily evaluated for a square well

$$\omega_{nN}(\lambda) = \frac{n\pi + N\alpha}{\sin\alpha} \frac{v_F}{R'} \quad (2.9)$$

where we have defined

$$Q_{nN}^{(L)}(\lambda, q) = \int_0^1 dx j_L(qR'(\cos^2\alpha + x^2\sin^2\alpha)^{1/2}) \cos[(n\pi + N\alpha)x - N \arctan(x \tan\alpha)] \quad (2.10)$$

The quantity in Eq. (2.8) is already semiclassical since it has been derived in the hypothesis that the equilibrium distribution in phase space is of the (zero-temperature) Thomas-Fermi type.¹¹ However, as discussed in Ref. 11, we can easily make a further step towards quantum mechanics by replacing the integration over angular momentum in Eq. (2.8) with a sum over discrete values: $\lambda \rightarrow (l + \frac{1}{2})\hbar$ and

$$\int_0^{\bar{\lambda}} d\lambda \lambda \rightarrow \hbar^2 \sum_{l=0}^{\bar{l}} (l + \frac{1}{2}) \quad (2.11)$$

Here \bar{l} is the maximum integer such that $\bar{l} + \frac{1}{2} < \bar{\lambda}/\hbar$.

The imaginary factor $i\eta$ in the denominator of (2.8) is, in principle, infinitesimal; however, since we want to compare our results with those of Ekardt, who gave a finite value to the analogous factor in χ^0 , we will take η small but finite. Actually we expect to need a slightly

$$\cos\alpha \equiv \lambda/\bar{\lambda} \quad .$$

The Fourier coefficients $Q_{nN}^{(L)}(\lambda, q)$ which appear in Eq. (2.8) are the classical limit of the quantum radial matrix elements for the transition operator¹³. They are obtained from Eq. (5.27) of Ref. 11 by taking the spherical Bessel functions $j_L(qr)$ for the external field $Q_L(r)$. For our square-well potential these coefficients can be expressed as

larger value of η than that assumed by Ekardt in order to reproduce his results. This is because, as discussed in Ref. 11, the Vlasov theory does not treat the continuum correctly. A somewhat larger value of η is a way of mimicking the escape width, which is automatically included in the quantum Green's function of Ref. 4, but not in the semiclassical expression (2.8).

Once the noninteracting propagator D^0 has been determined, we are still left with the problem of solving the integral equation (2.1) or (2.4). In general, this must be done numerically. For this purpose we use the Lanczos method, which has proved to be very useful for solving the RPA integral equation (2.1) both in its quantum¹⁹ and its semiclassical¹⁴ version.

The Lanczos method gives a continued-fraction expansion for propagator (2.4). The first few terms of this continued fraction are

$$D = \frac{D^0}{1 - \frac{D^1}{D^0} - \frac{\frac{D^2/D^0 - (D^1/D^0)^2}{(D^3/D^0) - 2(D^2/D^0)(D^1/D^0) + (D^1/D^0)^3}}{\frac{D^2/D^0 - (D^1/D^0)^2}{(D^2/D^0) - (D^1/D^0)^2}} \dots \quad (2.12)$$

where the quantities D^j are the terms of order j in the perturbative expansion of Eq. (2.4):

$$D_L^j(q, q', \omega) = \frac{1}{(2\pi)^3} \int_0^\infty dk k^2 D_L^0(q, k, \omega) \bar{u}(k) \times D_L^{j-1}(k, q', \omega) \quad (2.13)$$

Once the solution of the integral equation (2.4) has been determined, we can obtain the response function corresponding to the multipolarity L of the external field by taking the imaginary part of D_L :

$$S_L(q, \omega) = -\frac{1}{\pi} \frac{2L+1}{4\pi} \text{Im} D_L(q, q, \omega) \quad (2.14)$$

Here we limit our calculations to the dipole response ($L=1$). The electric polarizability $\alpha(\omega)$ is given by

$$\alpha(\omega) = -\lim_{q \rightarrow 0} \frac{3}{4\pi} \frac{e^2}{q^2} D_{L=1}(q, q, \omega) \quad (2.15)$$

III. RESULTS

First we briefly discuss the static polarizability. For $\omega=0$ it can be shown¹⁴ that the semiclassical single-

particle susceptibility $D^0(\mathbf{r}, \mathbf{r}', 0)$ given by the Vlasov theory reduces to a δ function inside the sphere of radius $R' = R + \delta$:

$$D^0(\mathbf{r}, \mathbf{r}', 0) = -\frac{1}{4\pi e^2} \frac{1}{r_{TF}^2} \delta(\mathbf{r} - \mathbf{r}') \Theta(R' - r) \quad (3.1)$$

TABLE I. Static polarizability for spheres of N alkali-metal atoms, in units of R^3 . Column 2, without electron "spill-out" ($\delta=0$); column 3, $\delta=2a_0$; column 4, including exchange-correlation effects. For each N the first row gives the analytical result (3.3), while the second row is obtained from the numerical solution of the integral equation (2.4).

