Small metal particles

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This review article is devoted to results of theoretical and experimental investigations of properties of nanometer metal particles. First, the modern theory of equilibrium structures and shapes of small particles is presented. The next Section deals with the thermodynamics of small particles. It reflects the present state of the theory of surface forces for small particles, including crystalline ones. Validity conditions are pointed out for the standard approach, and an alternative approach is described which is adequate for particles surrounded by their saturated vapor. In it the Laplace pressure is not a real physical force, but a formal quantity that describes the size dependence of the chemical potential. Specific features are described of melting and interphase fluctuations in small particles. In describing the electron properties of the particles emphasis is laid on the smoothed level density and the size dependence of the Fermi energy. Some effects caused by this dependence are presented, in particular the mutual charging of particles and so on. Magnetic properties of small particles are also described including macroscopic quantum tunneling of magnetization.

INTRODUCTION

Solid or liquid samples of size in the range from several nm to several tens of nm are referred to as small particles. In them the number of surface atoms is not negligibly small compared with that of bulk atoms: these quantities differ only by an order magnitude or even less. Since the total number of atoms in such particles still amounts to 10^3-10^4 , they possess properties of crystals or liquids. But due to relatively large fraction of surface atoms these properties may differ essentially from those of bulk samples.

This difference was discovered long ago, and it is used for various technical applications. A few examples may illustrate how wide is the range of applications of small particles. Powders of small particles often act as catalysts much better than bulk samples of the same material. Composite materials including small metal particles exhibit unique mechanical properties especially valuable in aero- and space engineering. Magnetic small particles play a vitally important role in modern electronics and military technology. The US Stealth bomber, for instance, which is virtually invisible to radar when in flight, is covered by a special composite material. It includes small particles which can trap and virtually absorb radar beams.

Sometimes one deals with small particles despite one's desire. For example, inhabitants of large towns are compelled to inhale small particles of harmful industrial pollutants together with air. In such cases an opposite task arises: not to produce but to suppress small particles.

Diversity of practical applications suggests by itself that small particle physics will remain prominent for many years to come. It suffices to point out the books (Refs. 105, 126, 128, 131) and review articles^{1,46,129,130} on this subject appearing only in the last decade and the vast number of original publications appearing each year. But the present review article is not devoted to the task to supplement the previous review articles with recent information. It overlaps with them only slightly. Its main subject is the basic physical properties of small particles: new developments in the thermodynamics and surface force theory, spatial quantization of the conduction electron levels in metal particles, specific features of their electrostatics, and phase transitions and fluctuations in them.

To be more specific, one should note that although the concept of Laplace forces was formulated already two centuries ago, the problem of the surface forces is far from having been finally solved. One might hope that Laplace forces can explain the properties of small particles, at least qualitatively. For example, one might expect that they are all compressed by the Laplace pressure in the thermodynamically equilibrium state. Meanwhile, the experiment shows that very often this is not the case: some particles are compressed but others are dilated. This means that not always the surface forces are equivalent to the Laplace pressure.

When analyzing surface forces one should differentiate between the equilibrium case when the shape of the particle corresponds to the minimum free energy, and the nonequilibrium case. A sample of a nonequilibrium shape tends to take on the equilibrium shape under the Laplace pressure, and here its reality is beyond doubt. But the thermodynamically-equilibrium case demands much more careful treatment. It shows that the Laplace pressure is a real physical force for a liquid particle in equilibrium with its saturated vapor if both the particle and its vapor may be treated thermodynamically.² In this case the change in the free energy caused by a change in the surface area of the particle is proportional to the surface tension and for this reason it can be expressed in terms of the Laplace pressure.

But the situation for crystalline particles is quite different Gibbs³ already noted the difference between the energies of the formation of a new surface due to the crystal splitting and of change in the area of the already existing surface due to its deformation. In microscopic terms, in the former case the number of surface atoms increases, in the latter case it remains unchanged. Gibbs proved that if in the former case the free energy change is determined by the surface tension, in the latter case it is determined by a different quantity called the surface stress. If the crystalline particle shape is in equilibrium its deformation may be caused only by the surface stress. Thus, the Laplace pressure proportional to the surface tension cannot be a real physical force causing the crystalline particle deformation.

Another origin of inadequacy of the concept of the Laplace pressure was pointed out only quite recently.¹⁸⁹ The question arises whether the condition that the particle and its surroundings should be subsystems of a united thermodynamic system is always met. Certainly, the condition is fulfilled for a crystalline particle in its own melt. But when a crystalline or liquid particle is surrounded by its saturated vapor, the vapor density is so small under typical conditions, that the standard thermodynamics described in Ref. 2 becomes invalid. This is the case for almost all metals close or below their melting points.

This is most clearly seen from the case of tin particles. Using experimental data from Ref. 7 with allowance for the exponential temperature dependence of the saturated vapor pressure, one finds that it is so low at 300 K that it corresponds to one tin atom in a volume comparable with the volume of the Earth. It is clear that there is no coexistence of the condensed phase with its vapor for particles of any size. Consequently, a new thermodynamics should be developed for such cases in which exchange of atoms between particles and their environment is absent. There are no reasons to believe that the Laplace pressure retains the meaning of a real physical force even for liquid particles in such a thermodynamics. The theory of Ref. 189 shows, in fact, that for liquid particles, too, the surface forces correspond not to the surface tension but to the surface stress.

The problem of the surface forces is closely related to the problem of the chemical potential of the finite-size samples. In the standard thermodynamics, if the particle is isotropic, it is the same as for infinite-size samples compressed by the Laplace pressure. But this well known result is by no means self-evident: the surface atoms with energies differing from the bulk atom energy might contribute to the chemical potential not via the Laplace pressure but in some other way. It may seem astonishing but the thermodynamics¹⁸⁹ leads to the same result. This means that in the general case the Laplace pressure is not a real physical force but a formal quantity describing the influence of the surface atoms on the the chemical potential of the particle.

The problem of the chemical potential for crystalline particles is much more complicated because atoms in a crystal may be located not only in regular sites but also in irregular positions (interstices and so on). On the other hand, vacancies should form at regular sites. For this reason expressions for chemical potentials of liquid and crystalline particles at extremely low saturated vapor pressures differ very strongly in their form and even in the dependence on the particle size.

Turning to the electron properties of small particles one should point out that their specific features are determined mainly by the spatial quantization of the electron levels. Whereas in the previous review articles the case of strong quantization $\delta \gg T$ predominated, here the emphasis will be laid on the opposite limit of weak quantization, $\delta \ll T$, where δ is the level spacing. The problem of strong quantization is extremely complicated for particles of irregular shapes. Beginning from Ref. 79 it was mainly treated using the Dyson level statistics. But one should keep in mind that conditions for its applicability are not known yet though cases of its validity, certainly, exist.⁸⁰ The question of applicability of the Dyson statistics to small particles will be extensively discussed in what follows.

On the other hand, even if the Dyson statistics are applicable, its possibilities are rather limited. This method is effective in calculating some low-temperature thermodynamic properties determined by spatially quantized levels closest to the Fermi level μ (the heat capacity, magnetic susceptibility and so on). But this method fails when one investigates such important properties of small particles as the size dependence of the Fermi energy and effects caused by it. In such cases the weak quantization approach turns out to be very useful.

This approach is based on the use of a coarse-grained density of states which is a continuous function of the energy.²⁵ The memory of the discrete structure of the energy spectrum is retained through a surface correction to the bulk density of states. This surface correction leads to the Fermi energy dependence on the size and shape of a particle. This dependence manifests itself in various physical effects, of which, first, the size dependence of the work function should be pointed out. It seems very strange that this fact so far was ignored by investigators, and the effect was fully ascribed to Coulomb forces whose role is, at least comparable, and in many cases much less than the role of the spatial quantization. To effects determined by the size dependence of μ one should add also similar dependences of the rates of chemical reactions on surfaces of small particles, the electric current flowing through them in electrochemical cells and so on.

It should be noted also that the size dependence of μ leads also to a cooperative quantum size effect which is the mutual charging of particles of different sizes and shapes if electron transfer is possible through the medium separating particles.^{23,27} As a result, particles attract each other much more strongly than via van der Waals forces which sharply increases their coagulation rate. Other manifestations of the mutual charging will also be discussed in the present review article.

In this review article some problems of the physics of small particles are discussed which have become pressing quite recently and are not elaborated sufficiently yet. The problem of melting of a small particle ensemble belongs to them. According to Berry's elegant hypothesis²⁵¹ particles entering the ensemble are divided into solid and liquid ones in such a way that each of them fluctuates between these two states being liquid or solid for a sufficiently long time. Such coexistence of phases is possible only inside a certain temperature range being forbidden outside it.

This physical picture resembles the quasimelting of small particles already discovered experimentally: well below the melting point a small particle fluctuates between the monocrystalline and the multi-twinned structures, being in each of the states for a macroscopically long time.

The quasimelting is, possibly, related to another interesting physical phenomenon which is the macroscopic quantum tunneling. But apparently, it may be most easily observed in investigating magnetic properties of small particles. As an example, spontaneous switching of the magnetization direction in ferromagnetic particles may be indicated. At low temperatures this switching should occur as a result of simultaneous coherent tunneling of all 10^5-10^6 electron spins of the particle.

Below throughout the review we have set $\hbar = 1$ and the temperature is stated in energy units.

1. STRUCTURE AND SHAPE OF SMALL PARTICLES

1.1. Particles of equilibrium shape

If the crystal structure of a particle is the same as for a bulk sample, the standard procedure for determination of the equilibrium shape of the particle consists in minimization of its surface free energy F_s with the particle volume being fixed. It is assumed that the surface free energy is given by the expression²

$$F_{\rm S} = \oint \alpha({\bf n}) {\rm d}s, \tag{1.1}$$

where α is the surface tension depending on the indices of the crystal face or, what is the same, on the direction of the unit vector **n** normal to the surface. Integration is carried out over all the surface area of the particle. But one should keep in mind that in certain cases (for example, due to quantum effects, Sect. 3.1, 3.4) the relation (1.1) does not hold. If the situation is typical, i.e. Eq (1.1) holds, the equilibrium shape of the finite-size crystals is determined from the Wulff geometric construction (see Ref. 2).

But as has been established by Landau² $\alpha(\mathbf{n})$ being a continuous function of the face direction has no definite value of its derivative at any point. If φ is the angle determining the direction of the face, then for any value of φ the quantity $\alpha(\varphi)$ has different values of $d\alpha/d\varphi$ for decreasing and increasing φ . If one takes this fact into account, one obtains that the equilibrium surface may consist not only of a few smooth faces (i.e. be polihedral) but it may be divided infinitely into more and more small facets and lines. The latter possibility at T = 0 has been proved rigorously by Burkov.¹⁹¹

Changes in the particle shape may occur with rising temperature. At nonzero temperatures curved interfacial regions may appear in addition to planar facets. As temperature increases, facets shrink and eventually disappear each facet at its own characteristic roughening temperature until at sufficiently high temperatures the crystal shape becomes everywhere smoothly rounded. From the mathematical point of view, at any finite temperature a finite number of surface tension singularities remains. They correspond to smooth faces connected by a rounded surface.

The problem of the crystal shape at temperatures where both facets and curved regions are present attracts much attention. To solve it, first the angular dependence of the surface tension should be established which was done in Ref. 192 taking into account the thermodynamic repulsion of steps on a rough surface. Results of Ref. 192 lead to the law $z \sim x^{3/2}$ for the rounded surface.^{193,194} General features of the diagram of states and the critical behavior near critical points of roughening transitions have been established in Ref. 195. In Ref. 196 a total shape of a rounded surface between two smooth faces was found, and the size of a smooth face was related to theoretical parameters using rather simplified models. But some relations obtained in Ref. 196 seem to be universal.

Though production of particles of the equilibrium shape is a very difficult experimental task it was successfully resolved. In Ref. 207 a long annealing made it possible to obtain small Pb particles of the equilibrium shape with coexisting rounded surfaces and faces. Their detailed investigation confirms the law $z \sim x^{3/2}$ obtained for rounded surfaces theoretically. Coexistence of faces and rounded surfaces in Pt particles was observed in Ref. 93. The curved region amounting to 35% of the surface has the structure typical of thermal roughening. Indium particles investigated in Ref. 148a had practically ideal spherical shape which may be a result of surface roughening. But in some particles, for example gold, the rounded surfaces were not observed, and transition between faces remains sharp at finite temperatures.²⁰⁷ In some cases reconstruction of the surface of small particles was observed instead of its roughening. So, the surface reconstruction of the (001) face of small Au particles was discovered in Ref. 208 where 5×1 and 3×1 structures were observed.

But the theory of the equilibrium state of a finite-size crystal based on the assumption that its structure and volume should remain unchanged may turn out inaccurate for very small particles, though for larger particles it works. It is due to the fact that in very small particles the surface energy is not negligibly small compared with the bulk energy. For this reason the total energy of the particle may be lowered by such a deformation of the crystal when a decrease in the surface energy will compensate increase in the bulk energy. The simplest case observed very often experimentally consists of a change in the lattice constant occurring without a change in the structure of the crystal. At first glance, it might appear that the particle should necessarily be compressed compared to a bulk sample as according to Eq. (1.1) at constant $\alpha(\mathbf{n})$ the compression decreases the surface energy. But in reality $\alpha(\mathbf{n})$ depends on the deformation of the crystal, and for this reason it can not be asserted unequivocally that the particle will necessarily be compressed (Sect. 2.1, 2.3).

The tendency to lower the surface energy (1.1) may be realized also by a change in the particle crystallographic structure as compared with bulk samples. Certainly, such a change should increase the bulk energy of the particle. But it may be compensated by a gain in the surface energy if the surface tension in the changed structure is less than in the structure of a bulk sample. One may expect that the surface tension should be minimum for close-packed structures since for them the number of bonds broken by the surface is a minimum. For this reason the f.c.c. structure may turn out to be the most favored one for small particles. This is observed experimentally for many materials. Other changed structures were observed in small particles, too, in particular, hexagonal close-packed.

Although the authors of Ref. 46 claim priority in investigation of this effect, as far as the present author knows it was first observed in Ref. 209 where a new cubic structure was found in small Cr particles instead of the usual b.c.c. structure. It was established in Ref. 210 that Nb, Mo, W and Ta small particles of size from 5 to 10 nm have f.c.c. or hexagonal structure instead of the usual b.c.c. Later numerous other materials were found which exhibit the size-induced structure transformation: Y, Gd, Tb, Dy, Ho, Er (Refs. 226–228), Be and Bi (Ref. 211).

One should point out specially that small particles of some materials lose the crystalline structure and become amorphous. One may think that amorphization lowers the surface energy. This effect was observed in Cd, Se (Ref. 211) and Fe, Cr (Ref. 212). Formal conditions for stability of a changed crystallographic or amorphous structure are trivial and will not be presented here.

One might expect that a new crystallographic structure may result from adsorption of certain adsorbates on their surfaces: it tends to establish that structure for which the heat of adsorption and two-dimensional density of adatoms are maximum.²¹³

Finally, equilibrium particles may have a multitwinned structure (Refs. 197, 198). The reason for its existence is that such a structure may be bounded by surfaces of lowest surface tension. For example, in f.c.c. lattices α (111) is, as a rule, the least of all α (*ikl*) where (*ikl*) are the Miller indices. In the Wulff polihedron representing the equilibrium shape of the particle not only low-energy (111) faces are present but also (100) faces with a high surface tension. But this polyhedron provides a minimum for the particle energy only under condition of strain nonexistence in it. One may hope that strained structures are possible in which a loss in the deformation energy is compensated by a gain in the surface energy. An icosahedron constructed of 20 equivalent tetrahedrons which are bounded by the triangular (111) faces. But if the tetrahedrons of which the icosahedron is constructed, had been undeformed, they could not have been packed close to each other: gaps would have existed between them. These gaps are removed by tetrahedron deformation consisting of an increase of the solid angles of each terahedron. Multi-twinned structures were often observed experimentally in such materials as Au, Pd and so on.¹⁰¹⁻¹⁰⁴

1.2. Main properties of atomic clusters

The problem of the equilibrium shape of atomic clusters consisting of several tens or several hundreds of atoms is quite peculiar. It turns out that the most stable and, hence, the ones in equilibrium are clusters consisting of certain definite numbers of atoms called magic. So, the magic numbers for Pb and the inert gases are equal to 7, 13 and 19. This suggests that the most stable ones are the clusters with closest packing independently of their electron structure.²¹⁴ But this point of view contradicts the results for Na and K clusters. In Ref. 215, 12 different magic numbers were observed for them: 2, 8, 20, 40, 58, 92, 138, 196, 260, 344, 440, 558. The first five of them coincide with magic numbers found in Refs. 216, 217. This set of numbers is close to the total number $2n^2$ of electrons in the closed electron shell corresponding to a spherically-symmetrical potential, n being the main quantum number. On the other hand, in Ref. 90 quite other magic numbers were observed for metal clusters: 13, 55 and 147, which are difficult to relate to n.

According to the data from Ref. 215 presented above, magic numbers exist even for very large clusters. A similar result was obtained for Au particles: magic numbers exist in them up to size 10 nm.²¹⁸ The maximum stability of clusters with magic numbers agrees with the fact that the degree of the surface imperfection is minimum for them while being very significant for other clusters.⁹⁰

As for the equilibrium shape of metal clusters, it may be approximated by a sphere only at the complete filling of the electron shells. If the external shell is filled only partially, ellipsoidal deformation of the particle should take place, i.e. the Jahn-Teller effect. This is just the origin for Eq. (1.1) being invalid (Sect. 3.1). But so far these theoretical predictions have not been confirmed experimentally.

In order to interpret properties of clusters adequately, one should take into account the fact that, on a decrease in size, clusters cease to be metallic, unlike bulk samples of the same materials. Thus, the type of the chemical bonding depends on the cluster size. Experimental data on the sizeinduced metal-insulator transition are as follows. Photoemission from 6-atomic Pt clusters reveals that they are nonmetallic.²¹⁹ Au clusters consisting of less than 100 atoms are nonmetallic, too, which may be inferred from the sizedependence of the plasmon frequency.^{119,120} But they become metallic in the range from 150 to 500 atoms. Judging from the photoionization threshold, in Hg clusters the transition from a van der Waals crystal to a metal occurs in the range from 20 to 70 atoms.¹²¹ In Na clusters the surface plasmon frequency increases from 2.4 to 3.4 eV reaching almost the bulk value when the number of atoms increases from 10 to 300 (Ref. 122). Tunnel phenomena in Fe clusters on a GaAs substrate show that Fe_{13} is a nonmetal but Fe_{35} is a metal.²²⁰ Ionization potentials of Al_n and In_n (n < 80) as functions of the number of atoms n exhibit flattening in the vicinity of n = 5 after an initial linear increase with n (Ref. 221).

In mixed valency materials transition to the insulating state manifests itself in the valency equal to 2 whereas in metal clusters it has a value intermediate between 2 and 3. (This value may be found using the x ray technique). In Ref. 124 clusters of Pr, Nd and Sm in solid argon were investigated. Dimers and trimers are characterized by the valence of atoms equal to 2. But that of clusters consisting of more than 20 atoms is very close to 3 as in bulk metals. A change in valence occurs abruptly at n = 5 for Pr and Nd and at n = 13for Sm. Similar results were obtained in Ref. 125 where Sm clusters in solid Ne, Ar or Kr were investigated. For numbers of atoms less than 10 the valence is equal to 2, but at n = 13 it abruptly reaches 2.6. The tendency toward an increase in valence with cluster size was discovered in Ref. 123, too, where 3 nm Sm clusters were investigated.

Cooperative phenomena are possible in ensembles of clusters: one expects superfluidity of parahydrogen clusters consisting from 10 to 20 atoms.²²⁴

1.3. Particles of nonequilibrium shape

Under real conditions thermodynamic equilibrium may be reached only partially when producing small particles. Then crytalline particles may be of nonequilibrium shape which may remain frozen for an arbitrarily long time. As the relaxation time for particle shape greatly exceeds other characteristic times one may speak of thermodynamic equilibrium for a particle of any given shape. Firstly, the nonequilibrium shape may be caused by the procedure of producing particles. For example, if crystallization of a melt occurs well below the melting point, not only the shape but also the crystallographic structure may turn out to be nonequilibrium: the nucleation droplet often exhibits the b.c.c. structure instead of the equilibrium f.c.c. structure.²⁸¹ Au particles deposited on a NaCl substrate have the shape of a pyramid with a square or rounded basis. In some cases the pyramids are truncated.91 Sometimes clusters obtained by deposition from vacuum are of quite irregular shape.92

Often particles on a substrate are stressed very strongly.

In Ref. 225 the shape of preformed spherical clusters with radii varying from 1 to 6 nm has been studied with the scanning tunneling microscope after deposition onto flat substrates of the same material, i.e. Au. The deposited clusters are found to resemble spherical caps with radii of curvature greater than and not strongly correlated with the original free space radii. Measurements revealed that 80% of the clusters studied have a radius of curvature lying between 10 and 30 nm. A continuum model to interpret this result indicates that clusters with radii less than a critical value characteristic of the cluster material are stressed beyond their elastic limit and can deform so as to decrease their surface free energy even at temperatures well below their melting point.

In some cases the nonequilibrium shape may result from diminished stability of particles as in the case of clusters with nonmagic numbers of atoms discussed in the previous Section. Finally, particles of nonequilibrium shape may arise as a consequence of their coagulation. For example, in Ref. 155 colloid aggregates of 7.5 nm gold particles were observed.

To describe the surface roughness phenomenologically, it was proposed in Refs. 86–88 to use the mathematics of fractals of which a general theory is presented in Ref. 95. Such a description is far from being complete and is rather limited in its applications. Nevertheless, in some cases it may turn out to be useful. The main parameter determining the degree of surface roughness is its fractal dimensionality D. It may be introduced in the following way. Let us cover the surface by adsorbate molecules modeled by small squares of side r. Under certain conditions the number N(r) of molecules in the multilayer coverage increases as r^{-D} and r decrease. Obviously, for smooth surfaces the fractal dimensionality D is equal to 2 since for them $N(r) = S/r^2$ where S is the surface area.

Let us assume now that there are voids on the surface in which molecules of sufficiently small sizes may hide. Then it is clear that N(r) should increase more rapidly than as r^{-2} , on a decrease in r. Thus, D should exceed 2 for a rough surface.

One may go over from admolecules with the cross section $c \sim \varepsilon^2$ to a "ruler" with the scale ε with which the surface is measured. Then the fractal approach is expressed by the relation

 $S \sim \epsilon^{2-D}$.

It makes sense only if the surface is self-similar. This means that its main features must be reproduced if the scale is changed. Certainly, the requirement of self-similarity strongly restricts the class of surfaces for which the fractal approach is applicable. Much more broad is the class of surfaces for which it is applicable in a certain range of scales ε . It is the existence of such ranges that makes it possible to apply the fractal approach to real objects. Certainly, this approach is justified if the scale of surface defects exceeds the interatomic distance in the crystal. Thus, for example, the fractal approach is inapplicable to crystal surfaces with vacancies and other point defects on it.

