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**BCS superconductivity for weakly coupled clusters**

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Résumé. — La superconductibilité BCS peut avoir d’assez fortes températures critiques quand des agrégats de taille moyenne sont couplés faiblement pour faire un cristal. Cette remarque étend aux cas quasi zérodimensionnels une remarque faite initialement par Labbé dans les cas quasi unidimensionnels et par Hirsch, Bok et Labbé pour les cas quasi bidimensionnels. Des applications possibles sont envisagées pour les agrégats bidimensionnels (fullerènes) ou tridimensionnels (métaux, phases de Chevrel). Les conditions l’applicabilité optimale de ce schéma sont assez restreintes.

Abstract. — BCS superconductivity is expected to have fairly high critical temperatures when clusters of moderate sizes are weakly coupled to form a crystal. This remark extends to quasi zerodimensional cases, a remark initially made by Labbé for quasi onedimensional ones and by Hirsch, Bok and Labbé for quasi twodimensional ones. Possible applications are envisaged for twodimensional clusters (fullerene) or threedimensional ones (metal clusters, Chevrel phases). Conditions for optimal applicability of the scheme are somewhat restricted.

Introduction.

The observation of superconductivity in crystals made with C\(_{60}\) fullerene molecules suitably doped with alkali metals [1-3] leads necessarily to the question whether the high \(T_c\)'s observed could not be explained with a classical BCS theory, as was suggested for the earlier examples of chain (\(\beta\) tungsten structure) compounds [4, 5] and plane (copper oxide) ones [6, 7].

In all these cases, it could happen that conditions for a standard BCS weak coupling scheme apply to delocalised electrons, with a well defined density of states \(n\), leading to expressions of the critical temperature \(T_c\) and of the gap \(\Delta\) such that:

\[
\frac{2}{V} = \int_{-k_B T_D}^{k_B T_D} n(\varepsilon) \frac{1}{\varepsilon} \left( \frac{1}{2k_B T_c} \right) d\varepsilon = \int_{-k_B T_D}^{k_B T_D} n(\varepsilon) \frac{1}{(\Delta^2 + \varepsilon^2)^{1/2}} d\varepsilon
\]

(1)

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Here, $V$ is the effective electron-electron coupling, $T_D$ a cutoff temperature (i.e. Debye temperature for phonon mediated coupling) and energies $\varepsilon$ are counted from the Fermi level.

As initially remarked by Labbé [5, 8], such expressions can lead to values of $T_c$ and $\Delta$ well above the standard results:

$$1.76 \, k_B T_c^9 = \Delta^8 = 2 \, k_B T_D \exp - \frac{2}{n(0)\varepsilon}$$  \hspace{1cm} (2)

if $n(\varepsilon)$ peaks strongly enough in the range of the superconductive gap $\Delta$.

1. BCS superconductivity for weakly coupled molecular states.

We shall assume in this paper that the independent electron approximation and the weak scattering limit basic in BCS superconductivity, are valid, and return to this point at the end.

Let us then assume that the clusters considered are small enough for their (independent electron) states near the Fermi level to be separated in energy by amounts much larger than their width. This is due to the intercluster transfer integrals $t$, which then broaden each molecular state into a band.

Let us further assume that this broadening is less than $k_B T_D$.

In equation (1), one has then only to consider the occupied molecular band with the highest energy; and this can be replaced by a delta function centred on the molecular level $\varepsilon_0$.

Equation (1) then leads to

$$\frac{2}{fV} = \frac{1}{\varepsilon_0 \, 2 \, k_B T_c} = \frac{1}{(\Delta^2 + \varepsilon_0^2)^{1/2}}$$  \hspace{1cm} (3)

These expressions give a maximum of $T_c$ and $\Delta$ for

$$|\varepsilon_0| \ll \Delta$$  \hspace{1cm} (4)

with

$$2 \, k_B T_c = \Delta = \frac{fV}{2}$$  \hspace{1cm} (5)

In these expressions, the factor $f$ is given by

$$f = p/q$$  \hspace{1cm} (6)

where $p$ is the degeneracy of the molecular state and $q$ an average renormalisation factor.