N	α/R^3	α'/R^3	α_{xc}/R^3
20	0.69	1.18	1.52
	0.70	1.18	1.27
92	0.80	1.11	1.27
	0.78	1.08	1.13
198	0.84	0.96	1.03
	0.85	1.09	1.13

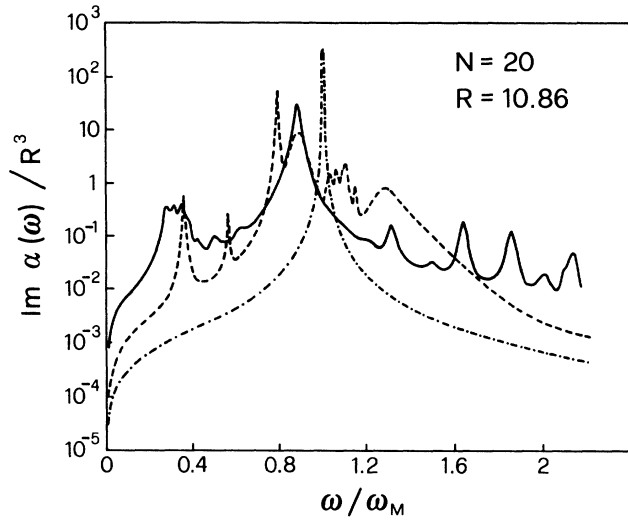


FIG. 1. Imaginary part of the dynamic polarizability, in units of R^3 , for $N=20$. The frequency ω is expressed in units of the Mie frequency (1.1), evaluated for $r_s=4$. The solid line shows the result of the present semiclassical calculation, while the dashed line shows the quantum result of Ref. 4. The classical Drude result of Ref. 4 is also shown for comparison (dot-dashed line).

Here r_{TF} is the Thomas-Fermi radius

$$r_{TF} = \left[\frac{\pi \hbar^3}{4e^2 m^2 v_F} \right]^{1/2} \quad (3.2)$$

and $\Theta(x)$ is the usual step function.

Equation (3.1) coincides with the approximation used by Lushnikov and Simonov for the polarization propagator.²⁰ These authors have shown that, if the interaction $u(\mathbf{x}, \mathbf{y})$ in Eq. (2.1) is assumed to contain only the

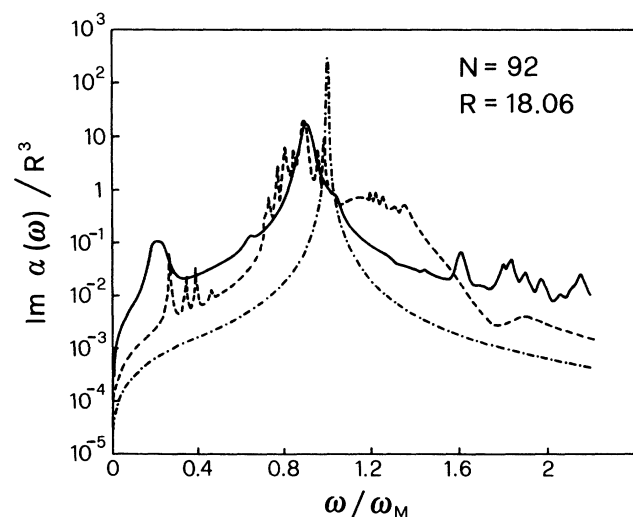


FIG. 2. Same as Fig. 1, for $N=92$.