In Ref. 89 an electron microscope method was developed which makes it possible to determine fractal dimensionality for small particles, and it was proved that the selfsimilarity condition is met for their surfaces. For Au particles deposited from vacuum onto an NaCl surface the value D = 2.130 was obtained, and for Pt particles D = 2.146. After carrying out the methanization reaction on the surface of the Pt particles, the surface becomes much more rough: D reaches 2.330. This example shows that the fractal approach may be quite useful for small particles.

In Ref. 155 the fractal approach was developed for aggregates of small particles which is based on the use of the density-density correlation function. In Ref. 233 it is established that a linear correlation exists between the fractal dimensionality and the atomic magnetic moment in aggregates of magnetic particles. Sometimes the fractal dimensionality is used for description of irregularity of dendrite-like particles. In this case it determines the linear size of such particles. So, it was established in Ref. 222 that the fractal dimensionality of Re supported Au particles is 1.72.

1.4. Size dependence of the wetting angle for supported liquid particles

The problem of nonequilibrium shape does not exist for liquid particles as nothing can prevent them from taking the equilibrium shape. Specific features of small particles manifest themselves only in the size dependence of the wetting angle.⁷² This dependence is a consequence of size dependence of the surface tension which will be introduced here phenomenologically. A microscopic theory of this phenomenon is presented in Ref. 72. The following assumptions will be made in what follows:

$$\alpha_{l} = \alpha_{l}^{\infty} (1 + gH), \ \alpha_{sl} = \alpha_{sl}^{\infty} [1 + (b/L)],$$
(1.2)

where α_i is the surface tension on the liquid-vacuum boundary, α_{sl} that on the liquid-solid substrate boundary, H is the mean curvature, and L is the radius of the contact area between the droplet and the substrate. The index ∞ denotes the corresponding quantity for a bulk sample. Phenomenological parameters g and b are of the order of the interatomic distance.

The equilibrium shape of the supported droplet is found from the condition of minimum free energy with the droplet volume kept constant. It seems quite obvious that the shape of the droplet is a spherical segment. Then the free energy functional with allowance for Eq. (1.1) in the isotropic version may be represented as a function of two parameters: the droplet radius $R = H^{-1}$ and the wetting angle θ ,

$$F = 2\pi R^2 \alpha_l^{\infty} \left[1 + (g/R) \right] (1 - \cos \theta) + \pi R^2 (\alpha_{sl}^{\infty} - \alpha_s) \sin^2 \theta + \pi R b \alpha_{sl}^{\infty} \sin \theta + (\lambda \pi R^3/3) \left[2(1 - \cos \theta) - \sin^2 \theta \cdot \cos \theta \right],$$
(1.3)

where α_s is the surface tension on the substrate-vacuum boundary, and λ is the Lagrange factor.

Minimizing F(1.3) with respect to R and θ and eliminating λ from the equations obtained, one finds the following expressions for the wetting angle:

$$\cos \theta = \cos \theta_{\infty} + (g/R) - (b\alpha_{sl}^{\infty} / 2R\alpha_{1}^{\infty} \sin \theta), \qquad (1.4)$$
$$\cos \theta_{\infty} = (\alpha_{s} - \alpha_{sl}^{\infty}) / \alpha_{l}^{\infty}.$$

Obviously, the last two terms on the right-hand side of Eq. (1.4) determine a correction of the order of 1/R to the bulk wetting angle θ^{∞} if θ is far enough from 0 and π . But this correction becomes anomalously large at $\theta \rightarrow 0$ or π . In the former case (complete wetting), if b > 0, the following



FIG. 1. Dependence of the wetting angle on the size of Au particles on a carbon substrate. 72

equality should hold

$$\sin(\theta/2) = (1/2)(b\alpha_{si}^{\infty}/R\alpha_{l}^{\infty})^{1/3}.$$
 (1.5)

In the latter case (complete absence of wetting), if b < 0, the wetting angle is given by the expression

$$\cos(\theta/2) = (1/2)(-b\alpha_{sl}^{\infty}/R\alpha_{l}^{\infty})^{1/3}.$$
 (1.6)

As follows from Eqs. (1.5), (1.6), the size dependent effect is proportional to $R^{-1/3}$ instead of R^{-1} . If wetting is absent for bulk samples it may appear for small droplets.

In Ref. 72 a systematic experimental investigation of wetting of inert carbon substrates by microparticles of some metals was carried out which reveals that the size dependence of the wetting angle is quite considerable. For example, the wetting angle for Au droplets diminishes from 140° to 120° when the droplet size diminishes to 10 nm (Fig. 1).

1.5. Surface relaxation of crystalline particles

So far only those properties of small particles were considered which may be described phenomenologically. But some properties of them cannot be described phenomenologically at all, and a microscopic treatment is required for them. Surface relaxation belongs to them. It consists in a change of atomic plane spacings close to the surface as compared with spacings inside the bulk. Though the surface relaxation decays with growing distance from the surface, it causes corrections to the particle volume and its thermodynamic quantities of order of 1/L where L is the particle size. Thus, their size dependence is similar to that of corrections caused by such factors specific for small particles as surface forces and so on. One should keep in mind that surface relaxation takes place not only in samples of equilibrium shape, but also in those of nonequilibrium shape.

Specific features of surface relaxation in small particles were established in Ref. 24. Firstly, it was found, that in a model of a crystal with elastic interactions only between the first neighboring atomic planes $V_1(r)$ surface relaxation is nonexistent. It becomes nonzero only if one takes into account the elastic interaction $V_2(r)$ between the second neighboring planes. If $Q = V_2''$ (2a) is negative and $P = V_1''(a) \ge 4|Q|$, then the relaxation decays inside the bulk exponentially with the inverse length q,

 $aq = \ln |b|$,

$$b = - [1 + (P/2Q)] \pm \{[1 + (P/2Q)]^2 - 1\}^{1/2}, \quad (1.7)$$

where a is the atomic spacing inside the bulk. The sign in Eq.

(1.7) should be chosen in such a way that |b| > 1. But if Q > 0, $P \ge 4Q$, then the relaxation not only decays with the exponent q (1.7) but also changes its sign with the period a.

Naturally, an exact expression for the positions of displaced atoms is very complicated because of superposition of relaxations of different faces bounding the crystal. Moreover, in the following range of the parameters tending to zero as the particle size goes to infinity,

$$Q < 0, 2|Q| \{1 + \cos[\pi a/(L-a)]\} < P < 4Q,$$

the solution exists for which, instead of an exponential decay, the surface relaxation displays a pure oscillatory behavior with the wave vector $k = -i \ln b$. Surface relaxation may both increase and decrease the total volume of the crystal depending on its elastic parameters and size.

Surface relaxation in metals displays very interesting peculiarities: oscillating, it decays not exponentially but in accordance with a power law.^{35,36} Physically, such a relaxation is related to the Friedel oscillations of the electron gas caused by the surface. (the Friedel oscillations are caused by any defects lifting the translation symmetry of the crystal, including two-dimensional defects, such as the surface). The electron-phonon interaction transfers these oscillations to the lattice causing changes in atomic plane spacings with a similar coordinate dependence. Such a "Friedel surface relaxation" is superimposed on the usual exponential relaxation. The former depends very strongly on the boundary conditions imposed on the electron wave function on the crystal surface. Their change caused, for example, by adsorption changes the phase of the Friedel oscillations.

Indeed, according to Ref. 36 the amplitude of the Friedel oscillations in the free-electron model decays with increasing distance from the flat surface according the law

$$f(g) \sim \frac{\sin(2k_0g)}{g^2} \left[\frac{4k_0x_0}{x_0^2 + k_0^2} + \frac{k_0^4 + 8k_0^2x_0^2 - x_0^4}{g(k_0^2 + x_0^2)} \right] + \frac{\cos(2k_0g)}{g^2} \left[\frac{x_0^2 - k_0^2}{k_0^2 + x_0^2} + \frac{x_0(3x_0^2 - k_0^2)}{g(k_0^2 + x_0^2)^2} \right], \quad (1.8)$$

where $g \ge 1$ is the number of the atomic plane, $k = k_F a (k_F)$ is the Fermi momentum, a is the lattice constant), $p = (\varkappa a)^{-1}$ with the parameter \varkappa entering the boundary conditions (3.10) for the electron wave function. As follows from Eq. (1.8), phases of oscillations are opposite for the cases when the wave function or its normal derivative vanish on the surface ($\varkappa \to \pm \infty$ and $\varkappa = 0$, respectively).

One should point out that oscillating surface relaxation was also obtained for metals by numerical calculations based on the pseudopotential theory.^{39–42} But in these papers decay of the relaxation was assumed to be exponential, i.e. the Kohn singularity leading to the Friedel oscillations was ignored. Relaxation of small particles was investigated in Refs. 70, 71, 199. In particular, it is shown in these papers that lattice anharmonism may lead to a strong temperature dependence of the surface relaxation.

1.6. Experimental data on spontaneous lattice deformation

To begin with, it should be noted that any comparison of the experimental data on the spontaneous deformation of the lattice of small particles with the theory presented in



FIG. 2. Dependence of the lattice parameter of Au(1), Ag(2) and Cu(3) on the particle size.^{68,69}

Secs. 1.5, 2.2 can, at best, be only qualitative. Usually experiment gives only the mean lattice constant of a crystalline particle. Judged by this parameter lattice compression was observed in many cases, for example, in Ag, Cu, Au, (Ref. 68) (Fig. 2), Pt (Ref. 69). The results of Ref. 55 for compression of Al particles with decreasing size are especially interesting because a coordinate dependence of the deformation (Fig. 3a) apart from the mean compression was also found in this paper (Fig. 3b). As seen from these figures, the lattice compression of Al particles is subdivided, in an obvious way, into surface relaxation whose magnitude depends on sample size very weakly, and bulk deformation which increases with decreasing size.

Unfortunately, experimentalists are not unanimous with respect to the properties of Al particles. In Ref. 56 the lattice constant of Al particles was found to exhibit no size dependence up to 3 nm size. Nor was it found for Pb particles in an aerosol up to 8 nm.⁵⁷ Similar results were obtained also in Ref. 59. Cu clusters in solid argon were investigated in Ref. 106. The lattice constant of a cluster of 5 nm diameter was found to be virtually the same as that of a bulk sample, but for clusters of 0.7 nm diameter it is 2% less.

Particles dilate instead of compressing in some cases (Refs. 60-63, 107) (Fig. 4). Small particles of diamond and Si also dilate (Refs. 229, 230). According to Ref. 60, a MgO particle with a clean surface is compressed, but it dilates after adsorption of hydroxide on its surface. There are many factors making the particle deformation depend on the adsorption: it may cause a change in the surface stress, relaxation and so on. Finally, there are some data on spontaneous compression of Au films⁵⁸ and data of Ref. 61 on the same subject but of the opposite sign (Au films dilate). Compression of small Au particles was found in Ref. 68. According to Ref. 62 Pt particles dilate, but according to Ref. 69 they are compressed. It was established in Ref. 146 that Gd, Tb and Ho particles of sizes below 30 nm have f.c.c. structure instead of the usual hexagonal structure of bulk samples. Their lattice constant increases on a further decrease in their size.

Before giving an unambiguous theoretical interpretation of the experimental data on the size dependence of the deformation of small particles, it is necessary that the experimental data of different authors should agree with each other. But at present this is not the case. To begin with, it seems important to make sure that the particles under investigation be really in thermodynamic equilibrium which is not always attained (Sec. 1.1).

Apart from bulk size dependence, surface relaxation has also been investigated in detail in many papers. As bulk samples were used data obtained in them seem quite reliable. In particular, oscillating relaxation was observed in a great many metals (Al, Fe, V and so on) on various crystal faces (e.g. Refs. 52–54). But the accuracy of the experiment does not make it possible to decide whether the relaxation amplitude decreases inside the bulk exponentially or more slowly (Fig. 5). For this reason their comparison with the theoretical results of Sec. 1.5 is impossible.

2. THERMODYNAMICS OF SMALL PARTICLES

2.1. Thermodynamics of isotropic two-phase systems

Discussion of the thermodynamics of small particles will be begun, as usually, by treating the thermodynamics of an isotropic particle in equilibrium with its vapor. The main attention will be paid to the problem which was not discussed in previous publications: the validity condition for the standard approach when the particle and its vapor are regarded as subsystems of a single thermodynamic system.

If the total volume of a single united particle-vapor thermodynamic system is V_t and the total number of atoms in it is N, the free energy F_s of the particle-vapor interface is given by an expression which is an isotropic version of Eq. (1.1):

$$F_{\rm S} = \alpha S, \ \alpha = \alpha (T, V_{\rm t}, N). \tag{2.1}$$

where S is the interface area, and α is the surface tension. It is implied here that, since the total free energy of the system F depends on its volume V_t , the quantity F_s must also depend on it. When V_t and N are given, the coefficient of surface tension α depends only on the temperature T (in the p and T variables the value of α , too, actually depends on only one of these variables since p and T are related to each other by the phase coexistence curve²).

Despite of the apparently self-evident linear relation between F_s and S, Eq. (2.1) is a thermodynamic postulate which should be substantiated microscopically. As shown in Secs. 3.1, 3.4, in some cases Eq. (2.1) is invalid.

Since a transitional region exists between the condensed phase and the surrounding vapor, the dividing surface (i.e. the surface separating the phases) is quite arbitrary. For



FIG. 3. a) Dependence of the mean lattice constant a of Al particles on a MgO substrate on the particle size R (Ref. 55); b) Dependence of the lattice constant a on the distance Z to the surface for Al samples of different sizes (Ref. 55).



FIG. 4. Dependence of the lattice constant of CeO₂ on the particle size.¹⁰⁷

further calculation it will be convenient to use the equimolar surface. It is defined by the condition that all the atoms be divided into atoms of the particle (phase c), their number being $N_c = n_c V_c$, and the atoms of the gas phase (phase g), their number being $N_g = n_g V_g$, without a transitional region between them. Thus, the following equalities should hold: where V_c and V_g are the volumes of the particle and vapor, respectively. With the accuracy to terms $\sim (S/V)$ inclusive, α does not depend on the choice of the dividing surface.⁹

The basic thermodynamic relations can be derived from the condition that the total free energy $F = F_c + F_g + F_s$ of a spherical particle of radius R be minimum with respect to variations of the volumes $\delta V_c = -\delta V_g$ and of numbers of the atoms $\delta N_c = -\delta N_g$ in both phases (F_c and F_g are the free energies of the condensed and gas phases without taking the surface into account) With allowance for Eq. (2.1) one obtains

$$\delta F / \delta V_{\rm c} = -p_{\rm c} + p_{\rm g} + p_{\rm L} = 0, \ p_L = 2\alpha/R.$$
 (2.2)

where

$$p_c = -\partial F_c / \partial N_c; \quad p_g = -\partial F_g / \partial V_g$$

After transition from densities to pressures in expressions for the chemical potentials μ_c and μ_g the second condition for minimum free energy takes the form

$$\delta F / \delta N_{\rm c} = \mu_0 (p_{\rm g} + p_{\rm I}) - \mu_{\rm g} (p_{\rm g}) = 0, \qquad (2.3)$$

where

$$\mu_{g} = \partial F_{g} / \partial N_{g}; \quad \mu_{c} = \partial F_{c} / \partial N_{c} \equiv \mu_{0} (n_{c})$$

and the approximate equality is used

$$\mu_0(p_g) + 2\alpha S/3N_c \approx \mu_0(p_g + p_L)$$



FIG. 5. Oscillations of the surface relaxation of Ni and Al (Ref. 54).

based on the Taylor series and the thermodynamic relation

$$1/N_{\rm c} = \partial \mu_0 / \partial p$$

Although the derivation of Eq. (2.3) just presented is standard, not always is the fact recognized that it is based on a basically important assumption of the particle density n_c being fixed in the main approximation in 1/R. This implies that a change in the surface area may occur only via exchange atoms between the particle and vapor. In the absence of this exchange Eqs. (2.2), (2.3) are invalid.

According to these equations the size dependence of the particle chemical potential is completely determined by the fact that the pressure p_c inside the particle exceeds the external pressure p_g by the Laplace pressure p_L . The functional dependence of the chemical potential on pressure inside the particle $p_c = p_g + p_L$ remains the same as for an infinitely large sample with $\mu_c = \mu_0 (p_g)$. Thus, the size dependence of the chemical potential is completely reduced to this dependence of the pressure inside the particle.

Conditions of applicability of Eqs. (2.2), (2.3) were analyzed in Ref. 189 where similar results were obtained by both a phenomenological and a microscopical analysis. In the first case one should take into account the circumstance that the variation δF_g of the vapor free energy caused by the change δV_g in the vapor volume was assumed to be a thermodynamic quantity when deducing (2.2), (2.3). Consequently, the volume δV_g must contain a number of atoms large enough. As this volume is restricted by the obvious inequality $\delta V_g \ll V_c$, this means that the inequality $n_g V_c \ll 1$ has to be satisfied.

In the second case when treating these conditions microscopically one should proceed from the requirement that the pressure exerted by the vapor on the particle should be a well defined physical quantity, i.e. that its fluctuations are small compared with its mean value. For establishment of an isotropic thermodynamically equilibrium compression of a particle under impacts of atoms from the vapor, the time interval between two consecutive impacts $\sim (n_g v_g S)^{-1}$ must be small compared with the time of the deformation spreading over the particle. The latter is of the order of R/s where s is the sound velocity in the crystal, v_g is the thermal velocity of atoms in the vapor. Uniting the phenomenological and the microscopic criteria just presented, one may write the following criterion for validity of the thermodynamic treatment described in this Section:

$$N_{gc} \equiv n_g V_c \gg \max\{1, s/v_g\}.$$
 (2.3a)

As follows from (2.3a), on decrease in the particle size, conditions for applicability of this treatment become more restrictive. The same is true if the pressure of saturated vapor diminishes. The latter should be expected with allowance for the fact that the relative fluctuation of the pressure is proportional to $p_g^{-1/2}$. Hence, at $p_g \rightarrow 0$ the fluctuations of the pressure greatly exceed the mean pressure, i.e., the pressure cannot be regarded as a thermodynamic quantity. Physically, breakdown of Eqs. (2.2), (2.3) at $p_g \rightarrow 0$ is a consequence of the fact that the atom exchange between the particle and its vapor is switched off. Breakdown of the inequality (2.3a) as $V_c \rightarrow 0$ is a consequence of the fact that, at any vapor pressure, the number N_{gc} of vapor atoms in the volume equal to that of the particle tends to zero also. Hence, its relative fluctuation increases and so does the fluctuation of the vapor pressure on the particle surface.

In addition to the thermodynamic derivation of the Laplace pressure, it was also derived using many microscopic models (see Refs. 8,9).

2.2. Thermodynamics of crystals in equilibrium with their melt or vapor

Unlike a liquid, the energy of a change in the surface area of a crystal depends on the way in which this change is produced. There are two different ways in which the area S can be changed. The first way consists in a change of the number of atoms on the surface of the crystal without stresses appearing in it. An increase in the number of surface atoms entails an increase in the number of interatomic bonds broken by the surface. The surface tension α , by definition, is proportional to the energy of broken bonds. Therefore, a change in the energy due to a change in the number of surface atoms (Gibbs³ calls it the formation of a new surface) is determined by α .

The second way consists in a deformation of the surface without any change in the number of surface atoms. The energy of the change in the surface area is determined in this case by elastic forces and for this reason has been described by a quite different quantity g referred to as the surface stress.⁴⁻⁶ Deformation of this kind arises spontaneously, and its origin is, in effect, the same as that of the surface relaxation discussed in Sec. 1.5.

First the case of a flat slab will be discussed in order to clarify this statement. As the elastic bonds of the surface atoms with neighbors "on the other side of the surface" are broken the interlayer distances near the surface differ the from bulk ones. But, although the thickness of the slab varies because of relaxation, the slab itself remains as flat as ever.

Now, if the crystal is initially cube-shaped, the atoms on its edges change their distances from their neighbors simultaneously in two mutually perpendicular directions in which their bonds are broken. The number of bonds broken on the edges in each direction differs from that far from the edges. Accordingly, it is as if the cube were stretched by the edges or, conversely, compressed along the edges, so that its faces are no longer flat. Such a deformation is proportional to the relative number of atoms along the edges, i.e., 1/L, where L is the edge length. Actually, it is proportional to the mean radius of curvature and in this respect is similar to the deformation brought about by the Laplace pressure. The difference consists in the fact that in the case discussed the deformation is proportional to the surface stress and not to the surface tension.

A mathematical description of the deformed surface of the crystal will be presented following Ref. 10. If the elastic deformation u_i is small, the crystal surface energy E_s changes by the quantity

$$\delta E_{\rm S} = -\int f_{\mu} u_{\mu} \,\mathrm{d}S_0 \,, \tag{2.4}$$

where f_{μ} are surface forces having only tangential (i = 1,2) components since the normal components are equal to zero in accordance with Newton's third law. Integration in Eq. (2.4) is carried out over the undeformed surface.

The force f can be represented as the divergence of a certain symmetrical tensor (the surface stress tensor):

$$f_{\mu} = \partial g_{\mu\nu} / \partial x_{\nu}, \quad \mu, \nu = 1, 2. \tag{2.5}$$

For this tensor the following expression has been derived in Refs. 4, 6, 21:

$$g_{\mu\nu} = \alpha \delta_{\mu\nu} + \partial \alpha / \partial u_{\mu\nu} \,. \tag{2.6}$$

It has been in Ref. 17 that Eq. (2.6) follows directly from the definition

$$Sg_{\mu\nu} d\mu_{\mu\nu} = d(S\alpha),$$

with allowance for the relation

$$\partial S / \partial u_{\mu\nu} = S \delta_{\mu\nu}$$

where $\delta_{\mu\nu}$ is the Kronecker symbol.

Eq. (2.6) assumes that the surface tension α depends on the surface deformation. In principle, α can also depend on the bulk deformation but under the equilibrium conditions this deformation is unambiguously determined from the equations of elasticity theory if the surface deformation is known. For a surface with a higher than second-order symmetry axis $g_{\mu\nu} = g \delta_{\mu\nu}$.

It was not ruled out in Ref. 4 that in the case of lowsymmetry crystals the components $g_{n\mu}$ of the stress tensor, where *n* is the index of the normal to the surface, may also differ from zero. But this point of view is wrong according to Refs. 10–12. A detailed analysis of the stress dependence of α is given in Refs. 12,13 where account was taken of the fact that a transition layer between the crystal and the liquid exists, the thickness of this layer being uncertain. Results of Refs. 10 to 13 are confirmed in Ref. 20 where it is shown that $g_{n\mu}$ vanishes only when the transition layer thickness is zero.

After substituting Eq. (1.5) into (1.4) and adding the surface energy (1.1), one obtains the following expression for the surface energy of a crystal (**n** is the normal vector):

$$E_{\rm S} = \int (\alpha(n) + g_{\mu\nu} u_{\mu\nu}) \, \mathrm{d}S_0 \,. \tag{2.7}$$

In order to reduce Eq. (2.7) to Eq. (2.1) for the liquid and to go over from the undeformed surface S_0 to the deformed S, one must put $g_{\mu\nu} = \alpha \delta_{\mu\nu}$. According to Eq. (2.4) this means that for a liquid the surface tension is deformation-independent. A qualitative explanation of this independence given in Ref. 4 is inadequate. The compression of a liquid, unlike that of a crystal, is thought in Ref. 4 to be accompanied by a decrease in the number of atoms on its surface. In reality, according to Eq. (2.13) this number for a spherical particle remains unchanged.