If $V$ is counted per atom, it is clear that, for a cluster of $N$ atoms,

$$q \approx N$$  \hspace{1cm} (7)

if we neglect corrections due to the possible angular and radial variation of the states considered. In fact the largest deviations from (7) occur for the occupied states of highest orbital degeneracy in threedimensional metal particles where Appendix A shows that

$$q \approx \alpha N^{1/3}$$  \hspace{1cm} (8)

with $\alpha$ of order unity.

The optimal values of $T_c$ and $\Delta$, are, in this scheme, directly related to the electron-electron coupling $V$. For the BCS analysis to be valid, $V$ must certainly be much smaller than the Fermi energy $E_F$, counted from the bottom of the valence band. This is the case for phonon mediated coupling, where $V$ is a fraction of $E_F$, itself of order 5 to 10 eV in the cases we shall consider [9]. Indeed $V$ is typically of order $10^{-1}$ eV to 1 eV. This allows for fairly high values of $T_c$ if the factor $f$ is not too small. This requires Fermi states of high degeneracy $p$ in not too large clusters. We shall consider in turn 3d metal clusters, then 2d fullerene ones.
2. Large metal clusters.

Compact 3d metal clusters, with spheroidal shapes, are known to occur in many metals and have been especially studied in alkali ones [10]. We shall only consider here the case where each cluster contains a large number of atoms. This is to simplify the algebra; but the discussion could be extended to smaller values of $N$, with no substantial changes.

If we treat the valence band as a gas of free electrons enclosed in a potential well of radius $R$, with a constant potential inside the well, a WKB standard analysis, recalled in Appendix A, shows that the quantised energy levels, measured from the bottom of the well, are

$$E_n^l = \hbar^2 k_n^l R / 2m$$  \hspace{1cm} (9)

with, for $l \gg n$,

$$k_n^l R = \sqrt{l(l+1)} \left[ 1 + \left( \frac{3(n\pi - \text{const})}{2\sqrt{l(l+1)}} \right)^{2/3} \right]$$  \hspace{1cm} (10)

Here, the nuclear notation is used: $1s, 2s, \ldots$ $ns$ for $l = 0$; $1p, 2p, \ldots np$ for $l = 1$ etc.

Taking into account that a $(n, l)$ level has a degeneracy $2l+1$, one sees that a special stability is obtained for states $(1l_M)$ just filled. Using the fact that, in the limit of large clusters, the total electronic density is independent of boundary conditions [11], one can write, for a metal of valence $v$ and atomic volume $v_a$

$$(k_n^{(1M)})^3 \approx 3\pi^2 v / v_a$$  \hspace{1cm} (11)

From (10), we deduce that the $(1l_M)$ state is just filled for a cluster of $N$ atoms such that

$$N v \approx \frac{4}{9\pi} l_M^3$$  \hspace{1cm} (12)

Such a condition is approximately followed experimentally up to $N \approx 10^3$ in Na clusters [12], where $v = 1$.

To reach the highest value of $T_c$ and $\Delta$ in superconductive clusters, we need the occupied state of highest energy to be half-filled. To have the highest possible degeneracy $p$, we then require that state to be a $(1l_M)$ state. The corresponding number of atoms only differs from (12) by a number of order $2l_M$, thus linear in $l_M$ and of the order of the terms neglected in (12) for large $N$ and $l_M$. Similarly, equation (12) remains approximately valid for somewhat ionised clusters, where the partial emptying of the $(1l_M)$ state is due to a charge transfer with another type of ion.

