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Electrons and vortex lines in He II, I. Brownian motion theory of capture and escape†

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Abstract. The Brownian motion theory of capture and escape, in the form given by L Onsager in 1934, is applied to the interaction of electrons and vortex lines in He II. Precise results are obtained to lowest order in the external field strength and certain misconceptions are clarified, laying the foundation for a reliable analysis of the available experimental data.

1. Introduction

A question which has fascinated physicists over a span of many years is that of the fundamental nature of superfluid helium. Due to the complexity of the problem, most theoretical discussions have by necessity been of a formal or qualitative nature. It is therefore of interest to apply simple concepts and push them quantitatively to the limits of their applicability in the hope that we may uncover new directions for research.

One method which has been used with great susccess by experimentalists in the field is the study of ions in He II. More specifically, the study of capture and release of ions by quantized vortices. These studies have occupied an important frontier of He II research, even playing an important role in questions of critical velocities and vortex nucleation (ie, nucleation of vortex rings by ions). The problem of capture and release of negative ions by vortex lines was first studied by Donnelly and Roberts (1969 and Donnelly 1967) and although they chose for their investigation the correct tool (Brownian motion theory), they did not derive results of sufficient strength to permit one to draw firm conclusions as to the limits of applicability of the basic theoretical assumptions. The criticism of their results may be summarized as follows:

(i) the capture cross section given by Donnelly and Roberts contains two arbitrary parameters left undetermined by theory; and

(ii) the resulting trapping lifetime, based upon a generalization of Kramers' method of escape over a potential barrier, cannot be valid except in the asymptotic limit $E \to \infty$ (E = external field strength in V cm^{-1}) whereas the available experimental data will be shown to fall within the domain of validity of the limit $E \to 0$.

Thus, our object is to derive the kinetic rate coefficients for capture and release in a 'weak-field approximation' of sufficiently large domain of validity that one can draw

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strong conclusions concerning the basic hypotheses. In order to begin this task, we assume the following:

(*a*) the bubble model of an electron in ^{4}He (Jortner *et al* 1965, Hiroike *et al* 1965, see also Careri 1961 and Ferrell 1956, 1957);

(*b*) the semi-classical model of a He II vortex (Onsager 1949, Feynman 1955);

(*c*) the hydrodynamic interaction between a bubble and a static vortex line with classical core structure; this interaction having been known to classical physicists (Thomson 1873) but appearing first in the present context in the work of Donnelly (1967), and

(*d*) Brownian motion theory in the Einstein–Smoluchowski approximation (Chandrasekhar 1943).

Qualitatively, these are the assumptions of Donnelly and Roberts. Our treatment of (*d*) will, however, differ in an important respect: we will apply a general theory of capture and release developed by Onsager in 1934 and by means of this general formalism a number of misconceptions will be corrected (Kramers' theory of escape (Chandrasekhar 1943, Kramers 1940) can be seen as an approximation of this theory in the limit $E \to \infty$ in two or more dimensions).

In the present communication, we formulate and solve the two relevant boundary value problems. In II, we discuss the comparison with the experimental data. The third paper, although by far the most speculative, is perhaps of the greatest interest. Based upon the results of I and II, we will show the necessity for considering the uncertainty in position of the vortex line due to thermal fluctuations and thereby suggest a resolution of a discrepancy concerning the temperature dependence of the trapping lifetime (McCauley 1974) (we also observe that the Heisenberg principle may play an important role in defining the 'core' of the quantum line, thus breaking with all previous treatments of the vortex core in terms of classical models).