As the sum of the bulk and surface forces should be equal to zero, the following equilibrium conditions for the surface (an analog of (2.2)) can be derived from Eq. (2.2):

$$\sigma_{nn} + \frac{g_{11}}{R_1} + \frac{g_{22}}{R_2} + p = 0, \quad \sigma_{\mu n} = \frac{1}{R_1} \frac{\partial g_{\mu 1}}{\partial \varphi_1} + \frac{1}{R_2} \frac{\partial g_{\mu 2}}{\partial \varphi_2}, \quad (2.8)$$

where $\sigma_{\mu\nu}$ is the stress tensor, p_g is the external pressure, R_1 and R_2 are the principal radii of curvature, φ_1 and φ_2 are the angles measured in the planes of the principal normal cross sections.

An important qualitative conclusion follows from Eqs. (2.7), (2.8): whereas α must be positive in order to ensure the stability of the crystal, there is no similar constraint for the signs of the components of the stress surface tensor. Consequently, the surface forces can, in principle, dilate the

crystal instead of compressing it like the liquid. But only experiment or microscopic calculations can show whether such values of $g_{\mu\nu}$ are really possible.

The change of the crystal volume due to surface forces was calculated in Ref. 14 for crystals of simple shapes and in Ref. 17 for those of an arbitrary shape. For instance, it was obtained in Ref. 14 for a cube with edge length L:

$$\frac{\Delta V}{V} = -\frac{4\varkappa g}{L},\tag{2.9}$$

where \varkappa is the compressibility of the crystal. As shown in Ref. 15, under certain conditions it is possible to introduce an excess pressure for a crystal $\Delta p = -2\langle g \rangle / \langle h \rangle$ where *h* is the distance between the fixed point of the crystal which does not change its position under surface forces and the face of the crystal, and the angular brackets denote averaging over the faces. This expression is a generalization of the Laplace pressure for crystalline systems.

As a generalization of Eq. (2.3) for a crystal in equilibrium with its vapor or melt, the following relationship for the chemical potential should hold:

$$\mu_0 + n_c^{-1} \left[p + \left(\alpha + \frac{\partial^2 \alpha}{\partial \varphi_1^2} \right) \frac{1}{R_1} + \left(\alpha + \frac{\partial^2 \alpha}{\partial \varphi_2^2} \right) \frac{1}{R_2} \right] = \mu_g, \quad (2.10)$$

where μ_0 is the chemical potential of the bulk sample.

Unfortunately, unlike the surface tension, the direct experimental methods for determination of the surface stress are nonexistant so far, and one should rely on its theoretical estimation using microscopical approaches and models. As an example, in Ref. 16, neglecting the anisotropy of the surface stress tensor, an expression was obtained relating g to the Poisson ratio ν

$$\frac{g}{\alpha} = \frac{3\nu - 1}{1 - \nu}$$
 (2.11)

Eq. (2.11) allows both positive and negative values of g. At v = 1/2 (incompressible liquid) it leads to the expected result $g = \alpha$. Nevertheless, Eq. (2.11) seems to be doubtful: since for most metals α is close to 1/3, the surface stress should be very small for them according to this equation, i.e. the size dependence of the lattice constant should be nonexistent. And yet in many metals it is, in fact, rather strong.

In Ref. 17 a numerical calculation of the quantities g and α for some metals was carried out using the pseudopotential method and Eq. (2.6). Values of α obtained in Ref. 17 are close to experimental ones. Values of g/α for (111) faces amount to 1.3 for Al, 1.6 for Ir, 2.5 for Pt and 2.2 for Au. According to these results, small particles of the above materials should be compressed even stronger than under the Laplace pressure.

The problem of dilatation of crystalline particles resulting from negative values of g remains unresolved so far. It is stated in Ref. 231 that g is negative for α -Fe₂O₃. In Ref. 232 the idea is advanced that g may be negative for those crystal faces where surface reconstruction occurs accompanied by an increase in the number of surface atoms. Experimental results presented in Sec. 1.6 suggest that a possibility for g to be negative should exist.

2.3. Thermodynamics of small particles with a fixed number of atoms

So far the situation was discussed when particles are surrounded with their saturated vapor with which they may exchange atoms. As a result of this exchange, the surface of a particle may change its area without changing its shape or density. This fact was used in deriving Eqs. (2.2) and (2.3). Thus, a particle was treated as a subsystem of the united particle-vapor thermodynamic system in Sect. 2.1.

A quite different situation arises at a vanishingly small pressure of the saturated vapor which is typical of metals and their compounds at room and lower temperatures. As already mentioned in the Introduction, the density of saturated tin vapor at 300 K is of the order of one tin atom per volume comparable with that of the Earth. The vapor density remains very low for most metals even in their liquid state close to the melting point. According to Ref. 7 for tin $n_{\rm g} \sim 10^{-6}$ cm⁻³ at this point, i.e., it is quite obvious that the standard two-phase thermodynamics is inadequate for liquid tin particles. For other metals n_g is of the order of 10⁶ to 10^{10} cm⁻³ at the melting point. Thus, at $R \sim 100$ nm the strong inequality (2.3a) given in Sec. 2.1 as the validity criterion for the standard two-phase thermodynamics becomes reversed here. This means that the fluctuations of the pressure on the surface of the particle are so large that one cannot speak of its definite value.

At such low pressures the number of atoms in each particle may be regarded as fixed with a very high accuracy. Thus, its thermodynamics should be different from that described in Sec. 2.1.

One may formulate a sufficient condition for treatment of the number of atoms in the particle as fixed. It consists in the requirement that the time of formation and disappearance of the fluctuation changing by v the number of atoms, t_v , be large compared with the measurement time. The number v should be large enough for the fluctuation to be regarded as thermodynamic.

First, the case v = 1 will be considered. The particle undergoes $\sim n_g v_g S$ impacts of atoms from the vapor per unit time. If W is the sticking probability for an atom colliding with the particle, then

$$t_1 \sim 1/W n_g v_g S$$

The time t_{ν} ($\nu > 1$) may be evaluated with allowance for the fact that the particle randomly emits and captures atoms from the vapor. Then, in accordance with the random walk theory,

$$t_{\nu} \sim \nu^2 t_1$$

Unfortunately, in the general case the order of magnitude of W is unknown. The lower bound for t_1 can be found, putting W = 1. Then at $v_g \sim 10^5$ cm/sec, $n_g \sim 10^6$ cm⁻³, $R \sim 5$ nm this lower bound should be ~ 10 sec, although its true value may be several orders larger. If one takes v = 10, then the lower limit for t_{10} exceeds 10^3 sec. This time is already macroscopically large, even without mentioning the true value of t_{10} which may be a huge quantity. This estimate justifies the picture of a particle with a fixed number of atoms.

If the number of atoms in the particle is conserved, and there is no vapor, the free energy F of the particle should depend on S and the number N of atoms in the particle. This property of the free energy resembles the free energy of the particle-vapor system (Sec. 2.1). But the dependence of F on the total volume of the system should be replaced by its dependence on the volume of the particle $V \equiv V_c$. Taking into account the fact that, at the volume given, the surface free energy F_s must be proportional to S, one can write (Refs. 66, 189)

$$F_{\rm S} = \alpha(V, N, T) \ S = \alpha(N/V, T) \ S.$$
 (2.12)

The second of equalities (2.12) follows from the condition that the surface tension α should be a zero order homogeneous function of the additive variables N and V. Basically important is the fact that α is a function not of a fixed total volume V_t but of the particle volume V which itself should be determined from the condition of minimum free energy.¹⁾ For this reason the quantity α in Eq. (2.12), unlike that in Eq (2.1), cannot be regarded as constant at a given temperature: it depends on the particle deformation the role of which is played by a uniform compression or dilatation.

Detailed dependence of α (2.12) on the atomic density n = N/V is determined by concrete physical models. As particular cases, Eq (2.12) allows proportionality of F_s to the surface area as in Eq. (2.1) or to the total number of the surface atoms determined by the equation

$$N_{\rm S} = S n^{2/3}, \tag{2.13}$$

(unlike the standard two-phase thermodynamics, N_s does not mean the number of atoms in the interphase layer. All the N_s belong to the same condensed phase as the rest of atoms). If one assumes that $\alpha \sim n^{2/3}$ one can write instead of Eq (2.1)

$$F_{\rm S} = \nu N_{\rm S}, \ \nu = \text{const.} \tag{2.14}$$

with c being constant at a given temperature. The particular cases (2.1) and (2.14) are equivalent only when the surface area changes while the particle density is kept constant. Then the change in the area is proportional to the change in the number of surface atoms. Certainly, such a process should lead to a change in the particle shape. Another way of changing the area consists in changing the density without changing the shape. In this case knowledge of the *n*-dependence of α is vitally important, and Eqs. (2.1) and (2.14) are incompatible.

If a spherical particle of radius R is placed in vacuum or in a gas of another chemical nature with the pressure small compared to the pressure p_c inside the particle, then the pressure p_c should be found from the condition of minimum free energy

$$F = F_{\rm c} + \alpha(n)S. \tag{2.15}$$

with respect to R with allowance for the equality $p_c = -\partial F_c / \partial V^{(2)}$

$$p_{\rm c} = \frac{2\gamma}{R}, \ \gamma = \alpha - \frac{3n}{2} \frac{\mathrm{d}\alpha}{\mathrm{d}n}.$$
 (2.16)

By analogy with Eq. (2.6), the quantity γ in Eq. (2.16) might be called the surface stress of the liquid. If the liquid is in thermodynamic equilibrium with its vapor, the surface tension and stress coincide.

According to Eq. (2.16), the pressure p_c coincides with

the Laplace pressure (2.2) only when α is independent of n. On the contrary, if the coefficient c in (2.14) is constant, the pressure inside the particle vanishes. But if the inequality

$$\frac{\mathrm{d}\alpha}{\mathrm{d}n} > \frac{2}{3} \frac{\alpha}{n}, \qquad (2.17)$$

is met, then the surface forces dilate instead of compressing the particle. Physically, dilatation occurs as, due to the inequality (2.17), on an increase in R, S increases slower than α decreases. Thus, F_S (2.12) also decreases.

Differentiating F with respect to N with S kept constant and going over from $\mu_c(n)$ to $\mu_c(p_c)$, one obtains the following expression for the chemical potential of the particle (cf (2.3)):

$$\mu_{\rm c} = \mu_0(p_{\rm c}) + \frac{3}{R} \frac{{\rm d}\alpha}{{\rm d}n} \simeq \mu_0(p_{\rm L}) \;, \qquad (2.18)$$

where p_L is the Laplace pressure.

The result (2.18) in the zero order approximation in n_g/n coincides with the well-known expression for the chemical potential of a particle in thermodynamic equilibrium with its vapor (2.3) regardless of the character of the *n*-dependence of α . But, unlike the latter, in the general case Eq. (2.18) cannot be interpreted in such a way that the size-dependence of μ_c is caused only by the Laplace pressure acting inside the particle. According to Eq. (2.16) such an interpretation is adequate only in the case when Eq. (2.1) holds, i.e., when $p_c = p_L$.

One should remember that Eq. (2.18) is obtained only for spherical particles. For particles of other shapes μ_c cannot be directly related to p_L even if Eq. (2.1) holds. As pointed out in Sec. 1.3, nonspherical particles are only partially in equilibrium. The chemical potential of such particles is a well defined quantity if the relaxation time for the shape of the particle greatly exceeds all other characteristic times. According to Ref. 2, the free energy of finite-size isotropic samples should depend on their surface area S. It loses the property of additivity with respect to N as the atoms on the surface are under different conditions than the bulk ones. For this reason the Gibbs free energy Φ is not a first order homogeneous function of N, and the equality $\Phi = \mu N$ does not hold for such systems. Correspondingly, one should assume that, besides p and T, μ should depend also on S and N. At $S/N \rightarrow 0$ this dependence should disappear. Thus, in the first order in S/N one may write

$$\mu = \mu_0 + \frac{2\alpha}{3} \frac{S}{N} .$$
 (2.19)

The coefficient in front of S/N in the second term in Eq. (2.19) is chosen from the condition that Eq. (2.19) should reduce to Eq. (2.18) for spherical particles.

As seen from (2.19), the size shift of the chemical potential is minimum at the equilibrium shape. It is nonzero even for systems with $p_L = 0$ (thin films). This means that in reality this shift is caused not by compression of the sample under surface forces, but by the very fact of the existence of surface atoms which are under conditions different from those for the bulk ones.

This is still more evident in the case of validity of Eq. (2.14) when according to Eq. (2.16) the pressure is zero inside the particle. Then the physical meaning of the result obtained for μ_c is deciphered by the binomial formula in Eq.

(2.18). The first term in this expression is the chemical potential of an infinitely large sample at the acting pressure $p_c = 0$ and the second term is a correction to it caused by surface atoms. In fact, it is proportional to the product of the relative number of the surface atoms N_S/N determined by Eq. (2.13), and the difference of the energies of a surface and a bulk atom proportional to α .

Thus, the Laplace pressure in the case under consideration is not a real physical force but a formal quantity which makes it possible to express the chemical potential of a finitesize sample μ_c in terms of that of an infinite-size sample μ_0 . The formal character of the Laplace pressure in Eq (2.18) manifests itself especially strongly at a sufficiently large $d\alpha/dn$: an apparent paradox occurs as the particle dilates but the size shift of its chemical potential imitates compression of the particle under the Laplace pressure.

Thermodynamic results of this Section will be confirmed by microscopic models in Secs. 2.4 and 3.6.

2.4. An atomic model of a crystal in vacuum and the chemical potential of atoms in crystalline particles

First, a microscopic model of a crystal will be discussed which exhibits neither surface nor bulk spontaneous sizedependent deformations. This model may be juxtaposed to phenomenological theories of Secs. 2.2, 2.3 simultaneously. A crystal is considered with a simple cubic lattice in which the potential energy of interatomic interaction U(a) goes through a minimum at a_0 and then sharply goes to zero as the atomic spacing a grows. Thus, only the interaction between the first nearest neighbors is essential. To make the picture maximally clear, it will be assumed that all the crystal faces are of the (100) type. For such a geometry the surface energy per atom is equal to the energy of its bond with the nearest neighbor broken by the surface. If the interatomic distances in the directions x and y along the surface subjected to a deformation **u** are equal to $a_x = a_0 (1 + u_{xx})$ and $a_{y} = a_{0} (1 + u_{yy})$ respectively one can write for the surface energy in the linear approximation in u_{xx} and u_{yy} :

$$E_{\rm S} = -U_0 N_{\rm S} = \alpha(u_{xx}, u_{yy}) S, \qquad (2.20)$$

$$\alpha(u_{xx}, u_{yy}) = \frac{|U_0|}{a_x a_y} \approx \frac{|U_0|}{a_0^2} (1 - u_{xx} - u_{yy}) U_0 = U(a_0, 0, 0),$$

where N_s is the number of surface atoms. In writing Eq. (2.20) account was taken of the fact that U depends on a_z which is equal to a_0 here.

In this nearest neighbor model the equilibrium distance between atoms is a_0 irrespective of the crystal size and shape. As Eq. (2.20) is a microscopic analog of Eq. (2.14), this provides a confirmation, in microscopic terms, of the thermodynamic theory presented in Sec. 2.3. According to it, in a system with the surface energy (2.14) the size-dependent deformation under surface forces should be nonexistent which is just the case for the model considered here.

On the other hand, the absence of a size-dependent deformation may be associated with the fact that in the model under consideration the surface stress tensor goes to zero according to Eqs. (2.6), (2.20). One should keep in mind that the notion of surface stress is valid not only for the case when the crystal is in thermodynamical equilibrium with its surroundings but also for the case of the crystal in vacuum. Though the crystalline particle is undeformed by the

surface forces in the model considered, the chemical potential of atoms in it, nevertheless, is size-dependent. But this size dependence sharply differs from that described by Eq. (2.10) which holds for the cases when the particle is in equilibrium with its environment. This statement will be proved in what follows, and it will be confirmed that the size-dependence of μ is caused not by the surface forces deforming the particle but by the very fact of presence of surface atoms whose energy of interaction with neighbors differs from that for the bulk atoms. (This statement is made in Sec. 2.3).

In calculating μ it should be borne in mind that, generally speaking, the thermodynamic relation $\mu = \partial F / \partial N$ cannot be applied to crystals because their free energy F is a nonanalytical function of the number of atoms N. The origin of this nonanalyticity is the fact that the atoms in the crystal may be located not only in regular sites but also in irregular positions (interstitial atoms and protruding atoms on the surface). The energy of atoms at regular sites is different from that at irregular sites. At T = 0 an atom can be added to the crystal only by placing it in an irregular position and removed only from a regular site of the crystal. Therefore

$$\left(\frac{\partial F}{\partial N}\right)_{+} = F(N+1) - F(N)$$
(2.21)

is not equal to

$$\left(\frac{\partial F}{\partial N}\right)_{-} = F(N) - F(N-1),$$

i.e., $\partial F / \partial N$ is not determined because there is a gap in the energy spectrum of the crystal equal to the difference between the energies of atoms in the irregular and regular positions.

Thermodynamics can be applied only if the transfer of atoms from regular to irregular positions may be neglected. This is precisely the case when atoms leaving the regular sites of the crystal into the environment play the dominant role, i.e., in the situation corresponding to Eq. (2.10). But if the saturated vapor is practically nonexistent the chemical potential should be found from the statistics. It must be of the same type as the statistics of electrons in semiconductors where the Fermi level is determined from the balance of numbers of elementary excitations. The interstitial atoms (analogs of the electrons in the conduction band) and vacancies (analogs of the holes) play the part of elementary excitations.³⁾ Since their numbers are small the Boltzmann distribution function is used with allowance for the fact that the sign of the energy and chemical potential of the vacancy is opposite to their sign for the atom.^{67,189,190}

Assuming that all the faces of the crystal are the same, μ can be determined from the condition that the number of bulk and surface vacancies be equal to the number of atoms in irregular positions (bulk and surface interstitial atoms and protruding atoms on the surface):

$$N_{\rm V} \exp \frac{\varepsilon_{\rm r} - \mu}{T} + N_{\rm S} \exp \frac{\lambda_{\rm r} - \mu}{T} = k N_{\rm V} \exp \frac{\mu - \varepsilon_i}{T}$$
$$+ \varkappa N_{\rm S} \exp \frac{\mu - \lambda_i}{T} + N_{\rm S} \exp \frac{\mu - \lambda_i}{T}, N_{\rm V} = N - N_{\rm S}. (2.22)$$

Here ε_r and λ_r are the energies of an atom in a regular site in the bulk and on the surface, respectively. Further, ε_i , λ_i and λ_e denote the energies of interstitial atoms in the bulk, on the surface and of a protruding atom on the surface, respectively. Notations k and \varkappa are used for the numbers of interstices per elementary cell in the bulk and on the surface, respectively. It is assumed that the number of atoms entering the surface from the bulk is small compared with the number N_s of sites of the first surface layer. This condition is, certainly, met for particles with sizes less than 100 nm. It is assumed also, that the roughening of the surface does not occur.

According to Eq. (2.22) in the high-temperature limit the surface part μ_s of the chemical potential proportional to the number of surface atoms N_s is a small correction to its bulk part μ_V :

$$\mu = \mu_{\rm V} + \mu_{\rm S}, \quad \mu_{\rm V} = \frac{1}{2} (\epsilon_{\rm r} + \epsilon_{\rm i} - T \ln k), \quad (2.23)$$

$$\mu_{\rm S} = \frac{T}{2L} \left(\exp \frac{\lambda_{\rm r} - \epsilon_{\rm r}}{T} - \frac{\varkappa}{k} \exp \frac{\epsilon_{\rm i} - \lambda_{\rm i}}{T} - \frac{1}{k} \exp \frac{\epsilon_{\rm i} - \lambda_{\rm i}}{T} \right)$$

$$L = \frac{N}{N_{\rm S}}. \quad (2.24)$$

Although μ_s (2.24) is proportional to 1/L this is the only similarity between Eq. (2.23) and Eqs. (2.10), (2.19): their dependences on the temperature and the surface tension $\alpha = (\lambda_r - \varepsilon_r)/a^2$ are quite different. In addition to α , μ_s depends also on the energies of atoms in irregular positions.

Still more drastic is the difference between μ determined from Eq. (2.22) and that given by Eqs. (2.10), (2.19) in the low-temperature limit. If $\varepsilon_i > \lambda_i$, λ_e , then the leading term in the expression for μ is the surface one, μ_s . The bulk term μ_V gives a small correction to it which is ensured by the obvious inequality $\lambda_r > \varepsilon_r$:

$$\mu = \mu_{\rm S} + \mu_{\rm V},$$

$$\mu_{\rm S} = \frac{\lambda_{\rm r}}{2} - \frac{T}{2} \ln \left[\varkappa \exp(-\lambda_i / T) + \exp(-\lambda_l / T) \right], \qquad (2.25)$$

$$\mu_{\rm V} = -\frac{TL}{2} \left\{ k \left(\exp \frac{\varepsilon_i}{T} \right) \left[\varkappa \exp\left(-\frac{\lambda_i}{T}\right) + \exp\left(-\frac{\lambda_l}{T}\right) \right]^{-1} - \exp\left(\frac{\varepsilon_r - \lambda_r}{T}\right) \right\}. \qquad (2.26)$$

A nontrivial size-dependence of μ (2.25) attracts attention: μ is linear in L, and not in 1/L. But the limit $L \rightarrow \infty$ is impossible in (2.26) since at L large enough the bulk term becomes dominating so that transition to Eq. (2.23) should occur.

At $\varepsilon_i < \max{\{\lambda_i, \lambda_e\}}$ the chemical potential cannot be separated into the bulk and surface parts. Such exotic terms as ln L appear in the size dependence of μ :

$$\mu = \mu_0 + \mu_1 \quad (\mu_0 >> \mu_1), \qquad (2.27)$$

$$\mu_0 = \frac{1}{2} \left[\lambda_r + \varepsilon_i - T \ln(kL) \right], \qquad (2.17)$$

$$\mu_1 = \frac{T}{2} \left[L \exp \frac{\varepsilon_r - \lambda_r}{2} - L^{-1} \left(\frac{\varkappa}{k} \exp \frac{\varepsilon_i - \lambda_i}{T} + \exp \frac{\varepsilon_i - \lambda_l}{T} \right) \right].$$

Finally, at intermediate temperatures, if $\varepsilon_i > \lambda_i$, λ_e , the situation is possible when the following relationship holds:

$$\mu = \mu_0 + \mu_1 \qquad (\mu_0 \gg \mu_1),$$

$$\mu_0 = \frac{1}{2} \left\{ \varepsilon_r - T \ln \left[\varkappa \exp \left(-\frac{\lambda_l}{T} \right) + \exp \left(-\frac{\lambda_l}{T} \right) \right] + T \ln L \right\},$$
(2.28)

$$\mu_{1} = \frac{T}{2} \left\{ L^{-1} \exp \frac{\lambda_{i} - \varepsilon_{r}}{T} - kL \exp \left(-\frac{\varepsilon_{i}}{T}\right) \left[\varkappa \exp \left(-\frac{\lambda_{i}}{T}\right) + \exp \left(-\frac{\lambda_{l}}{T}\right) \right]^{-1} \right\}.$$
(2.29)

As L increases, Eqs. (2.27), (2.28) also become inapplicable. Thus, Eqs. (2.26 to 2.29) are valid only for L not too large the range of which narrows with increasing temperature. As follows from these expressions, the chemical potential may not only increase but also decrease, on a decrease in L. The chemical potential of the electron gas also possesses this property, (Sec. 3.5).

