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# Theory of electrical noise induced in a wire loop by the thermal motions of ions in solution

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Continuous Markov process theory is used to model the electrical noise induced in a passive wire loop by the thermal motions of ions in a nearby solution. The ions, being charged particles in Brownian motion, generate a fluctuating magnetic field, and that in turn induces a fluctuating electromotive force (emf) that augments the loop's Johnson emf. It is shown that the spectral density function of the equilibrium current in the wire loop is thereby increased, for moderate cycle frequencies  $\nu$ , by approximately a factor  $(1 + \alpha\nu^2)$ , where  $\alpha$  is determined by the geometry of the system, the resistance of the loop, and the charges, diffusion coefficients, and concentrations of the solution ions. It is also shown that the temporal trajectory of the loop current becomes "thickened," in a randomly fuzzy way, by an approximate factor of the form  $(1 + \beta)^{1/2}$ , where  $\beta$  depends not only on the aforementioned parameters that determine  $\alpha$ , but also on the hydrated masses of the ions. These findings may be useful for estimating the intrinsic background noise in the detector coil of a medical magnetic resonance imaging machine, or any other sensitive electronic circuit that is required to operate in an immediate "salt water" environment. [S0021-8979(98)01506-0]

## I. INTRODUCTION

In a medical magnetic resonance imaging (MRI) machine, wire coils placed close to the human body being examined are used to detect weak magnetic signals emanating from excited nuclei inside the body. Efforts to improve the performance of MRI machines by making these detector coils more sensitive will ultimately be limited by thermal noise. In addition to the intrinsic and long understood Johnson noise in each detector coil, thermal noise also arises from ions, mainly  $\text{Na}^+$  and  $\text{Cl}^-$ , that are in solution inside the human body being examined. These ions will be in thermal or Brownian motion, and being also charged, they will give rise to a fluctuating magnetic field through each coil. That fluctuating magnetic field will induce a fluctuating electromotive force (emf) in each coil—a "noisy" emf that is superimposed on the Johnson emf. A similar noise enhancement would be encountered in any sufficiently sensitive electronic circuit that is required to operate in an immediate "salt water" environment. Although it is doubtful that such noise can ever be eliminated, the first step toward dealing with it in any wise is to gain a quantitative physical understanding of it.

We shall examine here what is perhaps the simplest physical system that exhibits ion-induced electrical noise. We consider a passive circular wire loop of resistance  $R$  and self-inductance  $L$  that is positioned just above, and coaxially with, a cylindrical beaker containing an ionic solution of known composition (see Fig. 1). The entire system is assumed to be in thermal equilibrium at some absolute temperature  $T$ . Our goal will be to determine explicitly the effect of the ionic solution on the electrical current in the wire loop. Our analysis will be entirely classical, ignoring not only

quantum but also relativistic effects. A summary of our key findings is given in Sec. VIII.

## II. BROWNIAN MOTION AND JOHNSON NOISE

Our problem conjoins two physical phenomena that, separately, have been well studied: Brownian motion<sup>1-5</sup> and Johnson noise.<sup>6,7</sup> A tutorial review of these two phenomena in the accommodating mathematical context of continuous Markov process theory may be found in Ref. 8; in this section we shall summarize from that reference some facts about Brownian motion and Johnson noise that will be required here. We shall use the notation  $\mathbf{N}(m, \sigma^2)$  to denote a normal random variable with mean  $m$  and variance  $\sigma^2$ , and we shall frequently invoke the fact that, for any two statistically independent normals  $\mathbf{N}(m_1, \sigma_1^2)$  and  $\mathbf{N}(m_2, \sigma_2^2)$ ,

$$\begin{aligned} a_1\mathbf{N}(m_1, \sigma_1^2) + a_2\mathbf{N}(m_2, \sigma_2^2) \\ = \mathbf{N}(a_1m_1 + a_2m_2, a_1^2\sigma_1^2 + a_2^2\sigma_2^2). \end{aligned} \quad (2.1)$$