In conclusion, for metal clusters, the optimal situation will occur if a $(1l_M)$ state is half filled. If the cluster keeps its spheroidal shape, the degeneracy of such state gives

$$p = 2l_M + 1 \approx 2 \left( \frac{9\pi N v}{4} \right)^{1/3}$$  \hspace{1cm} (13)

in the limit of large $N$'s. From (5), (8) and (A9), this leads to

$$k_B T_c \approx \frac{3vV}{8}$$  \hspace{1cm} (14)

Thus sizeable values of $V$, of at least 0.1 eV, usually met in such metals [9], could lead to values of $T_c$ above room temperature.
For such a relation to apply, a number of conditions must be realised, as pointed out above. First, the molecular state \((1l_M)\) considered must be separated in energy from its neighbours by more than the superconductive gap:

\[
\Delta = 2k_B T_c < \delta E_M
\]

(15)

where, from (10), one can estimate

\[
\delta E_M \cong \hbar^2 k_M \delta k_M / m
\]

(16)

with

\[
k_M R \cong 1_M
\]

(17)

and

\[
\delta k_M R \cong \pi.
\]

(18)

Thus one requires

\[
\frac{3vV}{8} < \pi \left( \frac{9\pi}{4} N v \right)^{1/3} \frac{\hbar^2}{m R^2}.
\]

(19)

With

\[
\frac{4\pi R^3}{3} \cong N v_a
\]

(20)

where \(v_a\) is the atomic volume, this gives

\[
V < \frac{\hbar^2}{2m} \frac{8\pi^2}{3} \left( \frac{2}{v_a v} \right)^{2/3} \frac{1}{N^{1/3}}
\]

(21)

With the approximate relation (exactly valid in the limit of large clusters)

\[
k_M^3 \cong \frac{3\pi^2 v}{v_a},
\]

(22)

this gives approximately

\[
\frac{V}{E_M} < \frac{5}{v^{4/3} N^{1/3}},
\]

(23)

a condition fulfilled at least up to \(N \cong 10^4\) as \(V < 10^{-1} E_M\).

Second, the cluster must remain spherical, although its \((1l_M)\) state is partly occupied only. One knows that a Jahn Teller distortion into an ellipsoidal shape lifts then the degeneracy of the \((1l_M)\) state and introduces a gap at or very near to the Fermi level [13]. The gain in \(T_c\) due to the high degeneracy of the \((1l_M)\) state would then be lost. One can imagine that quenching the clusters from a high enough temperature or reducing them by forming charge transfer compounds at very low temperatures might keep the spherical shape. There is another and simpler way to avoid the distortion: it is to use large enough clusters for their stability to be dominated by the atomic structure of the surface. In alkali metals \((v = 1)\), one knows that this happens for clusters larger than about \(10^3\) atoms [12]. However the polyhedral structure of the cluster would lift somewhat the degeneracy of the \((1l_M)\) states, in a way that would have to be analysed case by case. This would reduce the preceding estimate of \(T_c\) by a numerical factor typically smaller than 10.

Finally the band width due to the transfer integrals between clusters must be small than \(2k_B T_D\). Let the \((1l_M)\) states of two clusters be in coherent contact over an area of \(N_S\) atoms.
Let $t$ be an average transfer integral per atom pair. The probability of transfer from one cluster to the neighbour will be of order \[14\]

\[\tau_e \simeq (2\tau_M + 1) \frac{N_s}{q} t \] (24)

If each cluster has

\[r \simeq 12 \] (25)

neighbours, the corresponding band width will be of order \[14\]

\[w_e \simeq \left( \frac{6r}{2\tau_M + 1} \right)^{1/2} \tau_e \simeq 6 \left( \frac{2}{2\tau_M + 1} \right) \tau_e \] (26)

The condition

\[w_e < 2 k_B T_D \] (27)

then leads to

\[t < k_B T_D \frac{\alpha}{6N_s} \left( \frac{4N}{9\pi v} \right)^{1/6} \] (28)

The value of $N_S$ depends on the nature of contact. In the case of the polyhedral structure observed for large metal clusters, the least stringent conditions on $t$ would be obtained if the structure is such that the polyhedra touch by their summits. Then $N_S \simeq 1$ and, with $N \geq 10^3$, the condition (23) is that $t$ is no larger than $k_B T_D$. All other geometries of contact — spheres, polyhedra touching by their faces ... — would lead to larger values of $N_S$, thus more stringent conditions on $t$. As $k_B T_D \ll E_M$, these conditions imply that the clusters should touch only very loosely. This could be obtained in charge transfer compounds, if the metal clusters alternate with large enough negative ionic clusters. Another solution, perhaps more realistic, would be to obtain a contact through absorbed 0 or S or through a thin oxide layer.