It is assumed in the current theory of sintering of small particles that the vacancy density in the particle follows the same Thomson law as the density of the saturated vapor (it is $\exp(p_L/n_c T)$ times larger than over a flat surface²). Results (2.23 to 2.29) show that this assumption is not fulfilled in reality. Thus, the sintering theory should be revised.

If one carries out a calculation for two or more particles similar to (2.22) one finds that stationary states of such systems are possible which correspond to transfer of a relatively small number of atoms between particles of different sizes. Such a transfer makes it possible to equalize the chemical potentials of particles of different sizes. Certainly, such stationary states are metastable since the stability is reached when the particles coagulate. But they may influence the kinetics of coagulation.¹⁹⁰

It is worth noting that if one "forbids" transfer of atoms from regular to irregular sites and "allows" their exit from the crystal into their environment, then an expression for the chemical potential obtained similarly to Eq (2.22) reduces to Eq (2.3) only for

$$\lambda_{\rm r} - \varepsilon_{\rm r} \equiv \alpha S / N_{\rm S} << T \,. \tag{2.30}$$

In fact, if one assumes that the total number N_g of atoms in the gas phase is small compared with the number N_s of the surface atoms in the particle, and numbers of atoms in irregular positions are small compared with N_g , one obtains:

$$\mu = \mu_0 + T \ln \left\{ 1 + \left[\exp\left(\alpha a^2 / T \right) - 1 \right] L^{-1} \right\} / 2, \quad (2.31)$$

where μ_0 is the size-independent part of μ . Since αa^2 for real crystals is of the order of 1 eV, the inequality (2.30) is absolutely unrealistic. Apparently, the difference between Eqs. (2.3), (2.10), on one hand, and (2.30) on the other hand, is caused by the circumstance that the condition (2.3a) fails in the case considered.

One might expect that results obtained above may be extended to liquid particles, if one neglects the difference between the energies of regular and irregular positions, i.e., if one puts $\varepsilon_r = \varepsilon_i$ and $\lambda_r = \lambda_i$. But the relationship (2.18) may be obtained from Eqs. (2.23), (2.24) only if the condition (2.30) is also met.

Further development of the theory presented here should consist in taking surface roughening into account.

2.5. Melting and quasimelting of small particles

The section devoted to the thermodynamics of small particles should be completed by a discussion of the phase transitions in them. Strictly speaking, the notion of a phase transition has only an approximate meaning for them since genuine phase transitions may occur only in infinitely large systems. It is just in this sense that one should understand Pawlow's statement²³³ that the melting temperature T_m of a particle decreases with its size. The corresponding result may be readily obtained by equating to each other the chemical potentials of the solid and liquid phases. For them the expression (2.3) is used with corresponding parameters. Their expansion in terms of temperature and pressure in the vicinity of the melting point T_{m0} of a bulk sample with allowance for the thermodynamic relations

$$s_i = \partial \mu_i / \partial T$$
, $n_i^{-1} = \partial \mu_i / \partial p$,

leads to the result

$$(T_{\rm m}/T_{\rm m0}) - 1 = 2Q^{-1} \int (\alpha_2/n_2R_2) - (\alpha_1/n_1R_1)$$
, (2.32)
 $Q = T_{\rm m0}(s_2 - s_1),$

where s_i is the entropy of the *i*th phase per atom, the subscript 1 corresponds to the solid, and the subscript 2 to the liquid state. The surface tension α_2 for the liquid is essentially lower than that for the solid, α_1 . But the densities of both phases are close to each other. For this reason T is lower than T_{m0} .

This result has been confirmed by numerous experimental investigations. The melting points of thin films of Pb, Sn and Bi are considerably lower than those of the corresponding bulk samples, and very large supercooling which amounts to 20-30% was observed in them, on a decrease in temperature.²³⁴ Still earlier an anomalously large super cooling of Sn films was observed in Ref. 235. Lowering of the melting point was observed in investigating small particles of Sn (Ref. 236), Pb, In (Ref. 237), Ag, Cu, Al (Ref. 238), In (Ref. 239), Au, Ag (Ref. 240), Au (Ref. 241). The data of the last paper are reproduced in Fig. 6.

But one may expect that the specific features of melting of small particles cannot be reduced to only lowering of the melting point. As they are spatially-nonuniform, their melting may begin from their surfaces. This idea was confirmed by a computer simulation of the melting of particles consisting of several hundreds of gold atoms.²⁴² It was established that if the number of atoms exceeds 350, liquid skin appears on the surface as a precursor of the melting. A sharp decrease of the melting temperature with size was found in Ref. 242. Surface melting was found also by calculations performed in Refs. 243, 244. It exists if there is no reconstruction of the surface.



FIG. 6. Dependence of the melting point of Au particles on their size.²⁴¹

Experimentally, surface melting was observed in Refs. 245, 246 where Pb films were studied. Surface melting begins at 0.75 T_{m0} and the thickness of the melted layer increases with approaching to T_{m0} . The effect was observed also in Ar (Ref. 247), O₂ (Ref. 248), Ge (Ref. 249), Ne (Ref. 250).

A quite different physical picture of the melting of small particles was advanced in Ref. 251. Clusters containing a specific number of atoms N, may exhibit a sharp lower limit of temperature, T_{f} , for the thermodynamic stability of the liquid form and a higher sharp upper limit T_m for the thermodynamic stability of the solid form. Consequently, a collection of N-atomic clusters in thermal equilibrium acts as a statistical ensemble which, at temperatures and pressures within the coexistence region, behaves like a mixture of the two kinds of clusters: some solid and some liquid. Being in thermal equilibrium, these forms occur in a ratio K= [solid]/[liquid] = exp($-\Delta F/T$) fixed by the difference in free energy ΔF between the solid and liquid forms. But this is a dynamic equilibrium, with individual clusters passing between the two forms. If the two forms are to be observed coexisting in equilibrium like two phases or two chemical isomers, the mean frequency of passage between them must be low enough for the cluster to establish equilibrium values of their characteristic properties.

Results of Ref. 251 were obtained analytically by an analysis of the density of states of the cluster. The limiting temperatures T_f and T_m correspond to achievement by the free energy of a minimum or a maximum. In various papers (e.g. Ref. 252) results of computer simulations are described which confirm Berry results.²⁵¹ As for experimental confirmation of the Berry theory, possibly, it is given by the results of Ref. 253. It was found there that spectra of benzene-Ar_n clusters with the number of atoms between 18 and 25 showed both broad and sharp features in their spectra. These spectral features do not shift with temperature, and the sharp features become dominant as the temperature is decreased.

The Berry picture resembles a very interesting physical effect observed in small Au particles well below the melting point. If particle sizes are intermediate between stability ranges of single crystals and multiply-twinned crystals (Sec. 1.1) transitions from the single crystal to the multiply-twinned structure and reverse were observed when Au particles on the SiO₂ substrate were excited by an electron microscope beam. The lifetime of the structure was about 0.1 sec for a 2 nm particle. But the rate of fluctuations diminishes with increasing particle size, and beginning from 10 nm, the fluctuations disappear. The changes in the structure described above were accompanied by particle rotation or a motion of translation over the substrate.¹⁰⁴ Similar results were obtained in Ref. 254.

A theory of such a quasimolten state was developed in Ref. 96. But there were some doubts whether the effect observed in Ref. 104 is a genuine quasimelting or is caused by the electron beam which not only probes the particles but also charges and excites them. To elucidate the nature of the effect, an experimental investigation was carried out in Ref. 97. It was demonstrated that small Au particles on a MgO substrate sit in deep potential wells. The electron beam makes them leave these potential wells. Having become practically free the particles can quasimelt making transitions between various local minima on the shallow morphological free energy surface. The particles retain the unstable state for long intervals of time until they find another well on the substrate in which they can form a stable Wulff polyhedron shape. Fluctuation frequencies of 1 to 10 Hz were observed for 2 nm particles in agreement with Ref. 104.

Structure fluctuations observed in Refs. 104, 97 are characterized by macroscopic times. Thus, a question arises of whether they provide an example of macroscopic quantum tunneling discussed in Sec. 4.7 in connection with magnetic particles as appropriate objects for this phenomenon.

3. DENSITY OF STATES AND CHARACTERISTIC ENERGIES OF CONDUCTION ELECTRONS IN SMALL PARTICLES

3.1. Size-dependent oscillations of the shape and Fermi energy of almost-spherical particles

Specific features of the electron states in finite-size samples are determined by the spatial quantization of their levels. The quantization is expressed most clearly in spherical particles since due to a high degree of level degeneracy the level spacing is especially large in them. It will be shown in what follows that, in addition to the well known size-dependent oscillations of thermodynamic quantities,¹³⁸ quite other size-dependent oscillations are possible: oscillations of the shape of the particle.

At first glance, in the absence of external forces the equilibrium shape of liquid particles should necessarily be spherical. But in reality it may turn out to be unstable for metal particles, since their surface energy has a singularity for this shape due to the high degree of degeneracy of the electron levels. Indeed for liquid metals, as a rule, the almost-free electron approximation is quite adequate. For this reason each electron level is (2l + 1)-fold degenerate with respect to the projection m of the orbital angular momentum. If the radius R of the particle is small compared with the the electron wavelength k^{-1} , the typical orbital quantum number l is of the order of kR. Thus, the possibility arises to diminish the electron energy of the system by lowering its symmetry, i.e., by lifting the degeneracy. This should occur if the highest electron level is filled only partially.

On an increase in the number N of electrons, when the level with a given l becomes filled completely, the spherical symmetry should be restored, i.e., and then again disappear when a new partially filled level appears, i.e., the deformation of the shape is an oscillating function of N. In reality, an increase of N occurs as a result of an increase in R. Although the electron levels $\mathscr{C}_{nl}(R)$ are R-dependent their systematics does not change in the zero order approximation in deformation. For this reason states with different sets of quantum numbers (n,l,m) become occupied in the same sequence as for a constant R. But one should speak of shape oscillations as a function of N.¹⁸

This specifically quantum effect, in principle, may be observed even at temperatures so high that the metal is in the liquid state. This is caused by the fact that the level spacing in a spherical particle amounts to $\mu/k_F R$ where μ and k_F are the Fermi energy and momentum, respectively. For $\mu \sim 10$ eV, $k_F R \sim 10$ this spacing may reach values from 10³ to 10⁴ K. The situation becomes still more favorable for observation of this version of the Jahn-Teller effect due to the circumstance that small metal droplets may be supercooled by 30 to 50% in comparison with the melting point.¹³⁷

The fact that the surface energy of a spherical particle is not proportional to its surface area is reflected in size-dependent oscillations of the Fermi energy. Investigation of these oscillations is interesting by itself since they differ from their analog in thin films¹³⁸ by their quasistochasticity. It is caused by the fact that the electron energy in small particles depends on two quantum numbers n and l simultaneously. An analysis of the sequence of quantum levels in the spherical potential well shows no explicit regularity in the change in quantum numbers n and l with a change in the energy \mathscr{C}_{nl} in the case of its low values.¹⁹ The role of two independent variables in the appearance of a quasistochastic behavior is supported also by the well-known fact that such behavior displays the sum of two periodical functions with incommensurable periods.

The model of free electrons in an infinitely deep potential well will be used.¹⁸ In this model the electron momentum k is given by $k = \rho_{\ln}/R$ where ρ_{\ln} is the *n*-th root of the Bessel function $J_{l+1/2}(x)$. At $l \ge 1$ the approximate expressions for ρ_{\ln} are valid:

$$\begin{split} \rho_{ln} &\approx \pi n + (\pi l/2) \qquad (n >> l), \\ \rho_{ln} &\approx l \left\{ 1 + 2^{-1/3} (3\pi n/2l)^{2/3} \right\} \qquad (3.1) \end{split}$$

Oscillations of μ are a consequence of the fact that $\rho_{\rm ln}$ is independent of R. In fact, on an increase in R, the value of $\rho l_{\rm F} n_{\rm F}$, corresponding to μ remains constant at T = 0 as the radius changes by $\delta R = l_{\rm F} (l_{\rm F} + 1)/2\pi\nu R^2$ where ν is the electron density. For this reason the Fermi energy $\mu = \rho_{l_{\rm F} n_{\rm F}}/2mR$ in this range of R diminishes by an amount $\delta \mu \sim \mu \delta R / R \sim \mu (k_{\rm F} R)^{-3}$.

On a further increase in R, the Fermi level jumps up as the electrons begin to fill the next higher energy level. According to Eq. (3.1), states with n < l will be preferentially occupied. Thus, the value of $l_{\rm F}$, corresponding to μ , is of the order of $k_{\rm F}R$. The maximum jump of μ is achieved when the level (1, $l_{\rm F} + 1$) becomes occupied after the level (1, $l_{\rm F}$). This jump, being of the order of $\mu/k_{\rm F}R$ is as large as the parameter $k_{\rm F}R$ in comparison with a similar jump in a thin film.

The Jahn–Teller deformation of the sphere ε is found from the condition of minimum total energy consisting of the energy of the higher occupied electron level and the surface energy αS .¹⁸ Here S is the surface area, α is the surface tension determined by the ions and the electrons of the inner completely occupied electron shells. The assumption seems quite natural that the deformation should be uniaxial and occur without a change in the volume of the particle. Then the principal axes of the ellipsoid obtained from the sphere of R are of length radius $c = R(1+2\varepsilon)$ and $a = b = R(1 - \varepsilon)$. Then the change in the energy due to the deformation is related to the change δS in the surface area by the formula

$$\delta E = \alpha \, \delta S - k(n_0 l_0 m_0) (\, \delta S\,)^{1/2}. \tag{3.2}$$

An expression for the coefficient k(nlm) corresponding to a uniaxial deformation is given in Ref. 19:

$$k(n_0 l_0 m_0) = \frac{l(l+1)}{(2l-1)(2l+3)} \left[\frac{3m^2}{l(l+1)} - 1 \right] \delta_{nl}, \quad (3.3)$$

where \mathscr{C}_{nl} is the unperturbed energy of the level with quan-

tum numbers n and l. It is meant that these quantum numbers in Eq. (3.2) correspond to the Fermi energy.

If there are $2(2m_0 + 1)$ electrons in the upper shell, then one obtains from Eqs. (3.2), (3.3) the following expression for the deformation:

$$\varepsilon = \frac{5l(l+1)(2m_0+1)\mu}{14\alpha S_0(2l-1)(2l+3)} \left[1 - \frac{m_0(m_0+1)}{l(l+1)}\right].$$
 (3.4)

As seen from Eq. (3.4), if the highest level is occupied only partially the deformation is nonzero and positive. This means that the shape of the particle is a prolate ellipsoid. The deformation vanishes at the complete filling of the highest level. The deformation goes through a maximum at $\tilde{m}_0 \approx l_F / \sqrt{3}$. According to Eq. (3.3) the Fermi level does not practically shift at this m_0 but its filling decreases sharply: the electrons go over from it to lower components of the multiplet split by the deformation. Moreover, at larger fillings the deformation causes not lowering but, on the contrary, raising of the Fermi level. Nevertheless, the total electron energy decreases.

On an increase in the particle size, the deformation (3.4) diminishes as $\tilde{m}_0/S_0 \sim 1/R$. For this reason it may be noticeable only in small particles. At $\alpha = 60 \text{ erg/cm}^2$, (as in liquid Cs), $R = 5 \text{ nm}, \mu = 5 \text{ eV}, \nu = 10^{22} \text{ cm}^{-3}$ the quantity ε may reach 10%. The spontaneous deformation influences many properties of small particles. In particular, it enhances their capacity by 2ε times.

Earlier²² the possibility of ellipsoidal deformation of metal clusters consisting of a relatively small number of atoms was pointed out although it is not clear to what extent the spherical or ellipsoidal model is applicable to them at all. A corresponding calculation was carried out by analogy with that for nonspherical nuclei in the theory of the atomic nucleus. The one-electron potential used in Ref. 22 included several adjustable parameters. Only small *n* and *l* were treated which made it possible to establish the sequence of levels with different *n* and *l*. In contrast to theory of Ref. 19 according to Ref. 22 ellipsoids may be both prolate and oblate. Similar results were obtained in the jellium model.²⁵⁵

According to Ref. 22, the ellipticity should markedly increase the polarizability of small particles. It should manifest itself still more strongly in anisotropy of light scattering in plasma or liquid if an external electrical field is applied.

Elliptic deformation may play an important role for generation of cooperative electric dipole excitations of the type of surface plasmons in small particles as was discovered in Ref. 139. It was pointed out in Ref. 140 that in ellipsoidal particles of such metals as Na, a specifically quantum magnetic state is possible. The magnetism should be of orbital nature of the same type as in nonspherical nuclei. It is caused by a rotation of the electron system as a whole relative to the particle shell.

3.2. Electron level distribution in particles with bulk or surface imperfections.

If a sample is of a nonsymmetrical shape, then even in the absence of impurities the systematics of levels in it is very complicated. Still more complicated is the situation, if the sample is imperfect: bulk and surface imperfections jumble up the systematics. But not all problems demand that the density of states be completely known. For many important problems it suffices to know the correlation function between the nearest energy levels: the ground and the first excited levels. If one assumes that the probability $p(\omega)$ of the distance ω between the nearest neighboring levels is a continuous function of ω due to the level randomness, one may think that at $\omega \ll \delta \sim \mu/N$ the probability depends on ω according to a power law. The exponent *n* in the law $p \sim \omega^n$ may be determined from some general considerations. One may advance plausible hypotheses in order to guess the value of *n*. Naturally, the proportionality coefficient can be determined only by a direct calculation.

Considerations which make it possible to determine n, have already been passing for more than two decades since the publication of the pioneering papers on the subject (Refs. 78, 79, 81, 85, 203), from one review article to another. Hence, it is not reasonable to reproduce them again. The excellent review article of Ref. 129 may, for example, be recommended to become acquainted with them. But it makes sense to undertake a test of the statistical hypotheses adopted in these papers by making some quantum-mechanical calculations and by computer simulations (according to Ref. 78 n = 0, according to Ref. 203 n = 1,2 or 4).

The main question is, to what extent is the Kubo hypothesis justified, according to which there are no correlations in the level distribution (n = 0), or is the theory of Ref. 203 more favorable according to which level repulsion exists $(n \ge 1)$. It might seem that the Kubo hypothesis is supported by exact quantum-mechanical results obtained using a one-dimensional model of a particle moving in a random potential.⁸⁴ A rigorous proof of the inapplicability of the Dyson statistics²⁰³ to disordered one-dimensional systems is given in Ref. 282.

Quite similarly, the Poisson distribution for the energy levels (n = 0) is obtained for an ensemble of rectangular potential wells inside of which the electrons move.⁸² But the variables are separable in this model, and practically it also reduces to a one-dimensional model. On the other hand, the adequacy of results obtained for one-dimensional models for real three-dimensional particles is by no means self-evident.

In the opinion of the present author, papers of Refs. 76, 77, 83 deserve special attention. As shown in them, the theory of random matrices²⁰³ forming the basis for the theory of electron spectra of small particles⁷⁹ is valid in the limit of their very strongly imperfect surfaces. In Ref. 83 a coordinate transformation is introduced which transforms a particle of an arbitrary shape not very strongly differing from spherical into an exact sphere. After this transformation a term playing the part of an effective potential is added to the initial free-electron Hamiltonian. This effective potential is taken into account to the second order of perturbation theory. The difference of the initial shape of the particle from spherical is described by a linear combination of spherical harmonics. Its coefficients are considered as independent random variables for an ensemble of particles. If the surface is very rough (all the harmonics enter the linear combination with weights of the same order of magnitude) the energy level distribution corresponds to that predicted by the random matrix theory.²⁰³ But if the surface becomes smoother (the low order harmonics dominate), the level distribution differs from the Dyson one very strongly.

The same results were obtained in Ref. 77 analytically by an analysis of the stochastic equation of motion for random matrices occurring in an orthogonal ensemble. But, possibly, this coincidence is merely a consequence of the fact that appropriate assumptions were made in Ref. 77.

The paper of Ref. 80 is a very important one. In it the two-level correlation function is calculated for a particle with a regular surface but with a randomly fluctuating potential in the bulk. In the special version of the quantummechanical treatment adopted in Ref. 80 the correlation function is expressed in terms of a convolution of advanced and retarded Green's functions of the one-electron problem. Unlike the density of states, the correlation function diverges if it is calculated by an expansion in powers of the random potential. This difficulty was circumvented by using the supersymmetry method which makes it possible to find the correlation function $p(\omega)$ under the conditions $\tau \mu \gg 1$, $\delta \ll \tau^{-1}$ where τ is the electron mean free time. It coincides with the results of the theory of random matrices.²⁰³ In particular, the correlation functions for all three ensembles appearing in the Dyson theory (orthogonal with n = 1, unitary with n = 2 and symplectic with n = 4) turn out to be universal functions of the mean level spacing δ independent of the scattering potential.

But the results of Ref. 80 were obtained using a very particular model in which the scattering potential was assumed to be delta-correlated with the zero average value. Apparently, proof is still required that there exist physical situations described by this model (in Ref. 80 this question is not discussed). Nevertheless, the results of Ref. 80 provide evidence that the Dyson theory may be applicable in some cases in contradiction to the opinion that it is inapplicable at all, expressed in Ref. 205.

At the same time, the results of Ref. 80 reveal also the nonuniversality of the Dyson statistics. In fact, going beyond the framework of the Born approximation leads to a nonDyson form for the correlation functions, i.e., the Dyson statistics does not work in the case of strong electron scattering. Apparently, for its applicability a lower bound for the scattering intensity should exist. Therefore, one cannot take for granted the possibility to use the Dyson statistics for small particles in every case. Every time one should prove that conditions for its applicability are met for a concrete ensemble of small particles.