### A. The Ornstein-Uhlenbeck process

The most convenient mathematical description of both Brownian motion and Johnson noise is in terms of the Ornstein-Uhlenbeck (OU) type of continuous Markov process. By definition, the OU process  $X$  with relaxation time  $\tau$  and diffusion constant  $c$  evolves with time  $t$  according to a Langevin equation that can be written in either of the two equivalent forms

$$X(t+dt) = X(t) - \frac{1}{\tau}X(t)dt + c^{1/2}N(t)(dt)^{1/2}, \quad (2.2a)$$

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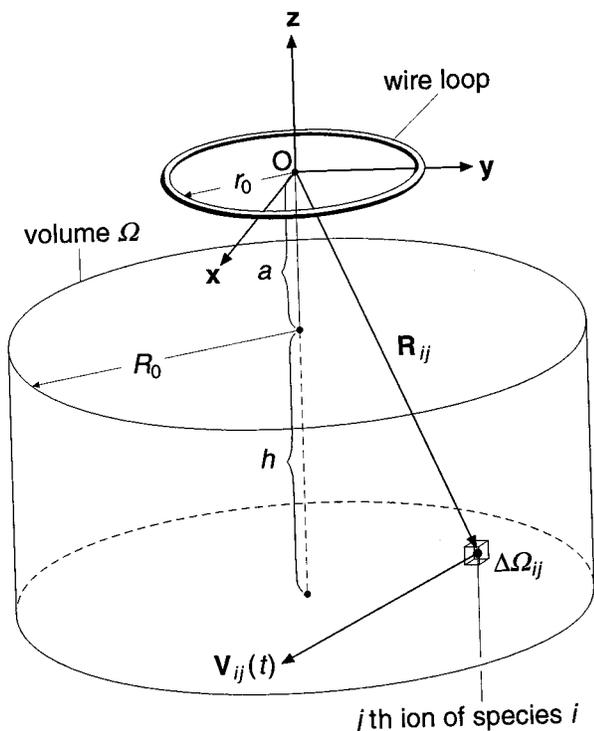


FIG. 1. Geometry of the circular wire loop of resistance  $R$  and self-inductance  $L$ , and the right circular cylinder  $\Omega$  that contains the ionic solution. The radius of the loop is  $r_0$ , the radius of  $\Omega$  is  $R_0$ , and the height of  $\Omega$  is  $h$ . The coordinate frame, with axis unit vectors  $\mathbf{x}$ ,  $\mathbf{y}$ , and  $\mathbf{z}$ , has its origin  $O$  at the center of the loop, with  $\mathbf{z}$  normal to the plane of the loop. The loop and the cylinder  $\Omega$  are coaxial, with the top of  $\Omega$  a distance  $a$  below the plane of the loop. The vector  $\mathbf{R}_{ij}$  locates the small subregion  $\Delta\Omega_{ij}$ , of volume  $1/\rho_i$ , which by definition contains the  $j$ th ion of species  $i$  at time  $t$ . The velocity of that ion is  $\mathbf{V}_{ij}(t)$ .

$$\frac{dX(t)}{dt} = -\frac{1}{\tau} X(t) + c^{1/2}\Gamma(t). \tag{2.2b}$$

In Eq. (2.2a),  $dt$  is a nonnegative infinitesimal variable, and  $N(t)$  is a temporally uncorrelated unit normal random variable—i.e.,  $N(t) = \mathbf{N}(0,1)$ , with  $N(t)$  and  $N(t')$  statistically independent if  $t \neq t'$ . In Eq. (2.2b),  $\Gamma(t)$  is Gaussian white noise, a temporally uncorrelated normal random variable with mean zero and variance  $\delta(0)$ , where  $\delta$  is the Dirac delta function. The equivalence of Eqs. (2.2a) and (2.2b) follows from the implication of Eq. (2.1) that  $(dt)^{1/2}\mathbf{N}(0,1) = dt\mathbf{N}(0,1/dt)$ . The solution to Eqs. (2.2) for the initial condition  $X(t_0) = x_0$  can be shown to be

$$X(t) = \mathbf{N}\left(x_0 e^{-(t-t_0)/\tau}, \frac{c\tau}{2} (1 - e^{-2(t-t_0)/\tau})\right). \tag{2.3}$$

If  $Z$  is a “stationary” stochastic process, in the sense that its mean is zero and its variance is a constant, then it will have an autocovariance  $\langle Z(t)Z(t+t') \rangle \equiv C_Z(t')$  that depends only on  $t' \geq 0$  (we use  $\langle \cdot \rangle$  to denote the averaging operation). The Wiener–Khinchine theorem states that the positive-frequency Fourier amplitude of this autocovariance, namely

$$S_Z(\nu) = 4 \int_0^\infty C_Z(t') \cos(2\pi\nu t') dt', \tag{2.4}$$

is such that  $S_Z(\nu)d\nu$  gives the amount of  $\langle Z^2(t) \rangle$  due to cycle frequencies in the (positive) interval  $[\nu, \nu + d\nu]$ ; so  $S_Z$  is called the spectral density function of  $Z$ . It is clear from Eq. (2.3) that the fully relaxed OU process,

$$X^*(t) \equiv \lim_{t_0 \rightarrow -\infty} X(t) = \mathbf{N}(0, c\tau/2), \tag{2.5}$$

is a stationary process. And one can show from Eq. (2.2a) that its autocovariance is given by

$$\begin{aligned} \text{cov}\{X^*(t), X^*(t+t')\} &= \langle X^*(t)X^*(t+t') \rangle \\ &= \frac{c\tau}{2} e^{-t'/\tau} \quad (t' \geq 0). \end{aligned} \tag{2.6}$$