2. Formulation of the boundary-value problems

We consider distributions of n_i free electron-bubbles, a lattice of n_v vortex lines and ν trapped electron-bubbles (all per unit area—we consider only the two-dimensional problem) and assume the kinetic equation (Onsager 1934)

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = -\frac{\mathrm{d}\nu}{\mathrm{d}t} = KA\nu - An_in_v \tag{1}$$

where A is the kinetic coefficient for capture of a bubble by a vortex line and $P = KA$ is the escape rate. The capture cross section and trapping lifetime are known once K and A are given by some microscopic theory. For $1\ \mathrm{K} \lesssim T \lesssim 2\ \mathrm{K}$, the dominant excitations are rotons with the roton density being sufficiently large that one may apply Brownian motion theory: we assume the roton–bubble collisions to be sufficiently frequent that the bubble may be treated as if in 'local thermodynamic equilibrium' with the roton gas at temperature T in which case the bubble has a probability distribution in velocity which is Gaussian with mean value (Chandrasekhar 1943)

$$-\boldsymbol{v}(\boldsymbol{r}, t) = D\nabla \ln f(\boldsymbol{r}, t) + \omega\nabla\phi(\boldsymbol{r}) \tag{2}$$

where f is the probability density to find the Brownian particle at $(\boldsymbol{r}, t)$, ω is the mobility ($D = \omega kT$) and ϕ the potential energy. Since we consider a vortex at the origin (polar coordinates (r, θ)) with external field along the x axis, we have $\phi = \phi_v + \phi_\epsilon$ where ϕ_v is the ion–vortex potential energy and $\phi_\epsilon = -eEx$. We have, then, the following continuity equation (Onsager 1934):

$$-\frac{\partial f}{\partial t} = \nabla \cdot f\boldsymbol{v} \tag{3}$$

or, with $u = \phi/kT$,

$$\frac{1}{D}\frac{\partial f}{\partial t} = \nabla \cdot \mathrm{e}^{-u}\nabla f\,\mathrm{e}^{u}. \tag{4}$$

Since, for weak fields, a Brownian particle may be considered captured wherever $|u_v| \lesssim \frac{1}{2}$ (Onsager 1934), we have

$$\nu = \int_{r<q} f\,\mathrm{d}^2 r \tag{5}$$

where q is the capture radius defined by $|u_v| = 2c/q^2 = \frac{1}{2}$. Thus,

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = \int_{r<q} \frac{\partial f}{\partial t}\,\mathrm{d}^2 r = \oint_{r=q} j_r r\,\mathrm{d}\theta \tag{6}$$

where $\boldsymbol{j} = D\,\mathrm{e}^{-u}\nabla\,\mathrm{e}^{u} f$ is the flux of ions into the vortex. K and A may be obtained by the solution of any two of the following three steady-flow boundary-value problems (Onsager 1934):

(i) the capture problem:

$$\nabla \cdot \mathrm{e}^{-u}\nabla f\,\mathrm{e}^{u} = -\frac{J}{D}\delta, \qquad f \to n_i n_v \quad \text{as } r \to \infty. \tag{7}$$

'δ' is the two-dimensional delta function and J the current ($J = \mathrm{d}\nu/\mathrm{d}t$) and since f represents the density of free particles we have

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = An_i n_v = \oint_{r=q} j_r r\,\mathrm{d}\theta \tag{8}$$

where the capture cross section is defined by

$$\sigma = \frac{An_i n_v}{|j_x|_\infty} = \frac{A}{\omega e E}.$$

(ii) The escape problem: we again solve (7) subject to

$$f \to 0 \qquad \text{as } r \to \infty$$

so that f represents a density of trapped particles (with $-J = P\nu$),

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = P\nu = -\oint_{r=q} j_r r\,\mathrm{d}\theta, \tag{9}$$

the trapping lifetime being given by

$$\tau = 1/P. \tag{10}$$

(iii) The steady-state problem:

$$\nabla \mathrm{e}^{-u} \nabla f \mathrm{e}^{u} = 0, \tag{11}$$

$$f \to n_\mathrm{i} n_\mathrm{v} \qquad \text{as } r \to \infty$$

(uniform flow from a source at $x = -\infty$ to a sink at $x = +\infty$). We will make the following useful approximation: for $r \lesssim q$ we may write (Onsager 1934):

$$f \simeq \alpha(E) n_\mathrm{i} n_\mathrm{v} \mathrm{e}^{-u} \simeq \alpha(E) n_\mathrm{i} n_\mathrm{v} \mathrm{e}^{-u_\mathrm{v}} \tag{12}$$