As emphasized in Appendix B, solution (5) is only valid if $w_e$ is typically less than $10 \Delta$. This condition can be expressed in detail as we have done for condition (27). However it is enough to remark here that we are discussing fairly high values of $T_c$, more than typically $1/10 T_D$. If superconduction is by phonon coupling, $T_D$ is the Debye temperature. If we are only considering $T_c$ larger than typically 30 K, then the above condition $w_e < 10 \Delta$ results from condition (27). The same remark will apply to the other cases considered.

In conclusion, compounds built up with fairly large metal clusters could lead to sizeable values of $T_c$, of at least 100 K. The conditions required are however not easy to meet. The most difficult is to reach the size and electron transfer conditions which correspond to a half filled $(1\tau_M)$ state, thus $2\tau_M + 1$ electrons less than the magic number corresponding to the filling of a $(1\tau_M)$ state. The cluster is then not particularly stable and tends to deform spontaneously if $N$ is less than typically $10^3$ atoms, except perhaps if it is encased in a strong enough surrounding of doping elements. If one chooses the solution of large clusters ($N > 10^3$), their polyhedral structure is used in an optimal way if they touch loosely through their summits.
3. Fullerene compounds.

A similar discussion can be made for nearly spherical \( C_N \) fullerene molecules and their doped compounds.

The main difference is about the degeneracy of the molecular states.

Thus, in the limit of large \( N \)'s, the atomic structure could be neglected, at least for the valence band [15]. The molecular (one electron) orbitals are the spherical orbitals \( (l) \) of degeneracy

\[
p = 2l + 1
\]

and energy

\[
E_l = P_l(0) = (2l + 1)\beta
\]

For neutral clusters, the Fermi level occurs at or just above level \( l_M \) such that

\[
N \leq 2 \sum_{l=0}^{l_M} (2l + 1) = 2l_M (2l_M + 1) \cong 4 l_M^2
\]

And a relation of the same order is valid for ionic clusters. Then, from (5), (6), (7), the optimal condition of a half filled \( (l_M) \) state gives

\[
2k_B T_c = \Delta = \frac{(2l_M + 1) V}{2 N} \cong \frac{V}{4l_M} \cong \frac{V}{2N^{1/2}}.
\]

The conditions of validity are similar to those for metallic clusters. Thus condition (15) gives, with (30):

\[
V < 2E_M
\]

which is well fulfilled as \( V \ll E_M \).

Condition (27) leads to

\[
t < \frac{k_B T_D}{3 N_s} N^{1/2}
\]

With \( N_s \) of the order of a few units and \( N \) of order \( 10^2 \), one finds again that the contact should be somewhat loose, with \( t \) of the order of \( k_B T_D \). As \( t \) is due to a transfer between \( \pi \) atomic states which are nearly parallel to each other, as in organic superconductors, condition (34) does not require a very loose contact.

Finally one could wonder whether here again doping away from the perfect filling of the \( (l_M) \) state should not produce a spontaneous Jahn Teller distortion which would lift its degeneracy. The occurrence of \( C_N \) molecules with ellipsoidal symmetry can possibly be related to such an effect. However, at least for the smallest value of \( N \) (60), there is strong evidence that the rigidity of the \( \sigma \) bonds prevents such a static distortion to be effective [16], although some small dynamic Jahn Teller effect might possibly exist [17].
4. The particular case of buckminster fullerene C$_{60}$.

This is the minimum possible value of C.

For such small values of $N$, one knows that the atomic structure splits the $(l)$ states into states of lower degeneracy [15, 18]. This effect is larger than in metallic clusters because of the 2d nature of C clusters.