Equation (2.4) then gives for the spectral density function of the fully relaxed OU process,

$$S_{X^*}(\nu) = \frac{2c\tau^2}{1 + (2\pi\tau\nu)^2} \quad (\nu \geq 0). \tag{2.7}$$

The integral  $Y$  of the OU process  $X$  is defined by  $Y(t+dt) = Y(t) + X(t)dt$ , and its variance,  $\langle Y^2(t) \rangle - \langle Y(t) \rangle^2$ , can be shown to satisfy the asymptotic relation

$$\text{var}\{Y(t)\} \approx c\tau^2(t-t_0) \quad \text{for } t-t_0 \gg \tau. \tag{2.8}$$

### B. Brownian motion

For a particle of mass  $m$  immersed in a fluid at absolute temperature  $T$ , a typical rectilinear component of the particle’s velocity  $\mathbf{V}(t)$  obeys the Newton’s second law equation

$$m \frac{dV_x(t)}{dt} = -\gamma V_x(t) + F_x(t). \tag{2.9}$$

Here, the  $x$  component of the force exerted on the particle by the molecules of the surrounding fluid has been expressed as the sum of a resistive term  $-\gamma V_x(t)$ , where  $\gamma > 0$  is the drag coefficient, and a zero-mean, temporally uncorrelated random term  $F_x(t)$ , which is assumed to be statistically independent of  $V_x(t' \leq t)$ . Given these assumptions, mathematical consistency can be shown to require that  $F_x(t)$  be proportional to Gaussian white noise, i.e.,

$$F_x(t) = f\Gamma_x(t), \tag{2.10}$$

where  $f$  is some constant. Equation (2.9) then takes the form of the OU Langevin equation (2.2b), implying that  $V_x$  is an OU process.

To determine the relaxation time  $\tau$  and diffusion constant  $c$  of the OU process  $V_x$ , two boundary conditions are imposed. First, classical statistical thermodynamics requires that  $V_x$  eventually be distributed in a Maxwell–Boltzmann fashion; thus,  $V_x(t \rightarrow \infty) = \mathbf{N}(0, kT/m)$ , where  $k$  is Boltzmann’s constant. And second, by the definition of the diffusion coefficient  $D$  of the particle (which is not to be confused with the diffusion constant  $c$  of the OU process  $V_x$ ), the integral  $X$  of  $V_x$  must satisfy  $\text{var}\{X(t \rightarrow \infty)\} = 2Dt$ . When these two boundary conditions are made to agree with the asymptotic properties (2.5) and (2.8) of an OU process and its integral, one finds that the relaxation time  $\tau$  and diffusion constant  $c$  of the OU process  $V_x$  defined by Eqs. (2.9) and (2.10) must be given by

$$\tau = \frac{Dm}{kT} \quad \text{and} \quad c = \frac{2}{D} \left( \frac{kT}{m} \right)^2. \quad (2.11)$$

With these expressions for  $\tau$  and  $c$ , an inspection of Eqs. (2.2b), (2.9), and (2.10) exposes the Einstein formula,  $\gamma = kT/D$ , and also the fluctuation–dissipation formula,  $f = (2kT\gamma)^{1/2}$ .

**C. Johnson noise**

The equation of motion for the current  $I(t)$  in a rigid wire loop of resistance  $R$  and self-inductance  $L$  is obtained by integrating the electric potential exactly once around the loop. That gives

$$-\frac{d[LI(t)]}{dt} + [-RI(t) + V(t)] = 0. \quad (2.12)$$

The first term on the left is the self-induced Faraday emf. The other term is the *thermal emf*, which arises from the interactions between the conducting electrons and the thermally vibrating atomic lattice of the wire. This thermal emf is assumed to be expressible as the sum of an ohmic term,  $-RI(t)$ , and a zero-mean, temporally uncorrelated random term,  $V(t)$ . The latter is called the *Johnson emf*, and it is assumed to be statistically independent of  $I(t' \leq t)$ . Given these assumptions, mathematical consistency can be shown to require that  $V(t)$  be proportional to Gaussian white noise, i.e.,

$$V(t) = b\Gamma(t), \quad (2.13)$$

where  $b$  is some constant. Equation (2.12) then takes the form of the OU Langevin equation (2.2b), implying that  $I$  is an OU process.