so that

$$\nu(E) \simeq \alpha(E) n_\mathrm{i} n_\mathrm{v} \nu(0)$$

where

$$\nu(0) = \int_{r \leqslant q} \mathrm{e}^{-u_\mathrm{v}} \, \mathrm{d}^2 r$$

is the zero-field bound-state partition function. Since $\mathrm{d}\nu/\mathrm{d}t = -\mathrm{d}n_\mathrm{i}/\mathrm{d}t = 0$ requires $KA\nu = An_\mathrm{i}n_\mathrm{v}$ (detailed balance condition), we have, whenever $A \neq 0$,

$$K(E) \simeq \frac{1}{\alpha(E)\nu_\mathrm{B}(0)}. \tag{13}$$

Thus, when $A(E) \neq 0$, the steady state may be represented as a superposition of two steady-flow source-sink problems defined by (i) and (ii), with detailed balancing imposed.

Except for the purpose of calculating $\nu(0)$, it is sufficient to consider the ion–vortex potential energy in the approximate form (Donnelly 1967, Pratt 1967)

$$u_\mathrm{v} \simeq -\frac{2C}{r^2} \tag{14}$$

valid for $r \gg R \gg a$ ($R \sim 16$ Å is the bubble radius and $a \gtrsim 2$ Å the vortex core parameter). The ion–vortex potential, first considered by Donnelly (1967), was given correctly by Thomson (1873), the force constant being

$$2C = \frac{3}{2} \frac{\rho_\mathrm{s}}{2} \frac{\kappa^2}{kT} \frac{4}{3} \pi R^3 \tag{15}$$

where ρ_s is the superfluid density and $\kappa = h/m$ ($m = {}^4$He atom's mass. The correction represented by the 3/2 factor has been mentioned by Pratt (1967) who uncovered it in Thomson (1873).) We will also use the notation

$$u_\epsilon = -2\beta x, \tag{16}$$

with

$$2\beta = eE/kT. \tag{17}$$

The small parameter upon which our perturbation theory will be based is

$$\beta q = 1{\cdot}3 \times 10^{-2} \left(\frac{\rho_\mathrm{s}}{T^3} \right)^{1/2} E \tag{18}$$

where $q = 2\sqrt{C}$ is the capture radius, the weak-field approximation being defined by $\beta q \ll 1$. (We have set $R = 16$ Å to obtain (18)).

At this point, we can state our objection to Donnelly and Roberts' trapping lifetime (rather, to its mis-application). Donnelly and Roberts (1969, Donnelly 1967) solved boundary value problem (ii) by a generalization of Kramers' method of escape over a potential barrier (Chandrasekhar 1943, Kramers 1940). This method, while exact in one dimension, is valid in two or more dimensions only in a certain limit (McCauley 1972). Donnelly and Roberts used the approximation

$$\oint j_r r \,\mathrm{d}\theta \simeq \int_{-\Delta y}^{+\Delta y} j_x \,\mathrm{d}y \sim \int_{-\infty}^{\infty} j_x \,\mathrm{d}y \tag{19}$$

where $\int_{-\infty}^{\infty} j_x \,\mathrm{d}y$ is evaluated at the saddle-point of the potential u, $2\Delta y$ being the 'width' of this saddle-point. It is obvious that (19) can only be valid when $\boldsymbol{j}$ is strongly directed along the x axis, ie in the asymptotic limit $E \to \infty$, whereas for the case $\beta q \ll 1$ the flow is almost symmetric and the saddle-point is irrelevant. Now, we need a result for P which is valid near $E = 0$. But $P(0)$ as given by (19) is finite and this contradicts the equation upon which (9) is based, for with $E = 0$ we have

$$f = c_1 \,\mathrm{e}^{-u_v} + J\,\mathrm{e}^{-u_v} \int_0^r \frac{\mathrm{e}^{u_v}}{s} \,\mathrm{d}s \tag{20}$$

where

$$P \propto J \propto \frac{1}{\int_0^\infty (\mathrm{e}^{u_v}/r)\,\mathrm{d}r}.$$

But

$$\int_0^\infty \frac{\mathrm{e}^{u_v}}{r} \,\mathrm{d}r = \infty$$

so that $P(0) = 0$ and $\tau(0) = \infty$. We will see in II that this divergence of the lifetime as $E \to 0$ is actually suggested by the experimental data, although it has heretofore been misinterpreted (Pratt 1967, Pratt and Zimmerman 1969). Finally, the result of Donnelly and Roberts may be relevant to ion–vortex ring experiments since these are often performed in the kilovolt range. For the case of ions and vortex lines, however, one generally finds $E \lesssim 100\ \mathrm{V\,cm^{-1}}$ and we will show that these results can be analysed by consideration of only the lowest-order approximation in the field strength.

