Size oscillations in the shape and Fermi energy of nearly spherical metal particles

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Liquid metal particles have an ellipsoidal shape with an eccentricity which oscillates with increasing size of the particles. The Fermi energy of the particles exhibits giant quasistochastic size oscillations.

In this letter we show that in addition to the well-known size oscillations in thermodynamic quantities, there can be size oscillations of a completely different type: in the shape of particles. At first glance, it would seem that the equilibrium shape of liquid particles in the absence of force fields would be spherical. However, a spherical shape is actually unstable for metal particles, since their surface energy in the case of spherical shape would have a singularity because of the high degree of degeneracy of the electronic levels. For liquid metals, the approximation of nearly free electrons usually holds well. Accordingly, each electronic level is $2l(l+1)$-fold degenerate in the angular-momentum projection m. Since the radius of the particles, R, is large in

comparison with electron wavelength k^{-1}, the typical orbital quantum number l is on the order of kR. There is accordingly the possibility of reducing the electron energy of a particle with a partially filled upper level by lowering its symmetry.

With increasing number (N) of electrons in the particle, and as the state with the given l becomes completely filled, spherical symmetry should be restored. When a partially filled level appears again, the symmetry will be lowered again; i.e., the deformation will be an oscillating function of N. In reality, the growth of N occurs during a growth of R. However, the electronic levels $E_{nl}(R)$ shift in the process, but in the zeroth approximation in the deformation there is no change in the level systematics. Accordingly, states with various (n,l,m) are filled in the same order as at a constant R. Instead of oscillations in the shape as a function of N, however, we should speak in terms of oscillations in the shape as a function of R here.

The possibility of observing this uniquely quantum effect at temperatures at which a metal is in a liquid state rests primarily on a large separation between degenerate levels in spherical particles, which reaches $\mu/k_F R$, where μ and k_F are the energy and Fermi momentum. At $\mu \sim 10$ eV and $k_F R \sim 10$, this separation os 10^3–10^4 K. The situation looks even more favorable when we note that small metal particles can be supercooled by an amount equal to 30–50% of the crystallization temperature.[1]

The fact that the surface energy of a spherical particle cannot be assumed to be proportional to the surface area is reflected in the size oscillations of the Fermi energy. A study of these oscillations is also of independent interest, since they are quite different from the size oscillations in μ in films (described in Ref. 2), because they are of a quasistochastic nature. The reason for this nature is that the electron energy depends on not one quantum number but on the pair of quantum numbers n, l. An analysis of the order of the quantum levels in a spherical well shows that there is no obvious regularity in the changes in n and l with increasing energy E_{nl} at small values of this energy.[3] The same comment applies at large values of this energy. The role played by two independent parameters in the onset of a quasichaotic behavior is also supported by the established fact that this behavior is exhibited by the sum of two periodic functions with incommensurate periods.

Calculations have been carried out for free electrons in an infinitely deep potential well, with $k = \rho_{ln}/R$, where ρ_{ln} is the n-th root of the Bessel function $J_{l+1/2}(x)$. Using the general expression for ρ_{ln}, we find, at $l \gg 1$,

$$\rho_{ln} \approx \pi n + \pi l/2, \qquad (n \gg l), \tag{1}$$

$$\rho_{ln} \approx l\{1 + 2^{-1/3}(3\pi n/2l)^{2/3}\}, \qquad (n \ll l). \tag{2}$$

The oscillations in μ follow from the independence of ρ_{ln} from R. Specifically, as R is increased, the value of $\rho_{l_F n_F}$ corresponding to μ remains constant at $T = 0$ as the radius changes by $\delta R = l_F(l_F + 1)/2\pi\nu R^2$, where ν is the electron density. The quantity $\mu = \rho^2_{l_F n_F}/2m^* R^2$ thus decreases by an amount $\delta\mu \sim \mu\delta R/R \sim \mu(k_F R)^{-3}$ (m^* is the effective mass of an electron) in this interval of R values.

