SMALL METAL PARTICLES AND THE IDEAL FERMI GAS

Mustansir Barma

Tata Institute of Fundamental Research
Homi Bhabha Road, Bombay 400 005, India

1. INTRODUCTION

In this paper, we are concerned with the electronic properties of small metal particles. By 'small' we mean a particle of a size intermediate between that of a few-atom cluster and the bulk solid – with a radius roughly in the range 5 to 50 Angstroms. More important than the actual numbers, perhaps, is the fact that the sizes of interest are much smaller than the typical mean free path of an electron in a bulk sample. This provides an a priori reason to expect size effects to show up strongly in electronic properties, and experiments show that they do.

The most important advance in this area in recent years has been an experimental one. It has become possible to use mass spectroscopy to separate small particles of an exactly determined mass without contamination by particles of close-by mass /1,2/. This has proved to be a very significant step because physical properties turn out to show oscillatory dependences on the size. In experiments on samples with a spread of sizes, oscillations are averaged out, and their effects suppressed.

A key experimental finding is the existence of shell effects – as typified by the occurrence of magic numbers /1-3/. These represent conglomerates of atoms which are especially stable. The stability is associated with the filling of electronic levels, rather than with structural stability coming from atomic close-packing. Magic numbers show up not only in relative abundances, but also in physical properties such as the ionisation potential, electrical polarisability and resonant optical response /1-4/. These experiments also provide indirect, but strong, evidence that clusters take on distorted, non-spherical shapes away from the magic cases. From the point of view of the present paper – which is primarily concerned with sorting out the size

dependences of various energy scales – magic numbers signify that there is a scale proportional to the inverse linear dimension of the particle. This is because magic numbers are relatively evenly spaced as a function of $N^{1/3}$ rather than N, the number of free electrons in the particle.

The simplest theoretical model of a small metal particle was first proposed by Kubo /5,6/. It consists of a number of noninteracting electrons (an ideal Fermi gas) confined to a finite volume. This model is simplified in several respects. It ignores band structure effects, electron-electron interactions and realistic surface potentials. But it does have the essential feature of the problem, namely the fact of finiteness, built into it. As such it is worth understanding in some detail. The advantage is that one can hope for an analytical understanding of overall trends in the size dependence, thus complementing numerical studies with more realistic starting points (e.g. self-consistent jellium calculations /7,8/ or cluster calculations /9,10/). We will explore some consequences of the noninteracting electron model in this paper.

2. GENERAL CONSIDERATIONS

Let us see what we can say about the Fermi gas model without any calculation at all. Since we are modelling systems in which the fermionic density does not vary too much as the size is changed (like nuclei, and unlike atoms) it makes sense, in the first approximation, to assign a size-independent value E_F to the Fermi energy. If L is a characteristic linear dimension and k_F the Fermi wave-vector, the number of one-electron states below E_F, which is an extensive quantity, is proportional to $(k_F L)^3$. The mean spacing between successive states is thus $\sim E_F/(k_F L)^3$. However, the mean spacing between successive energy levels (each of which may contain many states) may be quite different, as the degeneracy of a level near the Fermi energy may grow with the size.

The mean level spacing, which we denote $\delta_L(E)$, depends on the symmetries of the confining potential and also upon commensurability effects. If the confining region has an irregularly enough shaped surface, all degen-

eracies are lifted, and in that case $\delta_L(E)$ is given by $E_F/(k_FL)^3$ /6,11/. At the other extreme of regularity is an isotropic harmonic potential which is adjusted to keep the Fermi energy constant as the number of electrons is varied /12,13/. In this case, the degeneracy of a level near the Fermi energy is of order $(k_FL)^2$ while the spacing between levels is of order E_F/k_FL.

In between the irregular surface model which exhibits no degeneracies at all, and the harmonic model with its extremely large degeneracies, are confining potentials with intermediate symmetry. It is members of this class that are studied here. It turns out in such cases that there are two distinct size-dependent energy scales /14,15/. The inner scale is the mean level spacing $\delta_L(E)$, which was considered above. Besides, there is also an 'outer' energy scale Δ which describes an oscillatory structure in the density of states, on a scale which includes very many levels. Δ varies as E_F/k_FL, and is the energy scale which makes contact with the experimental observation of magic numbers and concommitant shell structure. An interesting consequence of having two distinct energy scales is that there are three regimes of temperature T. (i) If T is larger than Δ (but still much smaller than E_F), all oscillations are washed out, and normal metallic behaviour results. (ii) If T is of the order of or smaller than Δ, but larger than δ, the inner scale structure is averaged out, but not the outer scale oscillations. The system is metallic insofar as there are very many states within an energy T of the Fermi energy. However the shell-structure ripples in the density of states have observable effects. We refer to this region of temperature as the shell-metallic regime. (iii) Finally, if T is much smaller than δ, energy levels above E_F are populated with an exponentially small probability – giving rise to activated behaviour characteristic of a semiconductor.