As an example of microscopic calculations which do not fit within the Dyson statistics, the paper of Ref. 202 may be pointed out. In it a calculation is carried out of the level distribution in small particles in the limit of weak electron scattering by bulk or surface impurities when the shift in the level positions caused by impurities is small in comparison with the mean level spacing. Attention is drawn to a very important fact: if a sample is of a nonsymmetrical shape (e.g., rectangular parallelepiped with unequal sides), then its levels are nondegenerate even if the crystal is perfect. Therefore, the problem of level repulsion caused by impurities does not exist. But if a sample is of a symmetrical shape (e.g. two or even three sides of the parallelepiped coincide), then the unperturbed levels are degenerate, and a nonmagnetic impurity causes their repulsion with $p(\omega) \sim \omega$. But, in all other respects, the correlation function obtained in Ref. 202 differs from the Dyson one. In particular, it is not universal and the level correlation length depends on the number D of defects and the total number N of atoms in the particles as $\widetilde{U}D^{1/2}/N$ where \widetilde{U} has the meaning of the point defect potential if it is weak or the conduction band width if the defect is strong. (e.g., a vacancy). The ensemble width of nondegerate levels in nonsymmetrical samples turns out to be of the same order of magnitude.

The question arises whether the absence of level repulsion in nonsymmetrical samples is a consequence of the fact that in Ref. 202 parallelepiped-shaped particles were treated in which, even with allowance made for the periodic atomic potential, separation of variables is possible in the zero order approximation in the defect density. But, unlike the model of Ref. 82, due to defects the systems treated in Ref. 202 are also genuinely three-dimensional as the variables become nonseparable. Indeed the absence of level repulsion is a direct consequence of their nondegeneracy in ideally perfect samples of any nonsymmetrical shape if they are of finite size (for example, the level degeneracy for a sphere is lifted by its ellipsoidal deformation, see Eq. (3.3)).

Concretely, the Dyson statistics was applied for investigation of small particles in Ref. 79. It was assumed there that the electrons do not interact with each other but that they interact with defects. The orthogonal, unitary and symplectic ensemble was used for electron scattering by nonmagnetic impurities, magnetic impurities or in the presence of a magnetic field, and for systems with strong spin-orbit interaction, respectively. But in calculating the response of the particle ensemble to an external electromagnetic field, in Ref. 179 the screening effects were not taken into account.^{256,257}

3.3. The coarse-grained density of states for long-wave electrons

The fact that the electron levels in a particle are spatially quantized manifests itself most clearly at temperatures T that are low compared to the typical level spacing δ (the strong quantization limit). But for particles with numbers of atoms exceeding 1000 the opposite inequality $T \gg \delta$ should be met at room temperatures. But it is wrong to believe that the effects of spatial quantization disappear at high temperatures. In fact, it is instructive to consider the integral

$$\overline{f} = \int f(\mathfrak{G}) g(\mathfrak{G}) d\mathfrak{G} , \qquad (3.5)$$

where $f(\mathscr{C})$ is an energy function varying slowly over δ . The density of states $g(\mathscr{C})$ is a singular function of energy reflecting the spatial quantization:

$$g(\mathcal{E}) = \sum_{a}^{b} \delta(\mathcal{E} - \mathcal{E}_{m}). \tag{3.6}$$

In particular, $f(\mathscr{C})$ may be a function of \mathscr{C}/T . Using the Euler-Maclaurin summation formula, the following expression may be written for \overline{f} in the one-dimensional case:

$$\overline{f} = \sum_{a}^{b} f(\mathfrak{E}_{m}) = \int_{a}^{b} \mathrm{d}m f(\mathfrak{E}_{m}) + (1/2)(f(\mathfrak{E}_{a}) + f(\mathfrak{E}_{b})). \quad (3.7)$$

The first term on the right side of Eq. (3.7) corresponds to a continuous energy spectrum and the second term gives a quantum correction to it. Since the latter is relatively small, the case $T \gg \delta$ may be termed the weak quantization limit. But quantum corrections are of vital importance for small particles and thin films since they are the origin of the sur-

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face parts of the corresponding physical quantities.

One may try to introduce a continuous function $\tilde{g}(\mathscr{C})$ of energy which yields the same values for the integrals of slowly-varying functions of the energy \mathscr{C} as the singular true density of states $g(\mathscr{C})$:

$$\overline{f} = \int f(\delta) \widetilde{g}(\delta) \, \mathrm{d}\delta \,. \tag{3.8}$$

The function $\tilde{g}(\mathscr{C})$ is called a coarse-grained density of states and is obtained by averaging of $g(\mathscr{C})$ over intervals $\Delta \mathscr{C}$, such, that $T \gg \Delta \mathscr{C} \gg \delta$. Certainly, as seen from Eq (3.7), the coarse-grained density of states (DOS) cannot be introduced in the one-dimensional case. But it may be introduced in two- and three-dimensional cases. The coarse-grained DOS may be used for a degenerate electron gas at T = 0 if one is interested in integral quantities such as the Fermi energy μ or the electron surface tension α_e . This is justified by the very strong inequality $\mu \gg \delta$.

Essentially, averaging of $g(\mathcal{C})$ over the energy is equivalent to the Born-Oppenheimer approximation. It may be carried out if the wavelength $\lambda(\mathcal{C})$ of an electron with the energy \mathcal{C} is small compared with the minimum size L of a sample. Naturally, for very low-lying levels this condition is not met, and one cannot introduce the coarse-grained DOS.

A mathematical foundation for the procedure of the DOS averaging over the energy was given by Weyl.¹⁰⁹ To avoid dealing with fluctuations of $g(\mathscr{C})$ of infinitely large amplitude, instead of $g(\mathscr{C})$ Weyl considered its primitive $G(\mathscr{C})$., i.e., the number of states with energies less than \mathscr{C} . As \mathscr{C} grows, the primitive varies stepwise but its fluctuations with respect to the smoothed curve of G as a function of \mathscr{C} remain finite. If the dispersion law is quadratic, the summation over the energy gives the well-known asymptotic result $G(\mathscr{C}) \sim V\mathscr{C}^{3/2}$ when the volume V tends to infinity.

One may expect that this term is the leading one in the asymptotic expansion of the primitive $\tilde{G}(\mathscr{C})$ for the coarsegrained DOS $\tilde{g}(\mathscr{C})$. As pointed out in Ref. 25 the real expansion parameter is λ / L which proves the equivalence of the coarse-graining to the Born-Oppenheimer approximation mentioned above: as $\lambda \sim \mathscr{C}^{-1/2}$ for the quadratic dispersion law, such an expansion fails at small \mathscr{C} .

Obviously, the expansion is possible up to a term ~ 1 , since it is comparable with jumps of the step-like function $G(\mathscr{C})$. Moreover, if the sample is of a symmetrical shape, and electron states are degenerate, the jumps in $G(\mathscr{C})$ values are still larger. For example, if the particle is spherical, the jump of $G(\mathscr{C})$ equal to $2l \ 4 \ 1$ corresponds to degenerate states with the orbital quantum number l. A typical value of lat large energies is of the order of L/λ , i.e., of $\mathscr{C}^{1/2}$. Because of such large fluctuations of $G(\mathscr{C})$ in the case of a sphere, the coarse-grained function $G(\mathscr{C})$ can be expanded only up to the terms $\sim \mathscr{C}$ inclusive. Accordingly²⁵ $g(\mathscr{C})$ can be expanded only to a term independent of energy for a sphere and to a term $\sim \mathscr{C}^{-1/2}$ for other geometrical shapes.⁴⁾ In order to obtain terms $\sim \mathscr{C}^{-1/2}$, it is necessary to average $G(\mathscr{C})$ over the particle radii in a range of width $\sim \lambda$ (\mathscr{C}).

If the electron dispersion law is simple quadratic, the leading term in the expansion of $\tilde{g}(\mathscr{C})$ does not depend on the particle shape being proportional to its volume. The next term is a surface correction to it which represents the memory of the spatial quantization. It was first derived for the Dirichlet and Neumann zero boundary conditions in Ref. 109. This term depends only on the surface area of the particle.

It should be pointed out that the situation changes radically if one takes into account the crystalline structure of the particle and the band structure of its electron spectrum. Certainly, in this case the surface correction to the DOS should depend on the particle shape more strongly: via total areas of different faces. But much more striking is the fact that at certain energies an expansion of $\tilde{g}(\mathscr{C})$ in powers of λ / L is not possible at all.²⁷ This is a consequence of the fact that at these energies the DOS g_0 of a bulk sample exhibits the van Hove singularities $(dg_0/d\mathscr{C})$ is discontinuous or diverges) which belongs to the basic properties of the band spectrum. Definitely, $g(\mathscr{C})$ is nonanalytical close to the van Hove singularities. This implies that the particle energy cannot be divided into the bulk and surface parts if the Fermi level is close to these singularities.

Investigation of the DOS in the case of a quadratic dispersion law pioneered by Weyl¹⁰⁹ was continued in Refs. 110–112 and practically completed in the paper by Bloch and Bal'yan²⁵ where the coarse-grained DOS was derived for the wave equation

$$\Delta \psi + k^2 \psi = 0, \quad k^2 = 2m^{\delta} \tag{3.9}$$

under an arbitrary linear boundary condition

$$\frac{\partial \psi}{\partial \mathbf{n}} + \boldsymbol{x} \left(\rho \right) \psi = \mathbf{0} \tag{3.10}$$

on an arbitrary sufficiently smooth surface $(\partial \psi / \partial n)$ is the normal derivative of the wave function and ρ is the coordinate of a point on the surface). The surface smoothness condition consists of the inequality $\lambda \ll R_m$ where R_m is the minimum radius of curvature on the boundary.

The physical meaning of the parameter \varkappa in Eq (3.10) is as follows. If \varkappa is positive, it is the inverse decay length for the electron wave function outside the potential well which models the metal particle. Obviously, in the general case \varkappa should depend on the electron energy. The case $\varkappa \to \infty$ corresponds to an infinitely deep potential well. But a much more complicated situation may be realized when the electron potential energy is at a minimum on the surface of a particle growing sharply outside it. In this case the parameter \varkappa may have negative values. At $\varkappa < 0$, apart from solutions oscillating inside the bulk, there are solutions decaying inside the bulk. The latter correspond to a surface energy band.

The coarse-grained density of states was found in Ref. 25 using the Green's function for the problem (3.9), (3.10). It is represented as the sum of the Green's function in the infinitely large space G_0 and a correction to it G_1 which makes it possible to meet boundary conditions on the surface. This gives an integral equation for G_1 that can be solved by expansion in powers of λ / L . Coarse-graining of $g(\mathscr{C})$ is carried out using the Lorentz function. The final result of Ref. 25 for energies above the bottom of the bulk band is given by the following expression (the spin degeneracy of the electrons is ignored):

$$\widetilde{g}(k^{2}) = \frac{1}{4\pi^{2}} \left[Vk + \int_{S} d\rho \left(\frac{\pi}{4} - a \right) + \frac{1}{2k} \int_{S} \left(\frac{1}{3} + \cos^{2} a - a \operatorname{ctg} a \right) \left(\frac{1}{R_{1}} + \frac{1}{R_{2}} \right) \right] \equiv g_{0} + g_{1} + g_{2}. \quad (3.11)$$
$$a = \operatorname{arctg} \frac{\varkappa}{k}, \quad \& > 0,$$

where R_1 and R_2 are the principal radii of curvature of the surface S over which the integration is carried out.

Evidently, the first term, g_0 , in Eq. (3.11) is the bulk contribution to the coarse-grained DOS, while the second, g_1 , represents a surface correction to it. At constant \varkappa it is proportional to the surface area S. As for the third term, g_2 , unlike the second term, it depends on the particle shape quite strongly. In particular, it changes its form to some extent when the surface is ribbed. Thus, for a parallelepiped with edges \mathcal{L}_1 , \mathcal{L}_2 and \mathcal{L}_3 at $\varkappa \to \infty$ the third term is given by the expression

$$\Delta g = \frac{1}{8\pi k} (\mathcal{Z}_1 + \mathcal{Z}_2 + \mathcal{Z}_3). \tag{3.12}$$

When a surface band exists, the density of states is non-zero also for $\mathscr{C} < 0$:

$$\widetilde{g}(k^{2}) = \frac{1}{4\pi} \left\{ \int_{S} d\rho \theta_{-}((-k^{2})^{1/2} + \varkappa) + \frac{1}{2} \int_{S} d\rho \left(\frac{1}{R_{1}} + \frac{1}{R_{2}} \right) \times \left[\frac{\theta_{-}((-k^{2})^{1/2} + \varkappa)}{\varkappa} + \delta((-k^{2})^{1/2} + \varkappa) \right] \dots \right\},$$
(3.13)

 $\theta(x)$ is the Heaviside step function. Like g_2 in Eq. (3.11), the leading term in Eq. (3.13) at constant \varkappa is proportional to the surface area and does not depend on the particle shape.

However, it should be borne in mind that the above discussion does not take into account the difference between the electron density in the bulk and on the surface. An excess surface charge caused by this difference gives rise to an electric field which is not accounted for in the wave Eq. (3.9). Therefore, Eqs. (3.11 to 3.13) can be used only in cases when the effects caused by the electric field can be neglected.

The problem of the density of states for electrons with a quadratic dispersion law in finite-size samples is very similar to that for acoustic phonons with a linear dispersion law. The latter was treated in Refs. 113 to 117 but this treatment is less rigorous than in Ref. 25.

The main difference between these problems consists of the circumstance that one should take into account three different phonon modes intermixed due to the surface. If one neglects the difference between the transverse and longitudinal modes as is done in Refs. 113–115 then the expression for the coarse-grained phonon DOS differs from $\tilde{g}(k^2)/k$ (3.11) only by a constant. Just such a result was obtained in Ref. 113 for a parallelepiped (in that paper a term of a higher order in 1/L is also presented, but as discussed earlier this exceeds the accuracy of the coarse-graining method). Only the values $\varkappa = 0$ and $\varkappa \to \infty$ for the parameter \varkappa in (3.10) were considered in Ref. 113 corresponding to a free or to a pinned surface.

It was pointed out in Ref. 116 that, with allowance for the difference between the longitudinal and transverse phonons, the expansion of the coarse-grained phonon DOS should be of the form

$$g_{\rm ph}(\omega) = \frac{V\omega^2}{2\pi^2}c_3^{-3} + \frac{S\omega}{8\pi}c_2^{-2} + \frac{\omega}{4\pi}c_1^{-1}, \qquad (3.14)$$

where C_n is the *n*th order effective sound velocity. In the leading term in Eq (3.14) the longitudinal and transverse oscillations are not intermixed and, hence, $c_3^{-3} = 2c_t^{-3} + c_t^{-3}$ where c_t and c_t are the velocities of the

transverse and longitudinal oscillations, respectively. But the other coefficients in Eq. (3.14) can be found only by solving microscopic equations of motion.

3.4. The density of states and singularities of thermodynamic quantities with allowance for the band structure of the spectrum

The long-wave approximation presented in the preceding section is justified at small electron densities or at temperatures low enough if one deals with phonons or magnons. To go beyond these limitations, one must investigate how the finite size of a crystal influences the short-wave part of its spectrum. It is clear that extrapolation of the long-wave asymptotic expression into the short-wave region may lead not only to quantitative but also to qualitative errors.

First, as has been already pointed out, the van Hove and other singularities directly manifesting themselves in energetic and thermodynamic parameters of electrons will be lost as a result of such extrapolation. Second, it will be impossible to take into account the surface bands lying above the bulk ones, though the former should contribute significantly to the phonon and magnon thermodynamics at elevated temperatures.

Third, the long-wave asymptotic expressions (3.11 to 3.13) of the surface part of the DOS represents it as an energy function of fixed sign. Thus, this asymptotic expression might lead to the wrong conclusion that the DOS per atom for a finite-size crystal should be lower (or higher) than in the infinite size crystal at all energies. In other words, the total number of states in the crystal should differ from the total number of atoms (the spin degeneracy of the electrons is not taken into account, as well as higher energy bands). But such a conclusion is definitely wrong as in the one-band approximation both these numbers should coincide. This assertion remains in force, even if a surface band exists since its states arose from states of the bulk band. For this reason, for example, a decrease in the DOS in the long-wave part of the spectrum must be compensated for by an increase in the short-wave part which cannot be described by extrapolation of Eq (3.11).

Finally, a correct description of the short-wave part of the DOS makes it possible to take into account the crystal anisotropy which is ignored in Eqs. (3.11 to 3.13).

A general expression for the coarse-grained DOS of a finite-size crystal with an arbitrary dispersion law was first derived in Ref. 26 under the assumption that a crystal is an infinitely deep potential well for the conduction electrons. The density of states was expressed in terms of a contour integral of the reciprocal velocity. But this integral can be evaluated only for a quadratic dispersion law which excluded taking into account the real band structure of the spectrum. Not only extrema but also saddle points were treated in Ref. 26. But the procedure of Ref. 26 does not make it possible to point out the small parameters of the theory. For this reason the results of Ref. 26 were used without any justification for calculation of singularities of the thermodynamic quantities in cases when the Fermi level coincides with the van Hove singularity. But the surface part of the DOS formally exhibits a logarithmic divergence, i.e., the inequality $g_1 \ll g_0$ at which the procedure of Ref. 26 should work is replaced by the opposite one. But in the vicinity of extrema where the simple quadratic law holds the results of



FIG. 7. Bulk density of states for the simple cosinusoidal dispersion law for electrons (3.17).

Ref. 26 coincide with (3.11) in the first order in λ/L , as should be the case.

In Refs. 27, 28 a method was developed which makes it possible to obtain an explicit expression for the coarsegrained DOS for the simple cosinusoidal dispersion law with allowance for the difference of surface and bulk parameters, for example, for electrons with the Hamiltonian

$$H = B \sum_{g,\Delta} \bar{a}_g^* a_{g+\Delta} + 2Bv \sum a_s^* a_s; \qquad (3.15)$$

Here $a_{\mathbf{g}}^*$, $a_{\mathbf{g}}$ are the creation and annihilation operators for the conduction electron on the atom \mathbf{g} , Δ is the vector connecting the first nearest neighbors, s is the number of a surface atom (the spin index is left out). The integral representation for the δ -function is used when carrying out the calculation. If there are no surface bands in the spectrum, then

$$g(E) = 2\sum_{\mathbf{q}} \delta(\mathfrak{E} - \mathfrak{E}(\mathbf{q})) = \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{d}t l^{i\mathfrak{E}t} \sum_{\mathbf{q}} \exp(-i\mathfrak{E}(\mathbf{q})t),$$

$$\mathfrak{E}(\mathbf{q}) = 2B(\cos q_x a + \cos q_y a + \cos q_z a).$$
(3.16)
(3.17)

The allowed values of the quasimomenta q_i are determined from the boundary conditions which should be obtained using the Hamiltonian (3.15). Summation over q_i in (3.16) is carried out using the Euler-McLaurin formula (3.7) under the assumption that the second term in Eq. (3.7) is small compared with the integral term. Such an approach makes it possible to separate out the bulk contribution g_0 and the surface one, g_1 , to the coarse-grained density of states. The first of them (Fig. 7) coincides with the well known result of Ref. 118. It cannot be represented analytically but one sees singularities at points $\varepsilon = \pm 1$ (the van Hove singularities).

The surface term g_1 in some cases (v = 0, |v| = 0.5) can be expressed analytically as a combination of full elliptic integrals of the first kind of the form

$$K\left(\left[1-\frac{\left(\varepsilon\pm1\right)^2}{4}\right]^{1/2}\right) \text{ or } K\left(\left(\frac{9-\varepsilon^2}{8}\right)^{\pm1/2}\right), \ \varepsilon=\frac{E}{2B}.$$
(3.18)

If the crystal is bounded by the (100) or (110) faces, then, as seen from Eq. (3.18) and Fig. 8a,b in which g_1 is represented at v = 0 and v = -0.5 for (100) faces, the surface part of the DOS diverges logarithmically at points $\varepsilon = \pm 1$, in which g_1 becomes negative. Obviously this result is meaningless as the total DOS should be negative at this point. This means that in reality at $\varepsilon = \pm 1$ the coarsegrained DOS cannot be divided into bulk and surface parts.

At |v| > 0.5 the surface band appears in the spectrum (Fig. 8c) It manifests itself not only in the nonzero DOS outside the bulk band ($|\varepsilon| > 3$) but also in a jump in the DOS inside the bulk band (in Fig. 8c at ≈ 0.125 for v = -2). Jumps at the surface band extrema is caused by the fact that



FIG. 8. Surface density of states g_1 for the simple cosinusoidal dispersion law (3.17), $2D^2/a^2$ is the number of surface atoms²⁸ a) Faces (100) or (110), v = 0, b) Faces (100), v = -0.5, c) Faces (100), v = -2, d) Faces (100), $\beta = 2$.

the density of surface levels remains finite at them. Due to superposition of the bulk and surface bands, the DOS as a function of ε goes through a maximum inside the bulk band.

If the sample is bounded by the (110) faces, then, as seen from Fig. 8a and Eq. (3.18), although the surface DOS differs from that for (100) faces, the van Hove singularities are still located at points $\varepsilon = \pm 1$.

In Ref. 28 systems were investigated also with the Hamiltonian differing from (3.15) in that the surface perturbs not the diagonal but the nondiagonal matrix element between a surface atom and its nearest neighbor from the next atomic layer. If the perturbed nondiagonal matrix element $B' = B\beta$ is such that $\beta^2 \ge 2$, then two surface bands appear simultaneously lower and higher than the bulk band (Fig. 8d).

The singularities of the DOS just described are directly reflected in observable quantities since the electron heat capacity $C_e = \pi^2 T \tilde{g}(\mu)/3$ and the paramagnetic susceptibility $\chi = \tilde{g}(\mu)$ (the Bohr magneton is put equal to 1) are expressed in terms of $\tilde{g}(\mathscr{C})$). The surface contribution to χ which, as seen from Fig. 8, may be of both signs, may be interpreted as specific surface paramagnetism or diamagnetism. Influence of external factors may be observed both on χ and C_e . For example, adsorption or an external electrical field change the surface boundary conditions. Thus, under their influence the Fermi level may cross one of the singularities of the DOS sensitive to the boundary conditions, for example, the surface band extremum lying inside the bulk band. Then, together with a jump in $\tilde{g}(\mu)$, C_e and χ should reveal similar jumps.

3.5. The Fermi energy and the electron surface energy

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Results, obtained in Secs. 3.3 and 3.4 make it possible to calculate the Fermi energy and the surface energy of electrons in the particle. For the quadratic dispersion law one obtains from Eqs. (3.11), (3.12) to the first order in $S/k_F V$ (Refs. 47, 48):

$$\mu = \mu_{0} + \mu_{1},$$

$$\mu_{0} = (3\pi^{2}n)^{2/3} \frac{1}{2m}, \quad \mu_{1} \equiv \frac{S\zeta}{3V},$$

$$\zeta = 3 \left\{ k_{\rm F}^{-1} \left[\left(\mu_{0} + \frac{\varkappa^{2}}{2m} \right) \arctan \frac{k_{\rm F}}{\varkappa} - \frac{\varkappa}{k_{\rm F}} \mu_{0} \right] - \frac{\pi}{4} \frac{\mu_{0}}{k_{\rm F}} \right\} - \frac{3\pi\varkappa^{2}}{2mk_{\rm F}} \theta(-\varkappa),$$
(3.19)

where *n* is the electron density. On a decrease in particle size, according to Eq. (3.19) at $x \ge 1$ the Fermi level goes up due to the spatial quantization of the electron levels which makes them shift upwards. At $x \ll 1$ the Fermi level goes down. It is a result of the surface resonance due to which the DOS increases close to the band bottom, and the electrons "fall down," occupying them.