Thus for the C$_{60}$ M$_3$ compounds, where M is an alkali metal, the half occupied molecular state is a 3 fold $t_{1u}$ state. Equations (5) to (7) then lead to a maximum value

$$k_BT_c = \frac{1}{80}V$$

For the C$_{60}$ X$_5$ compounds, where X is a halogen, the partly occupied molecular state is a 5 fold $2h_u$ state. Then

$$k_BT_c \approx \frac{V}{50}$$

From this point of view, the optimal condition would be a compound with a charge transfer to C$_{60}^{19+}$, which would lead to partly occupied 1g$_g$ and 2h$_g$ states, with a degeneracy 7, leading to

$$k_BT_c \approx \frac{1}{35}V.$$  

However such large charge transfer might be unrealistic and the gain in $T_c$ rather minimal.

In these compounds as in isolated C$_{60}$ molecules, the energy differences between successive molecular states near the Fermi level are of the order of 1 eV, thus much larger than any possible superconductive gap. Condition (15) is thus amply fulfilled.

This is not necessarily so for condition (27), which gives

$$t < \frac{10\sqrt{2}}{\sqrt{PN_s}}k_BT_D$$

In C$_{60}$ M$_3$, $p = 3$ and $N_S = 2$ [16]. Then condition (27) leads to

$$t < 4k_BT_D.$$  

This is of the order of 0.1 eV if the electron coupling is through phonons.

Computed band widths $w_e$ for bands near the Fermi level are of order 0.2 eV for FCC crystals [17] of pure C$_{60}$, leading to $t \cong 0.4$ eV. In C$_{60}$K$_3$, where the intercluster distance is not much bigger [16] than in C$_{60}$, similar values are obtained [18] and condition (27) seems not to be fulfilled. However one expects $t$ to decrease fairly fast with increasing size of the metal ions. It is remarkable that indeed $T_c$ increases from 19 K for C$_{60}$K$_3$ [1] to 28 K for C$_{60}$Rb$_3$ [2] and 33 K for C$_{60}$Cs$_3$ [3].

Observed band widths, as deduced from electron excitations [17, 20], give also $w \cong 0.4$ eV; but, owing to a large Auger broadening, such values are only upper limits. Indeed angle resolved photoemission spectra seem to point to much smaller values of $w_e$, of the order [21] of 0.03 eV. Such a value would be in agreement with those deduced in C$_{60}$K$_3$ and C$_{60}$Rb$_3$ from measurements of the coherence length and penetration depth by magnetic measurement [22, 23] and, for C$_{60}$K$_3$, from muon depolarisation [24]. Thus condition (27) would be satisfied.

From this discussion, it looks as if the buckminster-fullerene compounds studied so far are borderline case where the band width $w_e$ is comparable with the cutoff energy band $2k_BT_D$.
if the electron coupling is through phonons. It is remarkable that, as expected in such a case (cf. Appendix B), the critical temperature varies sharply with the intercluster distance, thus apparently with the band width $\nu$, whether this variation is by pressure [23] or by change in doping agent [1-3].

Still higher $T_c$ could probably be obtained by suitable dopants increasing somewhat the distance between the $C_N$ molecules.

5. Limitations of the model.

There are obvious limitations to such a model.

First, the weak perturbation limit is certainly no longer valid [25] if the superconducting gap $\Delta$ is much larger than the band width $\omega_e$. This condition can be explicited in the various cases considered above. It always leads to a lower limit of the transfer integral $t$ somewhat less than $10^{-1}$ V. With usual values of $V$ for phonon mediated interactions, this is compatible with condition (27) only over a somewhat narrow range of couplings $t$. For smaller values of $t$, thus weaker intercluster couplings, the values of $T_c$ would drop much below the values discussed here [25], and tend rapidly to zero with $t$.

Second, the independent electron picture can be queried. There are various aspects to this question.

It is first clear that electron correlations are very weak within each metal cluster [26], while they are expected to be more sizeable in the $\pi$ bands of the fullerene [19, 27, 28]. Indeed they must be taken into account in a detailed study of electronic excitations [29].