3. The perturbation series

Onsager and Liu (1965), in a discussion of the dissociation of weak electrolytes, have suggested a perturbation scheme which, applied to our steady-state problem, may be stated as follows:

$$f = g\,\mathrm{e}^{-u_v} \tag{21}$$

$$(\Delta + \nabla u_\epsilon \cdot \nabla) g = \nabla u_v \cdot (\nabla g + g \nabla u_\epsilon) \qquad (\Delta \equiv \nabla^2). \tag{22}$$

We then assume an expansion for g in powers of the ion–vortex force constant C (the dimensionless parameter is really $\beta^2 C$)

$$g = g_0 + g_1 + \ldots \tag{23}$$

so that

$$(\Delta+\nabla u_\epsilon\cdot\nabla)g_0 = 0 \tag{24}$$

$$(\Delta+\nabla u_\epsilon\,.\,\nabla)g_1 = \nabla u_v\,.\,(\nabla g_0+g_0\nabla u_\epsilon) = \nabla u_\epsilon\,.\,\nabla u_v \tag{25}$$

($g_0 = 1$ where we take $n_i n_v = 1$ for convenience). g_0 represents uniform density and flow from a source at $x = -\infty$ to a sink at $x = +\infty$ and g_1 represents the perturbation due to addition of a vortex at the origin. The resulting g_1, however, does not behave correctly as $r \to 0$ (we must have $g \to$ constant as $r \to 0$ whereas the result given by (23) diverges logarithmically). This minor defect may be remedied as follows:

Setting

$$f = g\,\mathrm{e}^{-u_\epsilon}, \tag{26}$$

we assume an expansion for g as a power series in β (the dimensionless constant is $\beta\sqrt{C}$)

$$g = g_0+g_1+\ldots \tag{27}$$

so that

$$\Delta g_0+\nabla\,.\,g_0\nabla u_v = 0 \tag{28}$$

$$\Delta g+\nabla\,.\,g_1\nabla u_v = \nabla u_\epsilon\,.\,(\nabla g_0+g_0\nabla u_v). \tag{29}$$

(27) yields a good approximation near the vortex but our g does not satisfy the boundary condition at infinity. However, we can match f and $j_r = D\,\mathrm{e}^{-u}\nabla_r f\mathrm{e}^{u}$ as given by (21) and (26) on some suitable boundary, a circle of radius r_m being sufficient so long as $\beta q \ll 1$. We note that the right-hand side of (29) vanishes since $g_0 = \mathrm{e}^{-u_v}$.

For the capture problem, the following 'outer' expansion is convenient:

$$f = f_0+f_1+\ldots \tag{30}$$

$$(\Delta+\nabla u_\epsilon\,.\,\nabla)f_0 = 0 \qquad (f_0 = 1) \tag{31}$$

$$(\Delta+\nabla u_\epsilon\,.\,\nabla)f_1 = -\nabla\,.\,f_0\nabla u_v = -\Delta u_v \tag{32}$$

while the 'inner' expansion is again represented by (27)–(29). The perturbation f_1 here represents the addition of a sink at the origin and for the inner region we must choose $g_0 = 0$ since for $E = 0$ the boundary value problem does not exist.