With a further increase in R, the Fermi level increases abruptly, since a higher-lying energy level begins to be filled. According to (1) and (2), states with $n < l$ are

filled preferentially, so the value of l_F corresponding to μ is $k_F R$ in order of magnitude. The largest jump in μ is reached when the $(l_F + 1,1)$ level is filled after the $(l_F,1)$ level. This jump which is on the order of $\mu/k_F R$ than the jump in μ in a film. At nonzero but quite low temperatures, the oscillations in μ persist.

The Jahn-Teller deformation of the sphere, ϵ, is found by minimizing the sum of the energy of the highest electronic level containing electrons and of the surface energy, αS, where S is the surface area, and α is the surface tension, which is determined by the ions and the electrons of the completely filled inner shells. It is natural to assume that the deformation is uniaxial and that it occurs without a change in the volume of the particle. The principal axes of the ellipsoid are then $c = R(1 + 2\epsilon)$ and $a = b = R(1 - \epsilon)$, and the increase in the surface area due to the deformation is

$$\delta S = \frac{14}{5} \epsilon^2 S_0, \qquad S_0 = 4\pi R^2. \tag{3}$$

The change in the kinetic energy of electrons upon a deformation of this sort is given in Ref. 3:

$$\delta E_{nlm} = \frac{\epsilon l(l+1)}{(2l-1)(2l+3)} \left[\frac{3m^2}{l(l+1)} - 1 \right] E_{nl}. \tag{4}$$

If there are $2(2m_0 + 1)$ electrons in the upper shell, we find the following result from (3) and (4):

$$\epsilon = \frac{5l(l+1)(2m_0 + 1)\mu}{14\alpha S_0 (2l_F - 1)(2l_F + 3)} \left[1 - \frac{m_0(m_0 + 1)}{l_F(l_F + 1)} \right]. \tag{5}$$

It can be seen from (5) that the deformation corresponds to a prolate ellipsoid of revolution ($\epsilon > 0$). With increasing radius, ϵ decreases as $m_0/S_0 \sim 1/R$ according to (5). With $\alpha = 60$ erg/cm^2 (as for liquid cesium), $R = 50$ Å, $\mu \approx 5$ eV, and $\nu = 10^{22}$ cm^{-3}, and if we have $m_0 \approx l_F/\sqrt{3}$, we find that ϵ reaches 10%.

Apparently the simplest way to observe a size-dependent deformation of small particles would be by direct electron-microscopy method, whose accuracy would be completely sufficient for this purpose according to our estimate of ϵ. Experimentally, it would be convenient to place a large number of small particles on a substrate which they do not wet and which causes essentially no change in their shape.

A deformation of particles can also be observed by optical methods, e.g., by measuring the anisotropy in the scattering of light by particles in a plasma or a liquid in an external field F. If the field is parallel to the i axis, the dipole moment which it induces, P_i, is inversely proportional to the depolarization coefficient along this axis, $n^{(i)}$ (Ref. 4). Along the long axis, $n^{(i)}$ is at a minimum:

$$n^{(x)} = n^{(y)} = \frac{1}{3}\left(1 + \frac{6}{5}\epsilon\right), \qquad n^{(z)} = \frac{1}{3}\left(1 - \frac{12}{5}\epsilon\right). \tag{6}$$

Accordingly, the particles in the field tend to become oriented with their long axes along the field. Since the difference between the energies of the configurations $\mathbf{F} \| \mathbf{c}$ and $\mathbf{F} \perp \mathbf{c}$ is on the order of $\epsilon F^2 R^3$, at $T \sim 300$ K and $R \sim 100$ Å a field $\sim 10^5$ V/cm would be

required for an approximately complete orientation.

Since the cross section for the scattering of light is proportional to P^2, we conclude from (6) that the large number of oriented particles would scatter light which is propagating along their major axis more strongly than it would light propagating along their minor axis. The relative difference between the cross sections for scattering at right angles in these two cases is $3\epsilon/5$; i.e., the anisotropy in the scattering is nearly an order of magnitude greater than the anisotropy in the shape of the particles.

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