But more important are the effects of intercluster charge fluctuations. When an electron is transferred from one cluster to the next, the change of potential energy $e^2/\varepsilon_0 R$ is larger than the effective one electron band width $\omega_e$ if

$$\frac{t}{E_M} < \frac{N \nu^{-\frac{1}{3}}}{6\sqrt{2p\varepsilon_0 N} \nu^{1/3}}$$

where $\varepsilon_0$ is the dielectric constant and, as before, $\nu \approx 1/3$ for metals and 1 for fullerenes. The previous discussion shows that the above condition is always fulfilled in practical cases, especially in metals. This shows that electron correlation have to be taken into account in the intercluster jumps. One can expect qualitatively such correlations to slow down the intercluster jumps, thus to reduce the intercluster transfer integrals $t$. Such a renormalisation would work towards an easier fulfillment of condition (27).

But too small values of $t$ could lead to electron mediated superconductor couplings [19, 30], to magnetism [31] and finally to Mott insulation. That phonon mediated couplings can still prevail over electron mediated ones over a range of values of $t$ smaller than $4k_B T_D$ comes from the factor in $\ln (v_e/v_p)$ which then reduces the electron mediated coupling [32]. $v_e$ and $v_p$ are here characteristic speeds of electrons and phonons. Even when $v_e < k_B T_D$, this logarithmic factor can be large for two reasons.

The characteristic time associated with $v_e$ is that for an intercluster transfer; owing to the coherency of the molecular states across each cluster, $v_e$ contains a multiplicative factor proportional to the size of the clusters.

Optical modes are numerous in each cluster and therefore dominate the phonon spectrum; their low speed decreases $v_p$.

In conclusion, it seems that the transfer integrals $t$ which determine the intercluster coupling can decrease by one order of magnitude below the critical value for condition [27] without the
basic BCS assumptions to be violated. But still smaller values of \( t \) necessarily lead to (weak) electron mediated superconductivity, magnetism and finally insulation. A better knowledge of the electronic structure of these compounds, especially an understanding of their NMR properties, would be useful in this context.

One can ask in that context what is the situation of the Chevrel phases [33]. They fall in principle within the limits of the present scheme, with an attractive feature: the increased degeneracy of the molecular states in clusters due to using atoms with d or f character. The possible coexistence in such phases of magnetism and superconductivity shows however the importance of electron correlations.

Conclusions.

The conditions of quasi zero-dimensional compounds, where each band is deduced from one (degenerate) molecular state of the clusters involved could lead to fairly high values of the BCS superconductive critical temperature \( T_c \) if the width of the band is less than the superconductive gap. Such a condition of weak intercluster couplings is probably not exactly realised in any of the known \( \text{C}_{60}X_3 \) compounds. Thus an increase in observed \( T_c \)'s is expected in such compounds if the intercluster distance could be increased by suitable ionic dopants. One would be limited in this direction by a Mott insulator limit, when intercluster correlations become to large. Near such a limit, other theories than BCS might apply [19].

Another possible field of experience could be charge transfer compounds built up with metallic clusters. One is however limited in that direction by possible Jahn Teller distortion if the clusters are not more than about \( 10^3 \) atoms large.

We can conclude this discussion by stating that quasi zero-dimensional compounds present properties which have obviously not all be fully explored yet.

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Appendix A.

We schematise the metal cluster by a flat potential well of radius \( R \). The radial part of each spherical orbital multiplied by \( r \) is then solution of a one dimension Schroedinger equation with, inside the wall, a repulsive potential \( l(l+1) \frac{h^2}{2m} r^2 \). WKB quantum condition then writes [34], for an \((n l)\) state with \( l \neq 0 \):

\[
\int_{r_0}^{R} k \, dr = n\pi - \text{const} \quad (A1)
\]

with

\[
\frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k_n^2}{2m} - \frac{l(l+1)h^2}{2m r^2} \quad (A2)
\]

and

\[
\frac{l(l+1)}{r_0^2} = k_n^2 \quad (A3)
\]
The constant in (A1) depends on the boundary conditions at the surface \( r = R \) of the wall. For an abrupt and infinite wall, the constant is equal to \( \pi/4 \). For more smoothly varying walls, the constant would be somewhat larger but of the same order of magnitude.