Although intuitively appealing, these power series expansions in the force constants do not exist. g_1 and f_1, rather, are either $\mathrm{O}(\beta q \ln \beta q)^2$ or $\mathrm{O}(\ln \beta q)^{-1}$ to lowest order in βq (McCauley 1972). Therefore, the calculation of higher-order corrections is impossible and the validity of the lowest-order approximation may be called into question. Fortunately, there exists a generalization of the above procedure which yields results close to those of the above (incorrect) procedure, to *lowest* order in βq. We will now outline the correct procedure.

$$\nabla\,.\,\mathrm{e}^{-u}\nabla f\mathrm{e}^{u} = 0, \tag{33}$$

and setting

$$f = \mathrm{e}^{-u/2}\phi \tag{34}$$

yields

$$(\Delta-\beta^2-V_c)\phi = V_{\beta c}\phi \tag{35}$$

where

$$V_c = \tfrac{1}{4}(\nabla u_v) - \tfrac{1}{2}\Delta u_v = \frac{4C^2}{r^6} + \frac{4C}{r^4}$$

and

$$V_{\beta c} = \tfrac{1}{2}\nabla u_v \,.\, \nabla u_\epsilon = -\frac{4\beta C\cos\theta}{r^3}.$$

It will be convenient to write

$$V_{\beta c} = \lambda q(\boldsymbol{r})$$

where, for the present, λ is assumed arbitrary (λ will later be taken to be either $\beta^2 C$ or $\beta\sqrt{C}$, depending upon our choice of dimensionless variable).

Consider

$$(\Delta - \beta^2 - V_c)\phi_0 = 0, \tag{36}$$

which is separable in cylindrical coordinates and has the useful property that ϕ and ϕ_0 may be assigned the same boundary condition and also have the same form near the origin (ie for both (35) and (36) we have $(\Delta - \beta^2)\phi \sim 0$ as $r \to \infty$ and $(\Delta - V_c)\phi \sim 0$ for $r \to 0$). The 'cross-term' $V_{\beta c}$ in (35) is of the following form: $V_{\beta c}$ is dominated by V_c for small r, by β^2 for large r and within the intermediate region $V_{\beta c}$, V_c and β^2 are all dominated by thermal diffusion so long as the external field is weak ($\beta q \ll 1$). For either large or small r, then, we expect that there may exist some representation for ϕ in which $V_{\beta c}$ may be considered a perturbation. This will be useful because solutions of (36) are *in practice* obtainable, although perhaps at the cost of considerable labour. Noting that the Green function $K(\boldsymbol{r}, \boldsymbol{\rho})$ defined by

$$(\Delta - \beta^2 - V_c)K = -\delta \tag{37}$$

is expressible in the form

$$K(\boldsymbol{r}, \boldsymbol{\rho}) = \sum_{\mu=0}^{\infty} F_\mu(r_<)G_\mu(r_>)\cos[\mu(\theta - \theta')] \tag{38}$$

where (with solutions of (36) expressed as a cosine series) F_μ is the radial solution regular at the origin, G_μ is the radial solution regular at infinity, $r_< = \min(r, \rho)$ and $r_> = \max(r, \rho)$ (Ince 1956). Solutions of (35) may then be written in the form

$$\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) - \lambda \int K(\boldsymbol{r}, \boldsymbol{\rho})q(\boldsymbol{\rho})\,\mathrm{d}^2\rho, \tag{39}$$

where ϕ and ϕ_0 satisfy the same boundary conditions at infinity, and we may consider the Neumann series

$$\phi = \sum_{j=0}^{n-1} (-\lambda Kq)^j\phi_0 + (-\lambda Kq)^n\phi \tag{40}$$

(making use of an obvious shorthand notation) which converges whenever

$$\lim_{n\to\infty} (-\lambda Kq)^n\phi = 0 \tag{41}$$

(Whittaker and Watson 1963). Due to the dependence of K upon λ the problem of estimating the radius of convergence of (40) is non-trivial, but even in the event that the radius of convergence should vanish, we observe that (40) may still be useful as an asymptotic development for ϕ in the limit $\lambda \to 0$. We now turn to the generalization of the method of Onsager and Liu, based upon the approximation

$$\phi \simeq \sum_{j=0}^{n} (-\lambda Kq)^j \phi_0 \tag{42}$$

which is useful whenever $\lambda \ll 1$.