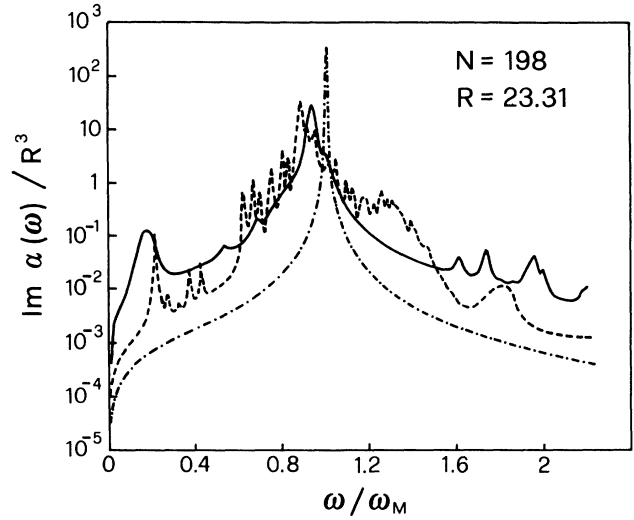


FIG. 3. Same as Fig. 1, for $N=198$.

Coulomb part, then, thanks to the simple form (3.1) of D^0 , the integral equation can be solved analytically for $\omega=0$. The resulting static dipole polarizability, in units of R^3 , is given by

$$\frac{\alpha}{R^3} = \left[1 + 3 \left(\frac{r_{TF}}{R + \delta} \right)^2 - 3 \left(\frac{r_{TF}}{R + \delta} \right) \coth \left(\frac{R + \delta}{r_{TF}} \right) \right] \left(\frac{R + \delta}{R} \right)^3. \quad (3.3)$$

In Table I we show the polarizability calculated according to this formula both for $\delta=0$ (α) and for $\delta=2a_0$ (α'). Clearly, the polarizability is increased, mainly because of the factor $(1+\delta/R)^3$. However, we want to

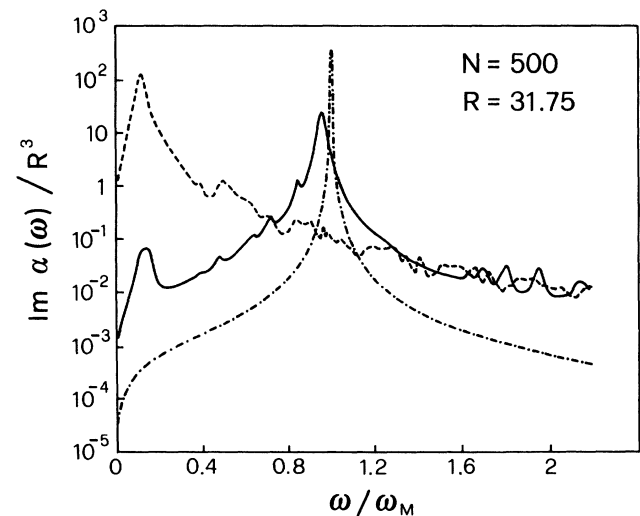
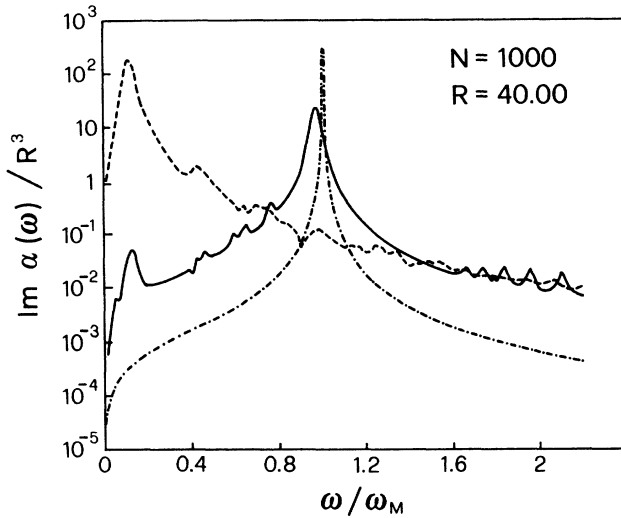