A straightforward integration then gives

\[
\sqrt{l(l+1)} \left( \frac{R}{r_0} \left( 1 - \frac{r_0^2}{R^2} \right)^{1/2} - \arccos \frac{r_0}{R} \right) = n - \text{const} \tag{A4}
\]

For \( n \gg l \), this gives the standard development

\[
\sqrt{l(l+1)} \left( \frac{R}{r_0} - \frac{\pi}{2} + 0 \left( \frac{r_0}{R} \right) \right) = n\pi - \text{const} \tag{A5}
\]

with

\[ r_0 \ll R. \]

But for \( n \ll l \), another development holds

\[
\frac{2}{3} \sqrt{2l(l+1)} \left[ \left( 1 - \frac{r_0}{R} \right)^{3/2} + 0 \left( \frac{r_0}{R} \right)^{5/2} \right] = n\pi - \text{const.} \tag{A6}
\]

valid for

\[ \frac{r_0}{R} \approx \frac{\sqrt{l(l+1)}}{k_n^l R} \approx 1 \]

In that limit, we can finally write

\[
k_n^l R \approx \sqrt{l(l+1)} \left[ 1 + \left\{ \frac{3(n\pi - \text{const})}{2\sqrt{l(l+1)}} \right\}^{2/3} \right] \tag{A7}
\]

We have also, for the \((l_m)\) states, with (12),

\[
\frac{R - r_0}{R} \approx \left[ \frac{3(n\pi - \text{const})}{2\sqrt{2} v N} \right]^{2/3}
\]

Hence the effective number of atoms where the amplitude of the \((l_M)\) orbital is important, in a shell near the wall, is

\[ N' \cong \alpha N^{1/3} \tag{A8} \]

where

\[ \alpha = \left[ \frac{3(\pi - \text{const})}{2\sqrt{2} v} \right]^{2/3} \tag{A9} \]

is a numerical factor near to unity.

It might finally be pointed out that, for \( n \ll l \) where it is valid, condition (A7) gives \( k_n^l R \approx 1 \). This is Balian and Bloch's semiclassical resonance conditions for a large number of reflections along the sphere [35].
Appendix B.

The progressive transition from usual BCS formulae (2) to the limit analysed in this paper can be easily pictured in a simple case.

Assume that the density of state has a constant value \( n \) over a width \( \omega = 2\delta \), and is zero elsewhere. Then equation (1) writes, for instance for the gap:

\[
\frac{2}{V} = \frac{2}{V} = n \int_{-\frac{k_B T_D}{\delta}}^{\frac{k_B T_D}{\delta}} (\Delta^2 + \epsilon^2)^{-1/2} \, d\epsilon \text{ if } \delta > k_B T_D \tag{B1}
\]

\[
\frac{2}{V} = n \int_{-\delta}^{\delta} (\Delta^2 + \epsilon^2)^{-1/2} \, d\epsilon \text{ if } \delta < k_B T_D \tag{B2}
\]

The solutions read

\[
\Delta = \frac{x}{\text{sh}(nV)^{-1}} \tag{B3}
\]

where

\[
\int x = k_B T_D \text{ for (B1) and } \delta \text{ for (B2).} \tag{B4}
\]

Formula (5) of the text is obtained for \( \delta \to 0 \). In fact it holds for \( \omega \) not very much larger than \( \Delta \). If, typically, \( \omega > 10 \Delta \), formula (B3) gives

\[
\delta \approx \omega \exp - \frac{2}{nV} \tag{B5}
\]

if \( \omega < 2 k_B T_D \), and saturates to the usual BCS formula (1) when \( \omega > 2 k_B T_D \).

References