The relaxation time  $\tau$  of the OU process  $I$  can be seen from Eqs. (2.12) and (2.2b) to be  $L/R$ . To determine the corresponding diffusion coefficient  $c$ , we invoke the equipartition theorem of classical statistical thermodynamics to conclude that  $\langle \frac{1}{2}LI^2(t \rightarrow \infty) \rangle = \frac{1}{2}kT$ . Comparing this with the asymptotic OU result (2.5) allows us to conclude that the relaxation time  $\tau$  and diffusion constant  $c$  of the OU process  $I$  are

$$\tau = \frac{L}{R} \quad \text{and} \quad c = \frac{2kTR}{L^2}. \quad (2.14)$$

With the expressions (2.14) for  $\tau$  and  $c$ , a simple inspection of Eqs. (2.2b), (2.12), and (2.13) exposes the fluctuation–dissipation formula,

$$V(t) = (2kTR)^{1/2}\Gamma(t). \quad (2.15)$$

And since  $\langle \Gamma(t)\Gamma(t+t') \rangle = \delta(t')$ , then it is easy to show from Eq. (2.4) that the spectral density function of  $V(t) = b\Gamma(t)$  is just  $2b^2$ ; hence, Eq. (2.15) implies that the spectral density function of the Johnson emf  $V(t)$  is

$$S_V(\nu) = 4kTR \quad (\nu \geq 0), \quad (2.16)$$

which is known as Nyquist’s formula.

With Eqs. (2.14), it follows from Eqs. (2.5) that the equilibrium current in the loop is

$$I^*(t) = \mathbf{N}(0, kT/L), \quad (2.17)$$

and from Eq. (2.7) that the spectral density function of this equilibrium current is

$$S_{I^*}(\nu) = \frac{4kT}{R} \left( \frac{1}{1 + (2\pi L\nu/R)^2} \right) \quad (\nu \geq 0). \quad (2.18)$$

Finally, if we integrate Eq. (2.6) over all  $t' > 0$  and then invoke Eqs. (2.14), we get

$$R^{-1} = \frac{1}{kT} \int_0^\infty \langle I^*(t)I^*(t+t') \rangle dt', \quad (2.19)$$

which is known as the conductance formula.

Our goal in what follows will be to see how the above results for an *isolated*  $R$ - $L$  loop will be altered when we place that loop over a beaker containing an ionic solution.

**III. THE ION-INDUCED MAGNETIC FLUX**

We suppose that a circular wire loop of resistance  $R$ , self-inductance  $L$ , and radius  $r_0$  lies in the  $xy$  plane, with its center at the origin  $O$  of a Cartesian coordinate frame with unit axis vectors  $\mathbf{x}$ ,  $\mathbf{y}$ , and  $\mathbf{z}$ . A right circular cylinder  $\Omega$  of radius  $R_0$  and height  $h$  lies coaxially below the loop with its top surface at  $z = -a$  (see Fig. 1). The cylinder is filled with an ionic solution that is at the same absolute temperature  $T$  as the wire loop. The solution is a well-stirred mixture of  $K$  different ionic species, there being  $N_i$  ions of species  $i$  ( $i = 1, \dots, K$ ). Although all the  $N_i$  are large compared to unity,  $\Omega$  is presumed to be large enough that the motion of each individual ion can be considered to be independent of all the other ions; thus, each species- $i$  ion, of charge  $q_i$ , hydrated mass  $m'_i$ ,<sup>9</sup> and diffusion coefficient  $D_i$ , is undergoing independent Brownian motion as described in Sec. II B. In this section we shall compute the instantaneous magnetic flux  $\Phi_i(t)$  through the loop due to the  $N_i$  thermally moving ions of species  $i$ .