3. THE MEAN LEVEL SPACING δ.

Consider an ideal Fermi gas confined in a finite region of volume V. We will study two shapes – spheres and cubes. The motivation for studying cubes is more theoretical than experimental, but as we shall see below both

geometries are regular enough to display broadly similar characteristics on both the inner (δ) and outer (Δ) scales of energy.

The edge length of the cube is taken to be $2\pi L$ while the radius of the sphere is $(6\pi^2)^{1/3}L$. With these definitions, a cube and a sphere with equal values of L have equal volumes. Single particle states have energies given by

Periodic Cube

$$\epsilon_{\vec{n}} = \frac{\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad n_{x,y \text{ or } z} = 0, \pm 1, \pm 2, \cdots \qquad (1a)$$

Hard-walled Cube

$$\epsilon_{\vec{n}} = \frac{\hbar^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad n_{x,y \text{ or } z} = 1, 2, 3, \cdots \qquad (1b)$$

Hard-walled Sphere

$$\epsilon_{n,\ell} = \frac{1}{(6\pi^2)^{2/3}} \frac{\hbar^2}{2mL^2} \alpha_{n\ell}^2 \qquad (1c)$$

where $\alpha_{n\ell}$ is the location of the n'th zero of the ℓ'th order spherical Bessel function.

For the sphere, each distinct pair of the radial and orbital quantum numbers (n, ℓ) identifies a level. Each level is $(2\ell + 1)$-fold degenerate, and moreover both quantum numbers n and ℓ depend linearly on $k_F L$ (as can be seen, for instance, by using the Debye approximation for spherical Bessel functions /12,16/). Since the number of states is proportional to $(k_F L)^3$ and there are $\sim k_F L$ states per level, the mean spacing between levels must be of the order of $1/(k_F L)^2$.

A similar conclusion holds for the cube, but the argument is different. From Eqs. 1a and 1b we see that except for a constant factor, ϵL^2 is given by the sum of three squared integers. Degeneracies arise because it is possible

for different sets (n_x, n_y, n_z) to result in the same value of ϵL^2. Now it is known /17/ that the fraction of integers which can be written in at least one way as the sum of three squares, approaches an asymptotic limit, 5/6. Since each such integer corresponds to a level, the mean spacing between levels is proportional to $1/L^2$. Moreover, the degeneracy of each level must be of order L in order to have an extensive total number of states.

How robust is the result $\delta_L \sim E_F/(k_F L)^2$, which we have seen holds both for the sphere and the cube? Consider a rectangular parallelopiped with sides $2\pi\alpha L$, $2\pi\beta L$ and $2\pi\gamma L$. If the ratios α/β, β/γ and γ/α are irrational, it is not possible for distinct sets (n_x, n_y, n_z) to be degenerate. (We are discounting the finite degeneracy coming from symmetry operations such as an interchange of n_x and n_y or a sign change.) Consequently, in contrast to the cube, no large degeneracies are possible, and the mean spacing varies as $1/(k_F L)^3$ in the incommensurate case.

What if α/β, β/γ and γ/α are rational but not unity? We have investigated this case numerically, and find that, as with the cube, the mean spacing varies as $1/(k_F L)^2$ for large enough values of $k_F L$. But for $k_F L$ lower than some characteristic crossover value, if the rational numbers in question are close to quadratic irrationals, the mean spacing appears to be $\sim 1/(k_F L)^3$. The crossover is being investigated at present.

One might wonder whether the rational case has any significance at all – after all, there are many more irrationals than rationals, and in that sense in the 'space of shapes' (even if restricted to cuboids), rationally related sides occur with zero probability. However, it may be argued that the shape should not be chosen at random from the set of all shapes, but rather in such a way as to minimize the energy. The most favourable shapes in this sense are quite likely to be determined by rational ratios – for instance, the relatively larger gap to the next excited level ($\sim 1/L^2$ in the commensurate case as opposed to $\sim 1/L^3$ in the incommensurate case) may indicate larger stability. In this general form, the argument should apply as much to ellipsoids (the presumed shapes of metal clusters) as to the rectangular

boxes under discussion in the previous paragraph, but this assertion is yet to be checked.