The quantity μ_1 changes its sign at some $\varkappa_c \sim k_F$. Evidently, at $\varkappa > \varkappa_c$ the charge of the surface is positive and at $\varkappa < \varkappa_c$ negative, i.e., μ_1 is linear in its charge.

In the limiting cases $\varkappa \to \infty$ and $\varkappa = 0$ the surface corrections μ_1 to μ_0 are of the same magnitude but of opposite signs. Obviously, $\mu_1 \sim \mu_0 / k_F R$. Using numerical values of the parameters entering Eq. (3.19) taken from Ref. 44, one finds at R = 5 nm the following values of the surface correction μ_1 for some metals: 0.29 eV for white tin, 0.22 eV for Ag



FIG. 9. The surface contribution μ_1 to the Fermi energy for v = 0 (faces (100) and (110)) and v = -0.5 (faces (100)) (Ref. 28).

and Au and 0.31 eV for Al, i.e., the effect is quite significant.

The surface shift μ_1 of the Fermi energy in the case of the cosinusoidal dispersion law (3.17) is found by numerical integration of the coarse-grained DOS represented in Fig. 8. As seen from Fig. 9, the Fermi energy depends on the type of crystal faces. At v = 0, on an increase in the band filling, the quantity μ_1 goes through a maximum, then changes its sign and goes through a minimum. Thus, unlike the free electron model, the sign of μ_1 depends on the band occupancy.

The change in the sign of μ_1 with band occupancy can be qualitatively explained as follows. At small occupancies the conduction electrons, and at large ones the holes are the charge carriers. Due to spatial quantization the Fermi levels of charge carriers of both signs shift upwards. But the sign of the chemical potential for holes is opposite to that for electrons. Therefore, the electron Fermi energy is shifted downwards at large occupancies. At v = -0.5 the surface potential acts on electrons and holes in a different way. For this reason the sign of μ_1 remains unchanged as the band occupancy increases.

Integration of μ_1 over the number N of electrons gives the surface part \mathscr{C}_1 of the electron energy. One obtains with allowance for Eqs. (3.19) (Refs. 23, 72):

$$\delta_{1} = \alpha_{e}S, \qquad (3.20)$$

$$\alpha_{e} = -(3n/2mk_{F}) \{ [(k_{F}^{2}/4) + (\varkappa^{2}/2) + (\varkappa^{4}/4k_{F}^{2})] \arctan(k_{F}/\varkappa) - (5\kappa k_{F}/12) - (\varkappa^{3}/4k_{F}) - \pi k_{F}^{2}/16 \};$$

$$k_{F} = (2m\mu_{0})^{1/2}.$$

As follows from Eq. (3.20), the electron surface tension α_e is positive as $\varkappa \to \infty$, but negative as $\varkappa \to 0$. The latter does not necessarily mean the instability of the system as the total surface tension may turn out to be positive due to the lattice contribution to it. In Ref. 72 corrections to α_e of the order of 1/R are found.

Not only spatial quantization but also Coulomb effects contribute to the size dependence of the Fermi energy of electroneutral small particles. The latter is caused by the nonuniformity of the electron density distribution over the particle. For example, as $\varkappa \to \infty$ the electron density vanishes at the surface, and the positive charge of ions remains uncompensated there. For this reason an electric double layer arises on the surface, its parameters being size-dependent.

It should be pointed out that taking the Coulomb interaction into account makes the problem of definition of the Fermi energy for a small particle quite nontrivial. Its standard definition as the derivative of the electron gas energy \mathscr{E} with respect to the number N of electrons, strictly speaking, has only a mathematical but not a physical meaning, as an infinitely small change in the number of electrons is impossible. But the minimum possible change in N (i.e., by 1) leads to charging of the particles. Unlike a bulk sample, the charge density in a singly-ionized particle is not an asymptotically small quantity. Correspondingly, the energy of the electrical field produced by the charged particle is not small compared to other characteristic energies. Meanwhile, from the point of view of its meaning, the Fermi energy is a characteristic of an electroneutral particle. Thus, in determining μ one must exclude the contribution to it of the electrical field of the ionized particle. This may be achieved by using the equation valid at T = 0

$$\mu = \delta(N) - \delta(N-1) + (e^2/2C\varepsilon_0) \approx \delta\delta/\delta N + \delta N \to 0,$$
(3.21)

where C is the particle capacity, and ε_0 is the permittivity of the surrounding medium. The Coulomb part of (3.21) is wholly caused by the electric double layer on the surface of the particle.

To find the size-dependence of the parameters of the double layer, this problem was solved in Ref. 200 for thin films, for which $C \rightarrow \infty$, and the entire Coulomb influence on μ is reduced to the double layer. The double layer size-dependence was found taking into account the spatial quantization of the electron levels in the mean field of the other electrons. Such a solution was obtained only for the parameters of films typical not of metals but of degenerate semiconductors. For this reason the quantitative results of Ref. 200 are not valid for metals. Nevertheless, the results of Ref. 200 are useful for metals, providing an insight into the physical mechanism which leads to the Coulomb contribution to the surface part of μ .

The interplay of the small parameters in Ref. 200 leads to the result that both as $x \to \infty$ and as $x \to 0$ the Coulomb effects reduce the size-dependent part of μ by a factor of two (in other words, the kinetic contribution to μ_1 (3.19) is twice as large as the Coulomb one, but their signs are opposite). It may turn out that the role of the Coulomb effects at electron densities typical for a metal will be less. This may be inferred from an analysis of the higher-order terms obtained. In any case, it is clear that the free-electron model gives a reasonable estimate for the size-dependent part of μ .

It should be noted that the free electron model with $x \to \infty$ in Eq. (3.10) was used in Ref. 33 for calculation of the disjoining pressure in thin films of liquid metals. This problem is related to the electron surface energy. To make the electron DOS a continuous function of energy, it was assumed that the energy levels are of finite width γ . But in the limit $\gamma \to 0$ the expression for DOS used in Ref. 33 differs from the quite reliable Eq. (3.11) by an extra term and for this reason is erroneous. On the other hand, there is no rea-

son for the energy levels to be of finite width in a finite-size sample. Any perturbing potential may change the systematics of energy levels but it cannot transform a discrete spectrum into a continuous one. For this reason the results of Ref. 33 are far from being reliable. Other critical remarks about Ref. 33 were advanced in Ref. 34 where the same problem was treated.

Naturally, the free-electron model used above for the calculation of \mathscr{C}_1 and μ cannot lay claim to quantitative agreement with experiment. Its aim is to establish the main regularities and to estimate characteristic quantities. Other methods are also widely used for the same aim. In particular, the density functional method is very popular. This method developed in Ref. 178 makes it possible, under assumption of a uniformly distributed compensating charge (the jellium model), to account for the nonuniformity of the electron gas caused by the surface or other factors. It was applied to small particles and related problems in Refs. 29–31, 145, 165, and other papers. Sometimes the still simpler Thomas–Fermi method³⁷ is used for the same problems as well as the pseudopotential method.³²

Returning to the density functional method, one should note that although the electron-electron interaction is taken into account in it, its accuracy is insufficient for obtaining reliable numerical data for concrete materials, contrary to claims of some authors using this method. Certainly, this method, as any numerical method, is inconvenient for obtaining qualitative results. Further, the nonuniformity of the electron gas is taken into account only by the gradient term which is appropriate only for a very slowly varying density. But in reality it changes sharply over distances of the order of the lattice constant near the surface. This excludes the possibility to obtain numerically accurate results. Strong limitations are imposed also on the boundary conditions used in the density functional method. In any case, in all the papers cited the possibility of surface bands or resonances is not taken into account. But the main shortcoming of the method consists in the circumstance that the spatial quantization of the electron levels is not taken into account in it. Meanwhile, as shown above, this factor is of vital importance for the size-dependence of the Fermi energy and for the surface tension. Similar shortcomings are inherent in other methods pointed out above.

3.6. Size-variable free electron model for an isotropic particle and general thermodynamic relations

The free electron model of a metal particle may be modified in such a manner that it may be used for confirmation of the thermodynamic relations of Sec. 2.3. For this purpose it is sufficient to treat the particle as deformable of which the volume should be found from the condition of minimum energy. Such a model may correspond to both a liquid or a solid particle. Its ionic frame may be taken into account implicitly by assuming that it should ensure the stability of the system against an infinitely large dilatation which leads to a decrease in the electron energy. The ionic frame also contributes to the surface energy. Conservation of the number of electrons and, consequently, of the number of atoms corresponds to a practically complete absence of the saturated vapor of the metal.

First of all, Eq. (3.20) manifests the truth of the basic thermodynamic relation (2.12) according to which the sur-

face tension α depends on the electron density, i.e. on the density of atoms. Qualitatively, this statement remains in force if one takes into account the contribution of the ionic frame to the particle surface energy. Thus, the surface tension remains constant in the case of a particle with a fixed number of atoms only if a change takes place in the particle shape (i.e. in S) and not in its density. But if the number of atoms in the particle is variable, as in the case of equilibrium between the particle and its vapor, then the surface tension may be constant also in the case of an unchanged shape of the particle, provided that the change in its size occurs at a fixed density.

Further, although the ionic frame, also contributes to the total surface tension α of the particle, situations are possible when the electron contribution to α and $d\alpha/dn$ exceeds that of the ions. Then the magnitude and sign of the spontaneous deformation of the particle is determined by electrons. In what follows, only the case of an infinitely deep potential well for the conduction electrons ($\kappa \rightarrow \infty$ in Eq. (3.10)) will be discussed in detail. Then according to Eq. (3.20) the electron part of the surface tension given by the expression

$$\alpha = \mu_0 k_{\rm F}^2 / 16 \,\pi \tag{3.22}$$

is proportional to $n^{4/3}$, i.e., the absolute value of the electron part of the internal pressure (2.16) is equal to the Laplace pressure but their signs are opposite to each other. In such a case the particle should dilate and not reduce its volume under surface forces, and this is often observed experimentally (Sec. 1.4).

It should be noted that the possibility in principle was pointed out earlier of a crystal dilatation due to the difference between the surface tension and stress (Sec. 2.2). But the origin of dilatation in the case considered is quite different. The conduction electrons which cause the dilatation form an electron gas and not an electron crystal, irrespectively of the particle being in the liquid or in the solid state. In the former case the "crystalline" mechanism of Sec. 2.2 does not work at all, but the "electron" one discussed above remains in force.

Finally, the validity of Eq. (2.18) for the chemical potential can be confirmed. A spherical particle of radius R is considered under the assumption that the electron contribution to α greatly exceeds the ionic one. Taking into account that the particle is expanded by surface forces which create the negative internal pressure p_c , one concludes that the surface part μ_s of the Fermi energy for the deformable particle is the sum of two terms. The first of them is the corresponding expression μ_1 (3.19) for an absolutely rigid particle which as $\varkappa \to \infty$ with allowance for Eq. (3.22) reduces to

$$\mu_1 = 3\pi \mu_0 / 4k_{\rm F} R = \frac{4\alpha}{n\,R}.\tag{3.23}$$

The second term is the difference between $\mu_0(p_c)$ and $\mu_0(0)$. Since as discussed above $p_c = -p_L$, in the case under consideration one obtains for the Fermi energy

$$\mu = \mu_0(p_c) + \mu_1(p_c) \approx \mu_0(0) + \tilde{\mu}_1, \qquad (3.24)$$

$$\tilde{\mu}_1 \approx \mu_1(0) + (\partial \mu_0 / \partial p) p_c = -(p_1 / n) + \mu_1.$$

Thus, it follows from Eqs. (3.23), (3.24) that

$$\mu = \mu_0(p_{\rm L}). \tag{3.25}$$

This means that although the particle is expanded its chemical potential imitates that of a particle compressed by the Laplace pressure. If the relation $\alpha \approx \alpha_e$ does not hold then the microscopic model under consideration is a twocomponent one and cannot be used for a quantitative comparison with Eq. (2.18) derived for a one-component system.

The size dependence of the Fermi energy may be caused by the surface relaxation occuring in deformable particles.³⁶

4. PHYSICAL EFFECTS IN SMALL PARTICLES

4.1. Work function and Coulomb explosion

Apart from the spatial quantization discussed in the previous Chapter the specific properties of small particles are determined by Coulomb effects arising due to the electron transfer from them or through them. If the appearance of an extra electron on a bulk sample practically does not change its electrostatic energy, the appearance of an extra electron on a small particle changes this energy by the quantity $\sim e^2/R$ which is large compared to T under normal conditions and for this reason cannot be discarded. In some cases Coulomb effects appear simultaneously with spatial quantization and even may be a consequence of the latter.

In this Section the size-dependence of the work function will be discussed. It is determined simultaneously by the Coulomb interaction and spatial quantization with both these factors leading to functionally the same size-dependence on R. We will follow the definition of the work function Φ given in Ref. 258:

$$\Phi = \Delta \delta / \Delta N = \delta (N-1) - \delta (N).$$
(4.1)

Then one obtains from Eqs. (4.1) and (3.21)

$$\Phi = -\mu + (e^2/2\varepsilon_0 C), \qquad (4.2)$$

$$\mu = \mu_0 + \mu_1 + \mu_c.$$

As was already pointed out in Sec. 3.5, the size-dependent terms μ_1 and μ_c , related respectively to spatial quantization and the electric double layer on the surface, yield corrections $\sim 1/R$ to the size-independent term μ_0 . But the second, "field" term in Eq. (4.2) exhibits the same R-dependence. It is maximum at $\varepsilon_0 = 1$ when, for example at R = 5 nm it amounts to 0.13 eV, i.e., is comparable with the sum $\mu_1 + \mu_c$ (see Sec. 3.5). But, depending on the boundary conditions (3.10) this sum may be of either sign. Correspondingly, although the last term in Eq. (4.2) is always positive, the size-dependent correction to Φ may be of either sign. This statement is all the more valid at $\varepsilon_0 \gg 1$ when the "field" term gives a contribution to the size-dependence of Φ which can be neglected in comparison with the contribution of μ . In the latter case the sign of the size-effect for Φ is completely determined by the spatial quantization.

Historically, in investigating the size-dependence of Φ , attention to the Coulomb contribution was drawn long ago, whereas the contribution of the spatial quantization has been ignored by most investigators up to now (apparently, its existence was first mentioned in Ref. 23). But differences of opinion still exist between different authors concerning the description of Coulomb effects.

Some authors¹³²⁻¹³⁴ relate the size-dependence of Φ to the electric image forces although these forces determine only the shape of the potential barrier and not its height.

Their reasoning is as follows. The energy ΔE of the electron transfer from the point $R_1 = R + \delta$ close to the charged sphere of radius R to infinity is the sum of the Coulomb energy and that of the images forces

$$\Delta E = \frac{R^3 e^2}{2R_1^2(R_1^2 - R^2)} - \frac{ze^2}{R_1} \approx \frac{e^2}{4\delta} - \frac{5e^2}{8R} - \frac{ze^2}{R}.$$
 (4.3)

It is assumed that $\Delta E = \mathscr{C}_z - \mathscr{C}_{z+1}$ where \mathscr{C}_z is the total energy of a sphere with charge z_e . The first term on the right-hand side of Eq. (4.3) diverging at $\delta \rightarrow 0$ is interpreted as the work function Φ_0 for a bulk sample. Putting z = 0 and z = 1, one obtains the electron affinity A and the work function Φ , respectively. The result (4.3) for the size dependence of the work function was obtained also in Ref. 29 using the density functional method.

The same method according to Ref. 135 gives the following expression for the work function and the electron affinity

$$\Phi = A = \Phi_0 \pm \frac{e^2}{2(R+a)},$$
(4.4)

which differs from the expression given by electrodynamics in that a microscopic length a, depending on the density of the particle, enters the denominator of the second term on the right-hand side of (4.4). The sign (+) corresponds to the work function and (-) to the electron affinity.

The approach of Ref. 135 seems to be more justified than that used in Refs. 132–134: the work function should depend on the height of the potential barrier and not on its shape. In addition, interpretation of the parameter δ in Eq. (4.3) is quite arbitrary. Perhaps, practically the difference between Eqs. (4.3) and (4.4) is not very essential. Much more essential is the fact that neither of these approaches makes it possible to take into account the spatial quantization of energy levels leading to Eq. (4.2). The same is also true of the size-dependence of the electric double layer ignored in Refs. 132–135. The linear dependence of Φ on 1/Rwas obtained also in a number of other papers, e.g., Refs. 29– 31, 145, 165 but all they reveal the same shortcomings.

Experimentally, the size-dependence of the work function was first discovered in investigating gold island films in Ref. 75 where their photoemission was measured (Fig. 10). On a decrease in the particle radius from 25 to several Å, the work function falls from 4 to 2 eV. In Ref. 137, on the contrary, enhancement of the work function of small Ag particles was observed which obeys the law $\Phi(R) = 4.37 + (5.4/R(\text{\AA})) \text{ eV with } \Phi_0 = 4.3 \text{ eV}.$ The order of magnitude of this shift agrees with that given by Eq. (3.19). Qualitatively similar results were obtained for Ag



FIG. 10. Size dependence of the work function of Au particles.⁷⁵

particles in Refs. 100, 176: the rise of Φ with decreasing R is characterized by the following values: $\Phi(30 \text{ Å}) = 4.55 \text{ eV}$, $\Phi(27 \text{ Å}) = 4.57 \text{ eV}$ and $\Phi(20 \text{ Å}) = 4.65 \text{ eV}$, with $\Phi_0 = 4.90 \text{ eV}$. Increase in Φ with decreasing R was also observed for Na particles.¹⁷³ The experimental fact that Φ may both diminish and increase with decreasing R agrees with Eq. (4.2) but not with the results of other theories described in this Section, according to which Φ can only increase. But one cannot exclude the possibility that the results of Ref. 75 are due to a transition of Au particles from a metallic to an insulating state, on a decrease in their size (see Sec. 1.2).

Multiple ionization of small particles or clusters can lead to their breaking up into singly charged fragments. This phenomenon is referred to as Coulomb explosion of small particles. It was first discovered in Ref. 158 where the critical number n_c of atoms in a cluster, starting from which doubly charged clusters become stable, was given: $n_c = 30$ for Pb, 20 for (NaI),, 52 for Ag. Later, however, doubly charged clusters Pb_7^{2+} , Pb_9^{2+} , Pb_{11}^{2+} and Pb_{13}^{2+} were discovered¹⁵ with sizes much lower than the critical value, and in Ref. 160 similar clusters Ag_n^{2+} with $n \leq 19$. Their existence was attributed to a chain structure of clusters. Clusters Pb_n^{3+} with n > 45 and Pb_n^{4+} with n > 60 to 70 are also stable.¹⁵⁹ Quite small doubly charged clusters Ni_3^{2+} , Au_3^{2+} and W_3^{2+} were observed in Ref. 157 although Cu_3^{2+} are unstable. According to Ref. 177 doubly-and triply-charged clusters are stable at much smaller n, than obtained earlier: n_c is equal to 3 for Pb_n^{2+} , 5 for Bi_n^{2+} , 9 for Ag_n^{2+} and Au_n^{2+} , 22 for Au_n^{3+} and Ag_n^{3+} , 38 for Bi_n^{3+} and 43 for Pb_n^{3+} . These values strongly depend on the experimental conditions under which clusters are produced.

A very simple calculation of charged cluster stability using a spherical or a chain model was carried out in Refs. 161–164. Equality of the cohesive energy of a surface atom and a change in the Coulomb energy caused by emission of a positive ion was taken as the stability criterion of a particle. The former was found from experimental data or by a calculation in the strong coupling approximation, and the latter was evaluated with allowance for a screened potential. The critical value of the number of atoms at which Coulomb explosion occurs is found to be equal to 30 for spherical Pb_n^{2+} clusters which is in agreement with the experimental data of Ref. 158. Pb_n^{2+} should be stable in the range from 6 to 13 atoms. But for Pb_n^{3+} and Pb_n^{4+} ions and for Ni_n^{2+} ions the critical values of *n* were found to be much in excess of their experimental values.

In Refs. 165, 166 a calculation of charged cluster stability was carried out using the density functional method. Although this method is inadequate for calculations of the surface energy and work function, it may give reasonable results for the problem being discussed. It was assumed in Ref. 165 that the charged cluster emits a singly-charged ion when exploding. But it was established in Ref. 166 that the most favorable channel for a Coulomb explosion corresponds to such fragments which consist of several atoms in agreement with the tendency that each fragment should contain the "magic" number of electrons (Sec. 1.2). If this is impossible, then the magic number of electrons must be in the smaller fragment. If this is also impossible, then the number of electrons in each fragment should be as close as possible to a magic number. This approach seems to be quite reasonable judging from the fact that sizes of maximally stable clusters

of Na and K obtained theoretically in this way in Refs. 167– 170 agree with experimental data of Refs. 167, 168 (these numbers are 8, 20, 40, 58 and 92). Sizes of such clusters for Mg and Al are calculated in Ref. 171. For Na_n^{2+} clusters the critical value of *n* should exceed 100.

In Ref. 174 the problem of Coulomb explosion was investigated theoretically under the assumption that a charged particle becomes ellipsoidal under electrostatic forces. The results of Ref. 174 agree with those of Ref. 157.

4.2. Mutual charging of small particles.

Size-dependent effects of Coulomb and quantum origin manifest themselves in properties not only of separate small particles but also of their ensembles. If the complete thermodynamic equilibrium between particles, which is reached on their coagulation, establishes much more slowly than their equilibrium with respect to electrons then a specific cooperative effect should arise: the mutual charging of small particles. It is realized via electron transfers between particles through the medium surrounding the particles. The electrons can go over from one particle to another by means of quantum tunneling or the usual electrical conductivity processes.

First of all, the electron transfer can be caused by the difference in the Fermi energies of particles of different size (see (3.19)). (One should keep in mind that a spread of particle sizes in an ensemble is inevitable). Then the minimum free energy is attained if electrons go over from a particle with larger μ to a particle with smaller μ . If the number of electrons transferred from one particle to another is large enough, one may speak of equalization of the electrochemical potentials of the particles.

At sufficiently high temperatures electron transfer between particles may occur as a result of a thermal fluctuation unrelated to the difference in the Fermi energies of the particles.

If the particles are mutually charged as a result of electron transfer, electrostatic forces arise between them. They are considerable if the screening length in the medium where the particles are located is large compared with the mean distance between the particles. These mutual charging forces cannot be reduced to the usual Coulomb forces as the particle charge depends on the particle separation. But up to the screening length their asymptotic expression is of the Coulomb form. For this reason, at sufficiently large interparticle distances, the mutual charging forces are much stronger than the conventional van der Waals forces with asymptotic behavior $\sim r^{-8}$. In fact, according to the Casimir formula⁶⁴ the latter are given by the expression

$$F_{\rm w} = r^{-2} q_{\rm w}^2(r), \quad q_{\rm w}^2 \approx 10\hbar c (R/r)^6. \tag{4.5}$$

With the minimum number of electrons going over from one particle to another (i.e., 1), and the permittivity $\varepsilon_0 = 1$, the van der Waals force F_W is less than the Coulomb one beginning from a distance three times larger than the particle radius R.