(i) 'Outer' region. Set $Z = \beta r$, $\lambda = \beta^2 C$ (we will now use the notation $\Delta = (1/Z)(\partial/\partial Z)Z(\partial/\partial Z)$). Then

$$(\Delta - 1 - \lambda^2 v_1 - \lambda v_2)\phi = \lambda q \phi \tag{43}$$

$$(\Delta - 1 - \lambda^2 v_1 - \lambda v_2)\phi_0 = 0 \tag{44}$$

$$(\Delta - 1 - \lambda^2 v_1 - \lambda v_2)K = -\delta \tag{45}$$

where $v_1 = 4/Z^6$, $v_2 = 4/Z^4$ and $q = -4\cos\theta/Z^3$. Then, by (42),

$$(\Delta - 1)\phi \simeq (\lambda^2 v_1 + \lambda v_2 + \lambda q)(\phi_0 - \lambda Kq\phi_0 + \ldots) \tag{46}$$

where the right-hand side, although not a power series, may be considered a perturbation series in the vortex potential. In practice, we will obtain the lowest approximation by assuming $\phi \simeq \phi_0 + \phi_1$, where

$$(\Delta - 1)\phi_0 \simeq 0 \tag{47}$$

and

$$(\Delta - 1)\phi_1 = \lambda q \phi_0 \tag{48}$$

whenever r is large and $\beta q \ll 1$.

(ii) 'Inner' region. Set $Z^{-2} = C/r^2$, $\lambda = \beta\sqrt{C}$. Then

$$(\Delta - \lambda^2 - v)\phi = \lambda q \phi \tag{49}$$

$$(\Delta - \lambda^2 - v)\phi_0 = 0 \tag{50}$$

$$(\Delta - \lambda^2 - v)K = -\delta \tag{51}$$

where

$$v = 4/z^6 + 4/z^4$$

and

$$q = \frac{-4\cos\theta}{z^3}.$$

As in (i), we may write

$$(\Delta - v)\phi \simeq (\lambda^2 + \lambda q)(\phi_0 - \lambda Kq\phi_0 + \ldots) \tag{52}$$

where the right-hand side may be considered a perturbation expansion in the external field strength. In practice, our lowest-order approximation (for small r) will be given by $\phi \simeq \phi_0 + \phi_1$ where

$$(\Delta - v)\phi_0 \simeq 0 \tag{49b}$$

and

$$(\Delta - v)\phi_1 = \lambda q \phi_0 (\sim 0). \tag{52b}$$

One can therefore solve (47), (48), (49*b*) and (52*b*) and match the resulting densities and (radial) current densities on a circle of radius r_m (r_m is yet to be determined).

4. Lowest-order approximation

Fortunately the lowest-order equations for ϕ_0 and ϕ_1 do not lead to results essentially different from those given by the first two terms in the improper expansion discussed earlier in § 3. Since the labour has already been performed for this latter case (McCauley 1972), we turn to the presentation of results.

(i) Steady state: (*a*) outer region

$$f \simeq e^{-u_v}(1+g_1) \tag{21b}$$

$$(\Delta+\nabla u_\epsilon\,.\,\nabla)g_1 = \nabla u_v\,.\,\nabla u_\epsilon. \tag{25}$$

The result is

$$f \simeq e^{-u_v}\left(1+e^{\beta x}\sum_0^\infty(\beta_m K_m(\beta r)+\pi_m(\beta r))\cos m\theta\right) \tag{53}$$

where I_μ and K_μ are Bessel functions of imaginary argument (Whittaker and Watson 1963) and π_μ is a sum of products of various combinations of I_μ, K_μ and inverse powers of r (McCauley 1972).

(*b*) Inner region

$$f \simeq e^{-u_\epsilon}(e^{-u_v}+g_1),$$

$$\Delta g_1+\nabla\,.\,g_1\nabla u_v = 0 \tag{29b}$$

and

$$g_1 = a_0\,e^{-u_v}+\frac{e^{-u_v}}{\sqrt{-u_v}}\sum_0^\infty b_m W_{-\frac{1}{2},m/2}\left(\frac{2c}{r^2}\right)\cos m\theta \tag{54}$$

where the $W_{\frac{1}{2},m/2}(2c/r^2)$ are Whittaker functions regular at the origin ($b_0 = 0$ since there is no source or sink at the origin). For $\beta q \ll 1$, it is sufficient to match only a few Fourier coefficients at $r = r_m$. In practice, the lowest-order approximation is given by the first three (McCauley 1972). Since dv/dt must vanish (detailed balancing), we calculate