4. THE OUTER ENERGY SCALE Δ

Now let us turn to the outer scale fluctuations in the density of states. The energy scale which characterizes these fluctuations is $\Delta_L(E)$, which we will see below, varies as E_F/k_FL. These outer scale oscillations are the ones which relate to the shell effects and magic numbers seen in experiment.

A general theory for these oscillations in spectral properties was formulated by Balian and Bloch /18/ and by Berry and Tabor /19/. Their results can be generalized /14,15/ to study the finite temperature properties of the Fermi gas, as sketched below.

The density ρ of fermions at temperature T and chemical potential μ is

$$\rho(L,\mu,T) = \frac{1}{V}\sum_i \frac{1}{e^{(\epsilon_i-\mu)/T}+1} \tag{2}$$

where i labels the one-electron states. For the regular systems under consideration here, i is specified by a set of quantum numbers denoted by $\vec{m}$. (For the box, $\vec{m}$ consists of the triad n_x, n_y, n_z; for the sphere it consists of the radial, and orbital quantum numbers n and ℓ but there is an extra factor of $(2\ell+1)$ in Eq. 2 to account for orbital degeneracy.) Let us recall the Poisson sum formula of Fourier transform theory: if a function is evaluated at all integer points and then summed, the answer is the same if the operation is repeated on its Fourier transform. On applying this result to the sum over quantum numbers $\vec{m}$ we get

$$\rho(L,\mu,T) = \frac{1}{V}\sum_{\vec{\tau}} \int d\vec{m} \frac{exp(2\pi i \vec{\tau}\cdot\vec{m})}{exp[(\epsilon_{\vec{m}}-\mu)/T]+1} \tag{3}$$

where $\vec{\tau}$ is the integer triplet (τ_x, τ_y, τ_z). (If the quantum numbers are restricted to be positive, as for the hard-walled box and sphere, appropriate step functions must be inserted before taking the Fourier transform).

The principal advantage of Eq. 3 over Eq. 2 is that it provides a large size expansion. To see this, notice firstly that the term with $\vec{\tau} = 0$ gives the familiar answer for the bulk or infinite volume limit. The other terms contain $\vec{m}$ in the exponent, and since $|\vec{m}|$ is typically of order of the size L of the system, the exponent oscillates rapidly and contributes successively less for larger values of τ. Thus keeping just a few terms in the $\vec{\tau}$ sum gives an accurate answer for large sizes.

Any particular term on the right hand side of Eq. 3 gives an oscillatory contribution to the density, with a period proportioned to $E_f/k_F L|\vec{\tau}|$. The longest finite period comes from $|\vec{\tau}| = 1$, and corresponds to the energy scale Δ.

For the periodic box the result is particularly simple and appealing /14,15/. From Eq. 3 one finds that the right hand side just involves the correlation function $< a_0^\dagger a_r >$ for the Fermi gas in the bulk. Thus, Friedel oscillations in the bulk system get linked to oscillatory functions in the density as a function of size.

Although both the cube and the sphere exhibit oscillations on the outer scale Δ, the amplitude of oscillation depends on the shape. For $k_F L \gg E_F/T$, the amplitude of oscillation dies down exponentially in both cases. But for $1 \ll k_F L \ll E_F/T$, the amplitude falls off as $1/(k_F L)^2$ for the cube but only as $1/(k_F L)^{3/2}$ for the sphere.

Shell effects, namely oscillatory effects on the scale of Δ, remain appreciable so long as T does not exceed Δ. It is important to realize that there are two ways in which shell structure can be probed: (i) as oscillations in physical properties as a function of size (ii) as an oscillatory feature in the density of states, for a fixed size. The experiments discussed in the introduction provide striking evidence for type (i) oscillations. It would be interesting to have evidence of shell structure from experiments in the second category as well. A calculation shows that the imaginary part of the dielectric constant $\epsilon_2(\omega)$ shows pronounced oscillations as a function of frequency /20/. But there does not seem to be unequivocal experimental

evidence for such oscillations as yet.