The idea of mutual charging of particles with different sizes was first advanced in Ref. 43. It was suggested there that particles of different sizes should have different Fermi energies due to the circumstance that the Laplace pressures for them are different, and the mutual charging should equalize their electrochemical potential. But the assumptions used in Ref. 43 are wrong. Surface forces acting on a crystalline particle are determined not by the surface tension but by the surface stress and for this reason cannot be reduced to the Laplace pressure (Sec. 2.2). The Laplace pressure has the meaning of a real physical force for small liquid particles only far from the melting point (Sec. 2.3), so that practically the assumption of Ref. 43 is inapplicable to them also. But if the Laplace pressure had been a real force it would have been insufficient to cause real interparticle electron transfer, as the difference in the Fermi energies of the particles caused by the Laplace pressure would have been too small for this purpose (see below).

But the situation changes drastically if one takes into account the spatial quantization leading to much stronger size-dependence of the Fermi energy. Obviously, this mechanism of the size-dependence of the Fermi energy is not related to surface forces and the spontaneous deformation of the particle caused by them. The idea that spatial quantization may cause the mutual charging of particles was advanced in Ref. 13. It was shown there that if the surface repels electrons ($\varkappa \rightarrow \infty$ in Eq. (3.10)) then electrons should go over from the smaller particle to the larger one. But if the surface attracts electrons ($\varkappa \rightarrow 0$ or $\varkappa < 0$) then the direction of the electron transfer is opposite.

The treatment of the mutual charging presented below is based on the thermodynamic expression for the probability W that N_i excess electrons are located on the *i*-th particle of an ensemble consisting of M particles. In the limit, when distances r_{ij} between particles greatly exceed their radii R_i , the probability is given by the expression (see (3.21)) (Ref. 206)

$$W \{ N_i \} = Z^{-1} \exp\left(-\frac{F\{N_i\}}{T}\right)$$

$$\approx Z^{-1} \exp\left[-\frac{1}{T} \sum_i \left(N_i \mu_i + \frac{e^2}{2\epsilon_0 R_i} N_i^2\right)\right], \quad (4.6)$$

$$Z = \sum_{\{N_i\}} W\{N_i\}.$$

At not very high temperatures for not very small work functions and not very large volumes of the surrounding medium one may neglect the electron transitions from particles to this medium. Then Eq. (4.6) must be supplemented with the condition of conservation of the electron number

$$\sum_{i=1}^{M} N_i = 0.$$
 (4.7)

As $T \rightarrow 0$ the set of numbes N_i should be realized for which the exponent in Eq. (4.6) is a minimum:

$$\pm \left[\left(\mu_i + \frac{e^2 N_i}{\varepsilon_0 R_i} \right) - \left(\mu_j + \frac{e^2 N_j}{\varepsilon_0 R_j} \right) \right] \ge (e^2 / 2\varepsilon_0) (R_i^{-1} + R_j^{-1}).$$
(4.8)

Evidently, for $N_i \ge 1$ relations (4.8) reduce to the conditions of equality of electrochemical potentials of all the particles of the ensemble. But for N_i comparable to 1 these conditions lose their meaning. One should take into account that N_i are discontinuous functions of particle parameters. For example, at M = 2 for transfer of N electrons from one particle to the other the following equalities should hold

$$k - \frac{1}{2} < N < k + \frac{1}{2},$$

$$k = |\mu_1 - \mu_2| \varepsilon_0 \left[e^2 \left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{r_{12}} \right) \right]^{-1},$$
 (4.9)

where $r_{12} \gg R_1$, R_2 is the interparticle distance. The terms of the following order in R/r are taken into account in writing Eq. (4.9) (Ref. 180). As follows from Eq. (4.9), as the particles approach each other, jumps of their charge should occur at certain distances. If one of the particles is spherical, then size-dependent oscillations of its Fermi energy (Sec. 3.1) should case similar oscillations of its charge.

Not the numerical estimates of the mutual charging will be presented. If the size-dependence of μ had been caused by the Laplace pressure then repeating the considerations presented in Ref. 43 one would have obtained that for any R_1 and R_2 the number of electrons going over from one Ag particle to the other would not have exceeded 0.05 to $\varepsilon_0 = 1$. It follows from the fact that in the case under consideration the quantity ξ in Eq. (3.19) should be put equal to $4\alpha \varkappa \mu_0/3$ where \varkappa is the crystal compressibility. These quantities for Ag are as follows (see Ref. 7); $\kappa = 10^{-6}$ atm, $\alpha = 930$ erg/ cm^2 and $\mu_0 = 5.5 eV$ (Ref. 44). Use of the condition of equality of the electrochemical potential instead of (4.8) as has been done in Ref. 43 then gives the estimate presented above. Meanwhile, the notion of electron transfer makes sense only if at least one electron goes over from one particle to the other. Thus, it is clear that the above mechanism of mutual charging does not work. Much more favorable estimates of the effect obtained in Ref. 43 are due to the fact that the deformation of Ag particles was overestimated by an order of magnitude there⁵) (by the way, in Ref. 46 the estimates are close to those presented here).

The mechanism of spatial quantization is much more effective: the number of electrons going over from one Ag particle to the other should exceed 1 at $\varepsilon_0 = 1$, if $R_1 \gg R_2$. In media with $\varepsilon_0 \gg 1$ this number may amount to several tens or even several hundreds. This follows from (4.8), (3.19).

As follows from (4.6), (4.8), the mutual charging forces are cooperative: since under conditions of thermodynamic equilibrium the electrochemical potential should be the same for all the particles of the ensemble, the equilibrium charge of each particle should be determined by the radii and positions of all the particles. Therefore, the interaction between any pair of particles should depend on the rest of the particles. Obviously, if an ensemble consists of two particles, the mutual charging forces are, by necessity, attractive. But in an ensemble consisting of a larger number of particles, a part of the particles has a charge of the same sign, and they repel each other. Nevertheless, attraction between particles predominates.

In order to estimate the cooperative effects in an ensemble with M > 2, let us assume that particle radii R_i are distributed uniformly over the range from $R - \rho$ to $R + \rho$. Then one obtains for averaged quantities with allowense for Eqs. (4.7), (4.8):

$$\overline{N_i^2} = -(M-1)\,\overline{N_iN_j} = \zeta^2 \rho^2 \varepsilon_0^2 / 3e^4 R^2.$$
(4.10)

As seen from Eq. (4.10), on an increase in M, the charge of each particle remains finite $(N_i^2 \text{ does not depend on } M)$. But the averaged force proportional to $\overline{N_i N_i}$, being attractive,

diminishes, vanishing as $M \rightarrow \infty$.

Mutual charging may also occur if the particles are of the same volume, but of different shapes. This follows directly from Eqs. (3.19) (4.9). Its origin may be the different degrees of imperfection of the particles that are otherwise identical, or even the differences in the distribution of an equal number of defects within them.²⁰²

Now another mechanism of mutual charging of small particles will be discussed which was called fluctuation charging.²⁰⁶ It is significant, as a rule, only at sufficiently high temperatures. But the fluctuation mutual charging, unlike the thermodynamically equilibrium one discussed above, is nonzero even in the case of identical or of nonmetallic particles. At low temperatures the fluctuation mutual charging is significant if the electrochemical potentials of the particles change only slightly after the electron transfer between the particles.

To estimate the fluctuation mutual charging, one may put all $R_i = R$, $\mu_i = \mu$. Then one obtains with allowance for Eqs. (4.6), (4.7) the following result for the thermodynamically averaged values at $T \gg e^2/\varepsilon_0 R$:

$$\langle N_i N_j \rangle = -\langle N_i^2 \rangle / (M-1) = -T \varepsilon_0 R / e^2 M.$$
(4.11)

For R = 10 nm, $\varepsilon_0 = 80$, T = 0.03 eV the average number of electrons going over between particles is close to 10. As $M \rightarrow \infty$ the fluctuation mutual charging forces

$$F_{ij}^{fl} = \frac{e^2}{\varepsilon_0 r_{ij}} \langle N_i N_j \rangle,$$

just as the equilibrium mutual charging forces proportional to $\overline{N_i N_i}$ in Eq. (4.10), disappear.

A calculation of particle motion in a vicsous liquid leading to their coagulation was carried out with allowance for the mutual charging forces in Refs. 27, 50. It was shown that these forces may accelerate the coagulation very strongly. In Ref. 45 the electrostriction caused by the mtual charging was investigated. This study reveals that, since the charge of a particle depends on its Fermi energy and this energy depends on the particle deformation, not only the standard expansion of the particles, but also their compression, is possible. Although the possibility was discussed in Ref. 45 of the Coulomb explosion of small particles due to their mutual charging, with realistic values of the parameters this problem does not infact arise: numerical estimates of the effect in Ref. 45 greatly overestimate it.

4.3. Screening by immobile particles

Keeping in mind subsequent comparison of the theory with the experimental data available, a situation will be studied here which corresponds to a very specific physics process: the mutual charging of particles in the case when all the particles of nonstandard sizes are located in a closed region surrounded by particles of a standard size.⁷³ Naturally, the charge inside the nonstandard particle rgion is distributed nonuniformly, and a layer of compensating charge should arise outside this region. In some sense one may say that the standard particles screen the nonstandard ones. But the problem of the potential distribution inside the small particle system differs essentially from the conventional problem of screening in a conducting medium. In the latter case the screening arises as a result of change in the density of charge carriers in motion in the vicinity of the screened charges. But in the case considered here the screening arises as a result of change in charges of motionless particles. Thus, unlike the standard situation, kinetic parameters cannot enter an expression for the screening length.

Strictly speaking, to ensure charge transfer between particles leading to equalization of their electrochemical potentials, there should be a number of electrons in the medium surrounding the particles. They should cause the conventional screening of charged particles. But in what follows, its number is assumed to be so small that the conventional screening length is very large compared with the size of the nonstandard particle region and with the screening length corresponding to immobile particles. For this reason the conventional screening will be neglected.

The model used below corresponds to a spherical region of radius ρ containing randomly distributed particles of radius R_1 and with the Fermi energy $\mu_1 = \mu(R_1)$. Particles of radius R_2 and $\mu_2 = \mu(R_2)$ are distributed randomly outside this region. The condition of the electrochemical potential equality between the particles can be represented as follows

$$(\mu_1/e) + (q_i/\varepsilon_0 R_1) + \varphi_1(r_i)$$

$$= (\mu_2/e) + (q_j/\epsilon_0 R_2) + \varphi_2(r_j) = \text{const}, \quad (4.12)$$

$$\sum_{i} q_i = -\sum_{j} q_j; \tag{4.13}$$

Here q_i is the charge of a type 1 particle at point r_i , $\varphi_1(r_i)$ is the potential at this point produced by all the other particles, q_j and $\varphi_2(r_j)$ are the corresponding quantities for the type 2 particles. The equality (4.13) accounts for the electrical neutrality of the system.

At rather high densities n_1 and n_2 of particles 1 and 2 spherically symmetric distributions of the charges and the potentials can be assumed allowing for the slow falling off of the Coulomb potential. Then with k = 1,2

$$\varphi_{k} = \frac{n_{1}}{\varepsilon_{0}} \int_{0}^{\rho} \frac{q_{1}(r') d^{3}r'}{|r'-r|} + \frac{n_{2}}{\varepsilon_{0}} \int_{\rho}^{\infty} \frac{q_{2}(r') d^{3}r'}{|r-r'|} \quad (k = 1, 2).$$
(4.14)

Then using well-known electrostatic theorems one obtains from Eq. (4.14)

$$\varphi_{1}(r) = \frac{n_{1}}{\varepsilon_{0}r} \int_{0}^{r} q_{1}(r') d^{3}r' + \frac{n_{1}}{\varepsilon_{0}} \int_{r}^{\rho} \frac{q_{1}(r') d^{3}r'}{r'} + \frac{n_{2}}{\varepsilon_{0}} \int_{\rho}^{\infty} \frac{q_{2}(r') d^{3}r'}{r'} \quad (r < \rho), \qquad (4.15)$$

$$\varphi_{2}(r) = \frac{n_{1}}{\varepsilon_{0}r} \int_{0}^{\rho} q_{1}(r') d^{3}r' + \frac{n_{2}}{\varepsilon_{0}r} \int_{\rho}^{r} q_{2}(r') d^{3}r' + \frac{n_{2}}{\varepsilon_{0}} \int_{\rho}^{\sigma} \frac{q_{2}(r') d^{3}r'}{r'} + \frac{n_{2}}{\varepsilon_{0}} \int_{\rho}^{\sigma} \frac{q_{2}(r') d^{3}r'}{r'} \quad (r > \rho).$$
(4.16)

As one sees from Eq. (4.16) with allowance for (4.13), $\varphi_2(\infty) = 0$.

The integral equations (4.12), (4.15) and (4.12), (4.16) can be reduced to exactly solvable differential equa-

tions by double differentiation with respect to the coordinate

$$\Delta q_1 = \varkappa_1^2 q_1, \ \varkappa_1 = (4\pi n_1 R_1)^{1/2}, \qquad (4.17)$$

$$\Delta q_2 = \varkappa_2^2 q_2, \ \varkappa_2 = (4\pi n_2 R_2)^{1/2}.$$
(4.18)

Their solution subject to the finiteness of the charge, the electrical neutrality condition (4.13) and the vanishing of $q_2(\infty)$ is given by the expression

$$q_{1} = A \frac{\operatorname{sh}(r \alpha_{1})}{r}, \quad q_{2} = \frac{C}{r} \exp(-\alpha_{2} | r - \rho |),$$

$$C = -\frac{n_{1} \alpha_{2}^{2}}{n_{2} (1 + \alpha_{2} \rho) \alpha_{1}^{2}} \left[\alpha_{1} \rho \operatorname{ch}(\alpha_{1} \rho) - \operatorname{sh}(\alpha_{1} \rho) \right] A$$

$$A = \frac{\mu_{2} - \mu_{1}}{e} \frac{R_{1} (1 + \alpha_{2} \rho) \varepsilon_{0}}{\alpha_{1} \operatorname{ch}(\alpha_{1} \rho) + \alpha_{2} \operatorname{sh}(\alpha_{1} \rho)}. \quad (4.19)$$

As seen from Eq. (4.19), for $\varkappa_1 \rho \ge 1$ virtually the entire charge of the internal region is concentrated close to its boundary and falls off inward inside the region over a length $\sim \varkappa_1^{-1}$. This length depends only on the geometrical parameters R_1 and n_1 and drops off with increasing particle density as $n_1^{-1/2}$. The particle charge at the internal boundary of the region is equal to

$$q_1(\rho) = \frac{\varepsilon_0(\mu_2 - \mu_1)R_1(1 + \varkappa_2 \rho)}{e\rho(\varkappa_1 + \varkappa_2)},$$
(4.20)

i.e., its typical order of magnitude is the same as for the particles that do not form regions but rather are distributed randomly among particles of normal size (see the preceding Section).

Outside of the boundary the potential falls off over the screening length κ_2^{-1} . This screening length vanishes as $n_2 \rightarrow \infty$. The particle charge will also vanish: $q_2(\rho) \sim n_2^{-1/2}$.

Using Eqs. (4.19), (4.15) and (4.16) one obtains the following expressions for the potential at the centre and along the boundary of the region:

$$\varphi(0) \approx (\mu_2 - \mu_1) \frac{1}{e},$$

$$\varphi(\rho) = \frac{\mu_2 - \mu_1}{e} \frac{x_{\nu} \operatorname{och}(x_1 \rho) - \operatorname{sh}(x_1 \rho)}{x_1 \operatorname{och}(x_1 \rho) + \rho x_2 \operatorname{sh}(x_1 \rho)}.$$
 (4.21)

As one sees from Eq. (4.21), the potential remains nearly constant throughout the entire nonstandard particle region $r < \rho$ for $\varkappa_1 \ge \varkappa_2$. On the other hand, it changes abruptly within this region for $\varkappa_2 \ge \varkappa_1$.

4.4. Experimental proof of mutual charging of small particles

Apparently, the very first evidence for the existence of mutual charging has been given by the results of Ref. 51 concerning coagulation of small Ag particles ($R \sim 5$ nm) in plasma. They reveal that their coagulation time is four orders of magnitude less than what it would be if the coagulation were governed by the van der Waals forces. But the coagulation rate of nonmetallic carbon particles of the same size was just the same as it should be the case for van der Waals forces. The fact that the plasma electrical conductivity is finite makes the mutual charging of Ag particles of different sizes quite possible. In carbon particles only the fluctuation mutual charging can occur but it is very weak in

plasma and, hence, cannot significantly influence coagulation kinetics. At the same time if the spread in the sizes of the Ag particles is considerable, can become mutually charged quite strongly. Unfortunately, no direct experimental confirmation of the Ag particles being charged was obtained in Ref. 51. Further investigations using an external electric field are required.

In Ref. 74 an attempt was made to explain the anomalously high coagulation rate of Ag particles found in Ref. 51 by adsorption on their surfaces greatly increasing the van der Waals forces between them. It is assumed in Ref. 74 that this increase is caused by interaction between surface plasma oscillations and electric dipole oscillations typical of adatoms. But concrete estimates, leading to the possibility for the van der Waals forces to increase by 3 to 4 orders of magnitude, were obtained only for a quite hypotethical case when a considerable part of adatoms is in an excited state with the excitation energy close to the surface plasmon frequency. Even if one allows for a high degree of coverage of particles by adatoms it is quite unrealistic to believe that these adatoms are very strongly excited.

A direct proof of the mutual charging of small particles was obtained in Ref. 73. We begin with a presentation of the results from visual observation of charged regions in island films. The studies were carried out at 300 K on island gold films fabricated by thermal deposition on the (001) cleaved faces of an NaCl crystal. Since the crystal surface is nonideal due to the cleaving process (for example, edge irregularities occur on the surface), the small-particle formation conditions differed throughout the surface. Therefore the island film may have had areas where particle sizes differed significantly from the averaged particle sizes. Electrical neutrality does not hold in such regions in accordance with the concepts outlined in Secs. 4.3, 4.4.

The studies were carried out using a scanning electron microscope and an electron-beam energy spectrometer. This method employs a comparison of the energy spectrum of the secondary electrons of the probed region with a reference spectrum of secondary electrons. Electrodes were attached to the film and the spectrum of the grounded electrode was used as the reference spectrum. The secondary electron spectrum may deviate from the reference spectrum for two reasons. First, any deviation of the local potential of the probed region from the reference potential will cause an energy shift of the local spectrum relative to the reference spectrum equal in magnitude to this potential which is then registered as a signal (the vertical beam deflection during its horizontal sweep). Second, electrically neutral substrate defects may also serve to distort the spectrum, and these also produce a signal. However, the apparent potential associated with such defects can be easily differentiated from the true potential by the behavior of the signal in an external electrical field applied to the electrodes.

Figure 11 shows the potential contrast signal plotted as a function of the coordinate along the scanning line. Curve Icorresponds to the case where no voltage is applied to the film. The features appearing on this curve have different physical origins. Indeed, when a voltage is applied to the film (curves 2 and 3 are obtained by applying a 0.5 and 1 V voltage to the film, respectively) the feature labeled by an arrow vanishes while the other features remain. When the voltage is removed the feature indicated by the arrow reappears. The



FIG. 11. Potential contrast cutves (a) for an island gold film deposited on the (001) cleaved face of a NaCl crystal at T = 300 K and a film voltage $U_f = 0$ (1), 0.5 (2) and 1 V (3); the left electrode is grounded. (b) repeat measurements showing the reproducibility of results.⁷³

potential contrast curves are recovered in their entirety in repeated measurements (compare Fig. 11a and 11b), are stationary in time and are independent of the energy and intensity of the probe electron beam. This suggests that they reflect the natural properties of the film and do not follow from changes in its state during the measurement process. Specifically, film charging by beam electrons is excluded.

Therefore, the potential contrast curves as a function of the coordinates reveal two types of features. Features of the first type remain unchanged upon application of a voltage to the film. Consequently, they are not related to film charges and are wholly determined by its morphology. The second type (it is the only one labeled by an arrow in Figs. 11a,b), on the other hand, exists when no voltage is applied to the film although it vanishes when the voltage level is raised. Consequently, it can be attributed to the electrical charges that accumulate in a specific region of the film. Given the electrical neutrality of the films, they must be screened by charges of opposite sign in the adjacent regions.

A drawback of this approach is that the measurements are carried out along a single scanning line. If a given step is selected and the spectal shift of the secondary electrons is converted into a digital signal and is then used to modulate the luminance of a television cathode-ray tube, it is possible to carry out measurements across the entire surface with the results presented as equipotential lines.

Figure 12 shows the equipotential lines from the application of a $U_{\rm f} = 3$ V voltage to the film as alternating dark and light lines. The potential difference between two neighboring light (dark) lines is 0.3 V. If the film were to contain no charged regions the equipotential lines would form a family of parallel lines. However, Fig. 12 clearly reveals a film region surrounded by a closed equipotential line (as indicated by the arrow). This behavior of the potential can be attributed solely to charges in this region. In order to avoid confusion, it should be emphasized that the results shown in Figs. 11 and 12 were obtained on different specimens. The fact that, unlike the first specimen (Fig. 11), the external field applied to the second specimen (Fig. 12) does not break down the charged region can be attributed to its geometrical proximity to the "B" electrode which is used to stabilize the specimen (the center of the region is negatively charged, while the "B" electrode is positively charged). Changes in elecrode polarity will cause the charged region to vanish;



FIG. 12. The equipotential lines in an island gold film, $U_{\rm f} = 3$ V, T = 300 K. The contact-island boundaries are designated A and B (Ref. 73).

this effect was observed in many specimens. It is important that the charged region shown in Fig. 12 does not vanish when the external field is removed, i.e., as the region in Fig. 11 it is produced by the intrinsic properties of the film.

The specimen whose equipotential lines are shown in Fig. 12 was also analyzed by scanning electron microscopy. It was established that the particle size within the charged region amounts to a few tens of angstroms, while it is an order of magnitude higher outside this region. Hence, the natural explanation is to attribute the charged region to the difference in the Fermi energies of the electrons in the localization region of the smallest particles and in the rest of the film.

Qualitatively, the experimental situation discussed here corresponds to the theoretical model investigated in the preceding section apart from the fact that the region occupied by smaller particles is here two-dimensional and not threedimensional. If one compares the theoretical results obtained there with experimental data just described, one should conclude that they correspond to the case $\kappa_1 \gg \kappa_2$.