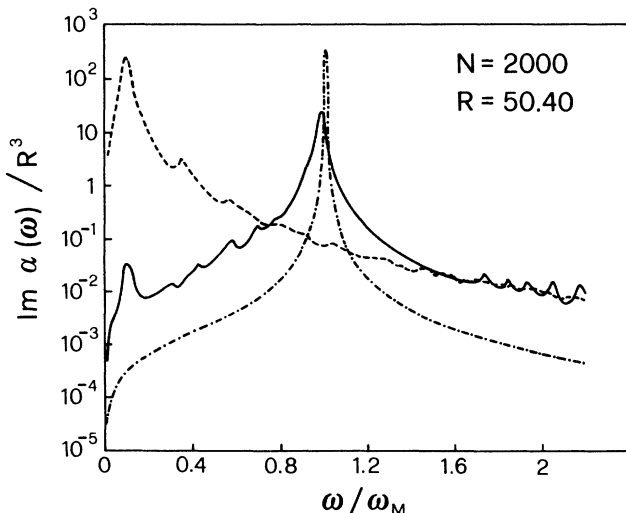
FIG. 4. Same as Fig. 1 for $N=500$, except for the dashed line, which now shows the single-particle polarizability.

FIG. 5. Same as Fig. 4, for $N=1000$.

stress here that a similar increase of the static polarizability is also caused by the exchange-correlation part of the interaction. The method of Lushnikov and Simonov can be immediately generalized to the case in which the interaction contains also an exchange-correlation term of the kind given by Eq. (2.2). In fact it can be easily shown that the polarizability is still given by Eq. (3.3), but with a modified Thomas-Fermi parameter

$$\tilde{r}_{\text{TF}} = (r_{\text{TF}}^2 - r_{\text{xc}}^2)^{1/2}. \quad (3.4)$$

The result of including the exchange-correlation term in the calculation of the static polarizability is shown in the last column of Table I. Also shown in Table I are the static polarizabilities obtained from the numerical solution of the integral equation (2.4). In the absence of the

FIG. 6. Same as Fig. 4, for $N=2000$.

exchange-correlation terms the polarizabilities agree within 1% or 2%, even if in the numerical calculation the angular momentum has been discretized according to (2.11). When the exchange-correlation interaction is taken into account, our numerical polarizabilities are considerably smaller than those given by Eqs. (3.3) and (3.4). This is because in the numerical calculations we are using the "softer" local-field correction (2.7) instead of (2.6).

Now we turn to the dynamic polarizability $\alpha(\omega)$. In Figs. 1–3 we compare the result of our semiclassical calculations (solid line) with the quantum calculations of Ekardt⁴ (dashed line). Our results have been obtained by taking a slightly modified version of Eq. (2.8) for D^0 [the sum over n has been truncated at $n_{\text{max}} = 10$ and the integration over λ has been discretized according to (2.11)]. The parameter η in the denominator of (2.8) has been given the value $\eta = 0.05$ eV, while Ekardt has used $\eta = 0.01$ eV. The interaction in momentum space has been taken of the form (2.5) with the local-field correction (2.7). The integral equation (2.4) has been solved numerically by using the Lanczos method.

It can be seen from Figs. 1–3 that our semiclassical calculations give a red shift of the surface plasmon which is similar to the shift obtained by Ekardt. The red shift is due to both the electron spill-out and the exchange-correlation interaction.

At large ω our semiclassical polarizabilities display secondary peaks in analogy with the results obtained by Ruppin in a classical approach.¹⁰ The similarity between the present semiclassical polarizabilities and those of Ref. 10 becomes more evident with increasing particle size, as can be seen from Figs. 4–6, where our results for spheres of $N=500$, 1000, and 2000 sodium atoms are shown. However, contrary to the results of Ref. 10, in which a blue shift of the surface plasmon is found, in our calculations the surface plasmon remains slightly red-shifted for large N also. The maximum of the calculated polarizability moves gradually from $\omega \approx 0.88\omega_M$ to $\omega \approx 0.98\omega_M$ when N changes from 20 to 2000.

IV. CONCLUSIONS

We have shown that a semiclassical theory based on the Vlasov equation can give electric polarizabilities of small sodium clusters in fair agreement with those obtained from quantum calculations. In particular, the enhancement of the static polarizability can be reproduced if the electron spill-out and the exchange-correlation potential are taken into account. Within the present semiclassical theory the static polarizability can be evaluated analytically (if the angular momentum is treated as a continuous variable) and the numerical effort required by the calculation of the dynamic polarizability is greatly reduced. As a consequence, calculations can be extended to heavier particles and the cluster behavior can be studied over a wide range of constituent atom number.

While the semiclassical point of view adopted here does not solve any of the problems concerning the position and width of the collective surface excitation, which

have been left open by the quantum-mechanical self-consistent calculations, nonetheless it can be useful in further work on the subject since it offers a more agile but sufficiently realistic approach to study the response of metallic particles.

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