However, the energy scale Δ does seem to show up in experiments on Mie scattering, though as a line width rather than as an oscillatory feature. Experiments show that the width Γ is inverse proportional to the radius /21,22/. The reason for this, it has been argued /22/, is that Γ is inversely proportional to the time τ a ballistic electron moving with the Fermi velocity v_F takes to hit the wall. Since, $\tau = A\times$ radius$/v_F$, where A is a constant, Γ should be proportional to (radius)$^{-1}$ /23/. Notice that the linewidth Γ determined thus is proportional to the outer scale of energy Δ.

5. CONCLUSIONS

For a Fermi gas confined in regularly shaped regions like a sphere or a cube, there are two size-dependent energy scales of importance.

The inner scale δ is the mean spacing between successive energy levels. It is given by $\delta \sim E_F/(k_F L)^2$ for both the sphere and the cube. For cuboids with irrationally related sides, $\delta \sim E_F/(k_F L)^3$. For cuboids with rationally related sides, $\delta \sim E_F/(k_F L)^2$ asymptotically, but there can be a crossover to irrational-type behaviour at smaller values of $k_F L$. The scale δ governs the very low temperature behaviour, which is semiconductor-like.

The outer scale Δ is associated with the shell structure that has been seen in experiment. When $\delta \ll T < \Delta$, thermodynamic properties show an oscillatory fluctuation around a smooth background as the size or energy is varied. The period of the fluctuations is set by Δ for both the sphere and the cube, but the amplitude is stronger for the sphere.

Existing experiments probe shell structure effects in physical observables as the size is varied. While the associated energy scale Δ also seems to show up as the linewidth of the Mie resonance, it would be interesting to have experimental confirmation of oscillatory effects on the Δ-scale in the energy spectrum of a system of a fixed size.

Acknowledgements:

I acknowledge the collaboration of V. Subrahmanyam on all aspects of the work reported here and thank him for comments on the manuscript.

REFERENCES

1. W.A. de Heer, W.D. Knight, M.Y. Chou and M.L. Cohen, Solid State Physics 40, 93 (1987)
2. T. Bergmann, H. Limberger and T.P. Martin, Phys. Rev. Lett. 60, 1767 (1988)
3. M.L. Cohen, M.Y. Chou, W.D. Knight and W.A. de Heer, J. Phys. Chem. 91, 3141 (1987)
4. K. Selby, M. Vollmer, J. Masui, V. Kresin, W.A. de Heer and W.D. Knight, Phys. Rev. B40, 5417 (1989)
5. R. Kubo, J. Phys. Soc. Japan 17, 975 (1962)
6. R. Kubo, A. Kawabata and S. Kobayashi, Annu. Rev. Mater. Sci. 14, 49 (1984)
7. J.L. Martins, R. Car and J. Buttet, Surf. Sci. 106, 265 (1981)
8. W. Ekardt, Phys. Rev. B29, 1558 (1984)
9. W. Andreoni in 'Elemental and molecular clusters' edited by G. Benedek, T.P. Martin and G. Pacchioni, Springer-Verlag, Berlin (1988)
10. P. Fantucci and J. Koutecky in 'Elemental and molecular clusters' edited by G. Benedek, T.P. Martin and G. Pacchioni, Springer-Verlag, Berlin (1988)
11. L.P. Gorkov and G.M. Eliashberg, Sov. Phys. JETP 21, 940 (1965)
12. A. Bohr and B.R. Mottelson, 'Nuclear Structure', Vol. 2, W.A. Benjamin, Reading (1975)
13. K. Clemenger, Phys. Rev. B32, 1359 (1985)

14. V. Subrahmanyam and M. Barma, J. Phys. A22, L489 (1989)

15. V. Subrahmanyam and M. Barma, Phase Transitions, to be published (1990)

16. M. Abramowitz and I.A. Stegun, Handbook of Mathematical Functions, Dover, New York (1965) p. 366

17. W. Sierpinski, 'Elementary theory of numbers', Mathematical Monograph of the Polish Academy, Warsaw, (1964)

18. R. Balian and C. Bloch, Ann. Phys. (N.Y.) 69, 76 (1972)

19. M.V. Berry and M. Tabor, J. Phys. A10, 371 (1977)

20. M. Barma and V. Subrahmanyam, J. Phys. Cond. Matt. 1, 7681 (1989)

21. U. Kreibig and L. Genzel, Surf. Sci. 156, 678 (1985)

22. U. Kreibig, J. Phys. F4, 999 (1974)

23. This prediction is confirmed by a quantum mechanical calculation of the optical response; see A. Kawabata and R. Kubo, J. Phys. Soc. Japan 21, 1765 (1966), and also Ref. 20.