The mutual charging effect can also be used in practice. If a dispersed metallic film is deposited on a dielectric substrate with the size of film islands varying monotonically from one electrode to the other, such a film will have diode properties due to the mutual charging of the particles. Indeed, the charge-induced initial potential relief of the film is added to (or substacted from) the applied voltage depending on its polarity, thereby producing asymmetry in the conductivity of such films. A necessary condition for this phenomenon is that the electical conduction of the medium through which which charge transfer from particle to particle occurs, i.e. the substrate, be of semiconductor nature.⁷³

The I–V characteristic shown in Fig. 13 corresponds to an island gold film with island sizes varying from several tens to several hundreds of angstroms. The characteristic is given for the $\pm 0.1 V$ range since the asymmetrical behavior of its branches corresponding to different voltage polarities across the film is particularly clearly expressed in this region.⁷³ This is consistent with the theoretical analysis outlined in Ref. 73. The forward current direction is the direction where current flows from large islands to small islands, as would be expected with the charge sign established for the small particles visually. At higher voltages both branches of the I–V characteristic converge and are accurately superim-



FIG. 13. The I-V-characteristic of a film with asymmetrical inhomogeneous island structure at T = 300 K (Ref. 73).

posed. In the initial section of the I-V characteristic the rectification ratio for the gold films exceeds a quantity of the order of 10 in individual cases.

4.5. Current through small particles and chemical processes in them

In what follows, some transport phenomena in which small particles take part, and in which effects of the spatial quantization or the Coulomb size-dependent effects manifest themselves will be discussed. First, the tunnel current through an insulating layer separating two electrodes in the cases when small metal particles are located inside the layer will be considered. Such a system consisting of two Al films separated by an Al₂O₃ film was investigated in Ref. 182. Small Sn particles were inside the insulating film close enough to one of the electrodes (correspondingly, far enough from the other one). This tunnel junction behaves at high temperatures like a conventional ohmic resistance. But at low temperatures (but exceeding the transition point to the superconducting state) the differential conductivity $\sigma = dV/dI$ reveals a sharp peak as $V \rightarrow 0$, i.e., current flow is hampered at small voltages V.

Qualitatively, the origin for this consists in the fact that the electron transition between electrodes occurs in two stages. At the first stage the electron goes over from an electrode to the small particle, and at the second stage from the small particle to the other electrode. But the electron transfer to the particle increases its Coulomb energy by $e^2/2\varepsilon_0 R$ (see Eq. (4.2)). This fact hampers the electron transfer: it becomes possible as $T \rightarrow 0$ only when the voltage between the electrode and the small particle exceeds this Coulomb energy. This effect is referred to as Coulomb blockade.

Treating the problem more accurately, one should take into account that at zero current an equilibrium charge transfer from the electrode to the particle should occur in order to equalize their chemical potentials. But their complete equalization is impossible, as only an integer number of electrons may take part in the charge transfer (see Sec. 4.2). As a result, a random equilibrium electrode-to-particle voltage arises which influences the detailed shape of the I-V characteristic. Existence of such quantum potential fluctuations leads to the conductivity dependence on the frequency ω of the external electrical field¹⁸³ and to quantum noise in the tunnel junction.¹⁸⁴ Experimental and theoretical investigations^{185,186} show that up to the region where the spatial quantization of levels is essential (eV, $T \ll \delta$), the conductivity σ depends on ω/T as $V \rightarrow 0$ and on ω/V as $T \rightarrow 0$. Here δ is the mean level spacing.

Recently quantum effects eroding the Coulomb blockade have been investigated intensively (e.g. Refs. 259-264). In particular, it was established that in moderate magnetic fields amplitude and peak positions of the tunnel junction resistivity reveal a periodic dependence on the magnetic field which is attributed to the field dependence of spatially quantized electron levels in small particles.²⁵⁹

If small particles serve as electrodes of an electrochemical cell, then the current density should depend on particle size.^{47,48} In fact, the current in an electrochemical cell is described by the Tafel equation:¹⁸⁷

$$\Delta \varphi = a(I_0) + b \ln I, \qquad (4.22)$$

where $\Delta \varphi$ is the potential shift from its equilibrium value, I_0 is the equilibrium atom exchange current between the particle and the electrolyte (in the electrolyte these atoms become ions, i.e. charge carriers),

$$I_0 \sim \exp\left[-\frac{1}{T}(\mu_c - \mu_a)\right],$$
 (4.23)

where μ_c and μ_a are the electrochemical potentials of the activated surface + atom complex and of the same atom in the adsorbed state, respectively.

At least one of these quantities, namely μ_a , should depend on particle size. For example, if adsorption of metal atoms from the electrolyte occurs according to a mechanism including electron transfer from the atomic level \mathscr{C}_A to the Fermi level μ of the small particle then the binding energy of the adatom with the particle is $Q = \mathscr{C}_A - \mu + E_i$ where E_i is the energy of interaction of the adatom ion with the particle.

The chemical potential of adatoms is linear in the adatom binding energy:

$$\mu_{\rm a} = Q + T \, \ln \sigma, \tag{4.24}$$

where σ is the degree of covering of the surface. Therefore, the size dependence of μ_a is opposite in sign and of the same order of magnitude as μ . Using estimates of the size-induced shift in μ presented in Sec. 3.5 this means that μ_a for a particle with $R \sim 5$ nm should differ from that for a bulk sample by a quantity ~ 0.1 to 0.3 eV. According to Eq. (4.23) such a shift may cause a corresponding change in the exchange current at 300 K by 4 orders of magnitude. This current may both increase and decrease with growing R depending on the sign of the derivative $\partial \mu_a / \partial R$.

The same estimate remains in force for the desorption rate, which also is proportional to $\exp(-Q/T)$. This is the simplest model of a chemical reaction, and it shows that chemical kinetics depends on the size of particles on surfaces of which a chemical reaction takes place. It is clear that the rate of a chemical reaction on small particles may be both higher or lower than bulk than on bulk samples, depending on the sign of the size induced shift in μ . There are numerous experimental data which give evidence of size-dependence of catalytic activity of small particles. They reveal that, really, its dependence may be of both signs.¹⁸⁸ But it is impossible to elucidate the microscopic mechanism of this dependence at present.

It should be noted that the boundary conditions for electrons on a metal surface change as a result of adsorption. For example, it may cause appearance of surface resonances if they were nonexistant before adsorption or, on the contrary, cause their disappearance if they existed before ad-

4.6. Magnetic properties of small particles

For a long time the main direction in the study of magnetic properties of small particles was paramagnetic susceptibility of nonmagnetic metals. Information on it makes it possible to draw some conclusions concerning the level statistics in smal particles (Sec. 3.2). Theoretical and experimental results on magnetic properties of nonmagnetic metal particles are fully discussed in the review articles of Refs. 129, 130 and its makes no sense to repeat them here. In what follows, the main emphasis will be laid on cooperative magnetic phenomena in small particles. They are possible not only in materials with spontaneous magnetic ordering of bulk samples but also in those without magnetic ordering.

The first problem to be discussed is the spin ferromagnetism of small particles consisting of nonmagnetic atoms. In fact, if the external (n,l) electron shell of a spherical particle is occupied by electrons only partially, then the spins of these electrons may form a united spin due to exchange interaction between them. It should be maximum for a given filling of the external shell and, hence, may amount to l/2. With allwance for the condition $l \sim k_F R \ge 1$ the magnitude of the united spin greatly exceeds the electron spin although it is small compared to the maximum possible spin of the particle (i.e., N/2).

The spherical shape of the particle favors the ferromagnetic ordering. For this reason this ordering competes with the Jahn-Teller effect which manifests itself in the ellipsoidal deformation of the particle (Sec. 3.1). The energy lowering in both cases is of the same order in $1/k_F R$. Indeed, according to Eqs. (3.2)-(3.4) the maximum change in the energy due to the deformation with allowance for $l \sim k_F R$ is of the order

$$E_{JT} \sim \frac{l^2 \mu^2}{\alpha S} \sim \frac{\mu^2 k_F^2}{\alpha}$$
 (since $l \sim k_F R$).

In the case of ferromagnetic ordering if one evaluates the exchange integral J using wave functions for an electron in a spherical potential well one obtains $J \sim e^2/Rl$. Correspondingly, the magnetic ordering energy E_F is of the order of $l^2 J \sim e^2 k_F$. Thus, in both cases the energy lowering does not depend on R.

Both these channels of energy lowering are mutually exclusive. For this reason the possibility exists when with the magnetic field nonexistent, the Jahn–Teller deformation occurs without ferromagnetic ordering. But a magnetic field causes an abrupt transition to the undeformed shape and ferromagnetic ordering.

Considerations just presented may explain the very interesting experimental result of Refs. 141, 142. The paramagnetic susceptibility of an ensemble of highly-symmetrical Hg_{13} clusters in the zeolite matrix in a field of 15 kOe is



FIG. 14. The magnetic moment of Hg_{13} clusters as a function of temperature. ^{141,142}

low and depends on temperature weakly. But in a field of 25 kOe as the temperature drops below 80 K, χ rises sharply and as $T \rightarrow 0$ reveals a 1/T temperature dependence (Fig. 14). The fact that the return of the system into the weakly magnetic state takes place with a hysteresis, points to the existence of two states, one of which is absolutely stable at a given field, and the other metastable. This effect should be justaposed to the fact that both zeolite and mercury bulk samples are diamagnetic.

Results strongly resembling those of Refs. 141, 142 were obtained for Na clusters in zeolite:²⁶⁵⁻²⁶⁷ at all field strengths, even at those when a complete alignment of magnetic moments of Na atoms should be achieved, χ obeys the Curie law. Meanwhile, metal clusters should behave as Pauli paramagnets.

Still more astonishing are the results obtained for Ag clusters in zeolite:²⁶⁸ in the temperature range from 4 to 300 K their susceptibility obey the Curie–Weiss law with the paramagnetic Curie temperature equal to (-80K). Similar behavior is also exhibited by Ce clusters in zeolite, but their paramagnetic Curie temperature is equal to (-40 K).

These results can be explained on the basis of the facts presented in Sec. 1.2: very small clusters of metal atoms are nonmetallic. Their external s-electrons are localized each on its own atom. For this reason the conventional exchange interaction is possible between atoms entering clusters which align their spins. This point of view is supported by the results of calculations in Ref. 143 according to which a moment of $5\mu_{\rm B}$ corresponds to the ground state of highly symmetrical Na clusters. The results of Refs. 141, 142 may be related also to other theoretical papers. An enhanced value of γ for a small metal particle was obtained, for instance, in Ref. 145 using the density functional method. According to Ref. 145, this effect should increase with increasing γ of a bulk metal sample, so that an almost-ferromagnetic metal being dispersed may become ferromagnetic. But the results of Ref. 145 should be treated with caution since the density functional method does not take into account surface effects related to spatial quantization (Sec. 3.5)

There are also other experimental data resembling those of Refs. 141, 142. Coexistance of the Pauli and the Curie-Weiss paramagnetism was discovered in small particles of V in Ref. 269. According to the NMR results of Ref. 270, this coexistence should be attributed to the conduction electron behavior in the bulk and on the surface of the Vparticle being different.

A considerable rise in the low-temperature susceptibility of Cu and Al particles of size of 6 to 10 nm with increasing field was observed in Refs. 153, 154 (actually the Knight shift proportional to χ was studied in Refs. 153, 154 using a NMR method). But the authors of these papers relate this enhancement of γ not to the almost-ferromagnetism of small particles but rather to the randomness in the level distribution in small particles. As levels are separated from each other by a gap $\sim \delta$, the initial susceptibility of systems with an even number of electrons should vanish as $T \rightarrow 0$. But for $\mu_{\rm B}H \gg \delta$ the level systems in spin subbands are displaced very strongly with respect to each other. For this reason levels of different subbands may be arbitrary close to each other, and in strong fields γ could tend to a finite value as for bulk samples. Experimental results on Al are more informative than those on Cu since, unlike Cu, in Al the spin-orbit interaction intermixing spin subbands is very weak. No thermal hysteresis is reported in Refs. 153, 154 which suggests that the physics of the effects studied in these papers differs radically from that in Refs. 141, 142.

The paramagnetic susceptibility of 1.5 nm Mg particles at not very low temperatures considerably exceeds that of bulk samples. As $T \rightarrow 0$ the susceptibility decreases sharply as should be the case for a system with an even number of electrons. A similar increase in χ with decreasing size was observed also for Os particles.¹⁷²

Now we proceed to materials with spontaneous magnetic ordering of bulk samples. Sometimes the spontaneous magnetization of small ferromagnetic particles should exceed that of bulk samples. In Ref. 147 it was established using the Monte-Carlo method, that small particles reveal no distinct phase transition to the paramagnetic state and at high temperatures the spontaneous magnetization increases with decreasing particle size. An analysis carried out in Ref. 148 shows quite satisfactory agreement between theoretical results¹⁴⁷ and experimental data¹⁴⁹ on Ni clusters of size up to 1.2 nm.¹⁴⁹

Enhancement of the magnetization with decreasing size may be caused also by a decrease in the role of magnetic dipole interaction. Because of it the magnetic state of a particle large enough cannot be uniform.¹⁵⁰ According to Ref. 151, a critical radius exists beginning from which a moment twisting should arise.¹⁵² A relatively small spontaneous magnetization component arises which is twisted along the particle surface. This component is superimposed on the uniform magnetization. But at radii less than critical the magnetization should be uniform.

On the other hand, there are experimental data according to which the spontaneous magnetization of small ferromagnetic particles is lower than that of bulk samples: for Fe clusters of 50 to 500 atoms²⁷¹ Co clusters of 20 to 200 atoms.²⁷² In Ref. 65 the saturation magnetization of small Ni particles is found to be less than that of bulk samples. Similar results were obtained in Ref. 146 for small Gd, Tb and Ho particles. The effect is significant even for R > 30 nm which, possibly, may be attributed to a very large indirect exchange length in these materials. Particles of smaller size exhibit a structure transformation from the hexagonal to the f.c.c. modification. Then the spontaneous ordering vanishes completely, and the magnetic susceptibility follows the Curie-Weiss law with the paramagnetic Curie temperature about (-10 K). These results have not obtained a theoretical explanation as yet. Possibly they are related to a high degree of imperfection of small particles leading to their spin-glass state.

The results of Ref. 146 should be juxtaposed to the results of Ref. 273 on magic numbers for magnetic properties of Gd_n clusters with *n* from 11 to 92. Magnetic moments of $3\mu_B$ per atom were found in clusters with magic numbers and their Curie point greatly exceeds that of bulk samples. These clusters behave normally, i.e. as superparamagnetic particles. But clusters of other sizes reveal a qualitatively different behavior including the deflection of a beam of them to the lower magnetic field side in passing through a Stern-Gerlach device. Possibly, this may be explained by the precession and nutation of clusters occuring under the condition of the magnetic moment being rigidly bound to the crystal lattice.²⁷⁵

In the opinion of the author of this review, contradictions in experimental results on properties of ferromagnetic particles may be explained at least, partially, by a difference in temperatures and cluster sizes used in the experiments. At temperatures, exceeding the Curie point of a bulk sample, when its spontaneous magnetization is zero, that of clusters may remain large enough. But at low temperatures the magnetization of small particles may decrease more rapidly than that of bulk samples, on an increase in temperature. This is caused by the fact that the relative weight of surface atoms tends to zero for bulk samples but remains finite for small particles. Meanwhile, the exchange interaction of a surface atom with its neighbors is reduced in comparison with a bulk one. One should also keep in mind the tendency of small Fe particles to amorphization (Sec. 1.1) due to which in some experiments particles were ordered and in other experiments disordered.

4.7. Macroscopic quantum tunneling of magnetization

Small ferromagnetic particles are single-domain. The magnetic anisotropy allows as a minimum two different directions for the magnetization at which the anisotropy energy is at a minimum (the easy axis case). Usually, the magnetization direction will switch from one easy axis direction to the other via a process of thermal activation. This process relies upon the system receiving thermal energy from its environment so as to surmount the energy barrier that separates one energy well from another. As the temperature is lowered, the available thermal energy obviously decreases. In fact, the switching rate, P, for this process decreases exponentially with the ratio of the energy barrier U to the thermal energy T.

The energy barrier is proportional to the particle volume. Thus as the temperature is lowered the thermally activated switching will be blocked for ever-smaller particles. But it was observed experimentally, that even at 1 K switching takes place. Obviously, it should be ascribed to a quantum subbarrier tunneling of magnetization. A single-domain particle consists of about 10^5 to 10^6 electron spins which are constrained by the exchange interaction between electron spins to behave dynamically as a single quantum spin. The result is that the single-domain particle can tunnel from one "macro-spin" state to another. Because of the huge number of degrees of freedom acting coherently, the tunneling process is an example of what has been recently referred to as macroscopic quantum tunneling.

Mathematically, if one considers the magnetization M as a spin operator, then the projection $(M \cdot e)$ onto one of the easy directions e does not in general commute with the Ham-

iltonian. This means that eigenvalues of $(\mathbf{M} \cdot \mathbf{e})$ are not conserved quantum numbers, which is not surprising because the magnetic anisotropy appears as a result of relativistic interactions. Consequently, M can tunnel between the energy minima.

Two mechanisms for the tunneling processes were suggested. The first one applies to relatively large particles whose size is greater than the domain-wall width. It consists of nucleation of a domain wall which subsequently sweeps across the particle switching the direction of its magnetization. Since the energy barrier between the two states is proportional to the volume of the particle, the tunneling rate due to this mechanism is extremely small. For particles of size smaller than the domain wall width, uniform subbarier rotation of the magnetic moment may take place. This is an analog for a particle subbarier tunneling if one takes into account that a moment of inertia associated with the rotation of **M** should exist.

A calculation of the latter process was carried out in Ref. 274. In particular, there a case of uniaxial anisotropy was considered, the energy of which is expressed in terms of the angles θ, φ which determine the direction of M (x is the easy axis):

$$E(\theta, \varphi) = K_1 \cos^2 \theta + K_2 \sin^2 \theta \cdot \sin^2 \varphi,$$

$$K_1 > K_2 > 0.$$
(4.25)

The rate of subbarrier tunneling in this case is given by the expression

$$P \sim \left(\frac{1-\lambda^{1/2}}{1+\lambda^{1/2}}\right) \frac{M}{2\mu_{\rm B}}, \qquad \lambda = K_2/K_1.$$
(4.26)

Since the ratio $M/2\mu_B$ is very large, tunneling is possible only for $\lambda \ll 1$. In the treatment presented above the dissipation of the energy due to the interaction of the system with a heat reservoir is not taken into account since it is very small.

The tunneling rate can increase in the presence of an external magnetic field directed along the easy axis which decreases the energy barrier. If this rate is large enough, the system may exhibit repeating tunneling back and forth between the two wells in a coherent fashion. This is a case of what is referred to as macroscopic quantum coherence (MQC). But, if the field is sufficiently strong, the system will end up trapped within the deeper well. Trapping requires some way of getting rid of excess energy, usually via dissipation. The general problem of the macroscopic quantum coherence (MQC) is discussed in Refs. 275, 276.

The physical manifestation of this phenomenon is as follows. In the absence of a magnetic field, given that the energy wells are deep, there is negligible probability to find the magnetization in other than an up or down direction. Furthermore, initially, there is equal probability for a singledomain particle to be in either of these two states. With negligible dissipation present, coherent tunneling back and forth between the two states leads to a sinusoidal oscillation of the two-time correlation function for the magnetization $C(t) = \langle \mathbf{M}(t)\mathbf{M} \rangle$ at double the MQC tunneling rate *P*. According to the Kubo formula the frequency-dependent magnetic susceptibility $\chi(\omega)$ is essentially the Fourier transform of C(t). Thus, this susceptibility should exhibit a resonance at frequency 2*P*. But dissipation should strongly affect this resonance.



FIG. 15. Dependence of the coercive force of $Tb_{0.5}Ce_{0.5}Fe_2$ on temperature for different measurement times τ (Ref. 280).

A number of possibilities exists for the behavior of C(t)as the time approaches infinity, among them being the following: 1) The resonance can be "underdamped," so that C(t) decays to zero in an oscillatory fashion. The resonance peak in $\chi(\omega)$ will then essentially be merely broadened. 2) The resonance can be "overdamped," so that C(t) decays to zero without oscillations. 3) C(t) remains equal to its initial value for all time. This case is special in that the magnetization is trapped with its initial orientation. Most theoretical studies indicate that with sufficiently strong dissipation, trapping will occur at absolute zero temperature.

Switching is also a very important process in small antiferromagnetic particles. As is shown in Ref. 277, quantum tunneling in them should be more intensive: the temperature T_c of crossover from the thermally activated regime to the quantum tunneling regime should be two orders of magnitude higher than in ferromagnets. To observe the tunneling process, no bias magnetic field is required.

There are already some experimental data which, apparently, confirm the existence of quantum tunneling in small particles. In Ref. 278 a sharp peak in $\chi(\omega)$ was found when studying ferromagnetic particles containing 10⁶ spins. The resonance frequency decreases with increasing particle volume. Such behavior agrees with the picture of quantum tunneling. The same is true for the temperature dependence of the height of this peak: it increases with decreasing temperature, reaching a more or less constant value below a temperature of about 0.1 K. But a numerical analysis of the results of Ref. 278 carried out in Ref. 279 casts doubt upon their correspondence to the theory of macroscopic quantum tunneling.

More definite are the results of Ref. 280 where the temperature dependence of the coercive force H_c of small ferromagnetic particles of $Tb_{0.5} Ce_{0.5} Fe_2$ was studied. An analysis shows that at $T \gg T_c$ the coercive force should strongly depend on temperature, but at $T \ll T_c$ it should be temperatureindependent. Both these regimes were observed experimentally with the crossover temperature T_c equal to 1.2 K (Fig. 15). Estimates of the tunneling volume show that it is much less than the particle volume but larger than the domain wall volume. Thus, it was suggested in Ref. 280 that quantum tunneling consists here in sweeping of the domain wall across the particle. The domain wall appears as $H \rightarrow H_c$, being, apparently, pinned to the particle surface. It means that it is in a state of metastable equilibrium.

- ¹⁾ To avoid misunderstanding, it should be stressed that the dependence of α (2.12) on V has nothing in common with the formal dependence of α (2.1) on V which follows from the ambiguity in the choice of the surface separating the phases (see Ref. 9). The point is not that the latter dependence is very weak ($\sim (S/V)^2$): in the one-phase case the notion of a separating surface has no meaning at all.
- ²⁾ By analogy with g (2.6) the quantity γ in (2.16) may be called the surface stress of a liquid. For a liquid in thermodynamic equilibrium with its vapor the surface tension and stress coincide.
- ³⁾ Their density under typical conditions, actually, may greatly exceed the density of atoms in the vapor which in the vicinity of the melting point amounts to only 10⁶-10¹⁰ cm⁻³ (Sec. 2.3). The bulk vacancy density may reach 10¹⁹ cm⁻³ according to Ref. 44. Conditions for the formation of surface vacancies are much more favorable than for bulk ones.
- ⁴⁾ In order to obtain terms ~ 𝒞^{1/2} for a sphere, one should average G(𝒞) over radii in a range ~λ(𝔅)
- ⁵⁾ The authors of Ref. 43 refer to experimental data of Yu. F. Komnik on thin films obtained in 1963, 1964. Unfortunately, there are misprints in the references to these papers presented in Ref. 43. This hinders us in using the original Komnik papers for elucidating the origin of such a huge effect. But it is clear that it cannot be related to the Laplace pressure. According to recent experimental data,⁶⁸ the relative compression of Ag particles of 5 nm size amounts to only 0.2% which is only half of what would be obtained according to the expression (2.2) for the Laplace pressure.
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