$$\frac{dv}{dt} \propto b_1 \propto (4C-r_m^2)\beta^2 \tag{55}$$

and find our matching condition to be

$$r_m \simeq q = 2\sqrt{C} \tag{56}$$

to lowest order. The radius q gives the minimum of the zero-field probability density $r\,e^{-u_v}$ and is known in the theory of electrolytes as the 'Bjerrum radius' (Onsager 1934). For $\beta = 0$, we see that the vortex dominates for $r < q$ while diffusion dominates for $r > q$. For larger fields, r_m will depend upon $\beta\sqrt{C}$. It is this 'Bjerrum radius' and not the Kramers saddle-point which determines capture and escape in weak fields.

Since $\alpha(E) = 1+a_0$, we have

$$(K(E)v(0))^{-1} \simeq \alpha(E) \simeq 1-2\beta^2C(\ln\beta q)^2-4\beta^2C\gamma'\ln\beta q-7\beta^2C \simeq 1 \tag{57}$$

$(-\gamma' = 0{\cdot}1159)$.

Hence, the E dependence of the trapping lifetime will be given entirely by $A(E)$ for weak fields.

(ii) Capture: (*a*) outer region:

$$f \simeq 1+f_1 \tag{30b}$$

$$(\Delta+\nabla u_\epsilon . \nabla)f_1 = -\Delta u_v. \tag{32}$$

Setting $f_1 - u_v = g_1$, we once more obtain (25).

(*b*) Inner region:

$$f \simeq e^{-u_\epsilon} g_1 \tag{58}$$

and

$$g_1 = \frac{e^{-u_v}}{\sqrt{-u_v}} \sum_0^\infty b_m W_{-\frac{1}{2}, m/2}\left(\frac{2C}{r^2}\right) \cos m\theta. \tag{59}$$

Matching the first three Fourier coefficients yields

$$b_0 = \frac{1-u_v(q)}{u_0-\gamma'-\ln \beta q} = \frac{3/2}{0{\cdot}577-\ln \beta q} \tag{60}$$

where $u_0 = e^{-u_v(q)}\int_0^q e^{u_v}/r \, dr$ and $-u_v(q) = 2C/q^2 = \frac{1}{2}$. Since

$$A(E) = 2\pi D b_0 \tag{61}$$

the capture cross section is given by

$$\sigma \simeq \frac{2\pi b_0}{\beta} \tag{62}$$

and the trapping lifetime is

$$\tau \simeq \frac{v(0)}{2\pi D b_0}. \tag{63}$$

We will see in II that (62) and (63) do a good job of explaining the field dependence of both σ and τ. Note that τ and $(E\sigma)^{-1}$ have the same field dependence. This fact will be used to determine which of two contradictory sets of cross section data is likely to be closer to the truth.

5. Summary

We have applied the general theory of Brownian motion (Onsager 1934) to the calculation of the capture cross section and trapping lifetime in the limit of weak external fields. We have proposed a systematic perturbation expansion in the weak-field parameter βq ($\beta q \ll 1$) as a generalization of the technique suggested in a similar context by Onsager and Liu (1965), and have derived results to first order in βq, representing the limit $E \to 0$.

Regarding the trapping lifetime, the theory previously employed in analysing the experimental data (Donnelly and Roberts 1969, Donnelly 1967, Pratt and Zimmerman 1969) is based upon Kramers' theory of escape over a saddle-point, which theory we have observed to be valid only in the limit $E \to \infty$ if the dimensionality is greater than one. In contrast, we find the experimental data to be described by the limit $E \to 0$

(McCauley and Onsager 1975), while the zero-field lifetime is actually infinite. Our calculation of the capture cross section is based upon the recognition that a Brownian particle may be considered trapped whenever the thermal kinetic energy is dominated by the interaction energy, so long as the external field is sufficiently weak (Onsager 1934).

These results will be used in a future communication to analyse and discuss the available experimental data (McCauley and Onsager 1975).

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