Our assumption that the ionic solution is “well-stirred” implies that the species- $i$  ions are distributed in a randomly uniform manner throughout  $\Omega$  with an average density  $\rho_i = N_i/|\Omega|$ , where  $|\Omega| = \pi R_0^2 h$ . We idealize the situation somewhat by assuming that, at any instant  $t$ , the region  $\Omega$  can be subdivided into  $N_i$  nearly cubic cells  $\Delta\Omega_{ij}$  ( $j = 1, \dots, N_i$ ), all of equal size

$$|\Delta\Omega_{ij}| = |\Omega|/N_i = 1/\rho_i, \quad (3.1)$$

such that there is *exactly one* species- $i$  ion—by definition the  $j$ th species- $i$  ion—inside cell  $\Delta\Omega_{ij}$ . The position of cell  $\Delta\Omega_{ij}$  relative to the origin  $O$  will be denoted by

$$\mathbf{R}_{ij} = \mathbf{x}x_{ij} + \mathbf{y}y_{ij} + \mathbf{z}z_{ij}. \quad (3.2)$$

Since the cell  $\Delta\Omega_{ij}$  is so small (because  $N_i \gg 1$ ),  $\mathbf{R}_{ij}$  can also be regarded as the position of the  $j$ th ion of species  $i$  at time  $t$ . The velocity of that ion will be denoted by  $\mathbf{V}_{ij}(t)$ .

As we show in Appendix A, the  $j$ th ion of species  $i$  at point  $(x_{ij}, y_{ij}, z_{ij})$  will, by virtue of its charge  $q_i$  and velocity  $\mathbf{V}_{ij}(t)$ , induce through the loop at time  $t$  a magnetic flux  $\Phi_{ij}(t)$  given by

$$\Phi_{ij}(t) = \frac{\mu_0}{4\pi} q_i Q(r_{ij}, z_{ij}; r_0) V_{ij\eta}(t). \quad (3.3)$$

Here,  $r_{ij}$  is defined by  $r_{ij} \equiv (x_{ij}^2 + y_{ij}^2)^{1/2}$ ;  $Q$  is the function defined in quadrature form in Eqs. (A2); and  $V_{ij\eta}(t)$  is the component of  $\mathbf{V}_{ij}(t)$  in the direction of the unit vector  $\boldsymbol{\eta}_{ij} \equiv \mathbf{z} \times \boldsymbol{\xi}_{ij}$ , where  $\boldsymbol{\xi}_{ij} \equiv (\mathbf{x}x_{ij} + \mathbf{y}y_{ij})/r_{ij}$ . It should be noted that the derivation of Eq. (3.3) makes the simplifying *approximation* that the magnetic field produced by the moving ion is given by the simple Biot–Savart law, and propagates with essentially infinite speed.

Equation (3.3) shows  $\Phi_{ij}(t)$  to be directly proportional to  $V_{ij\eta}(t)$ . As discussed in Sec. II B,  $V_{ij\eta}(t)$  can be regarded as an OU process whose relaxation time  $\tau_i$  and diffusion constant  $c_i$  are given by [see Eqs. (2.14)]

$$\tau_i = \frac{D_i m_i'}{kT} \quad \text{and} \quad c_i = \frac{2}{D_i} \left( \frac{kT}{m_i'} \right)^2. \quad (3.4)$$

Now it is easy to show from the normal random variable property (2.1) and the OU formula (2.3) that if  $X(t)$  is an OU process with relaxation time  $\tau$  and diffusion constant  $c$ , then  $\beta X(t)$  will be an OU process with relaxation time  $\tau$  and diffusion constant  $c' = \beta^2 c$ . So, from Eq. (3.3) we may conclude that  $\Phi_{ij}(t)$  is an OU process with relaxation time  $\tau_i$  and diffusion constant

$$c'_{ij} = \left( \frac{\mu_0}{4\pi} \right)^2 q_i^2 Q^2(r_{ij}, z_{ij}; r_0) c_i. \quad (3.5)$$

The instantaneous flux  $\Phi_i(t)$  through the loop due to *all* the  $N_i$  species- $i$  ions in  $\Omega$  is

$$\Phi_i(t) = \sum_{j=1}^{N_i} \Phi_{ij}(t). \quad (3.6)$$

The OU processes  $\Phi_{i1}(t), \Phi_{i2}(t), \dots$  being summed here are statistically independent of each other, this by virtue of our assumption that the ionic solution is dilute enough to render the motions of all the ions independent. Using again the normal random variable property (2.1) and the OU formula (2.3), it is easy to show that if  $X_1(t)$  and  $X_2(t)$  are statistically independent OU processes with a common relaxation time  $\tau$  and respective diffusion constants  $c'_1$  and  $c'_2$ , then  $X_1(t) + X_2(t)$  will be an OU process with relaxation time  $\tau$  and diffusion constant  $c' = c'_1 + c'_2$ . So  $\Phi_i(t)$  in Eq. (3.6) will be an OU process with relaxation time  $\tau_i$  and diffusion constant

$$\begin{aligned} c'_i &= \sum_{j=1}^{N_i} c'_{ij} \\ &= \rho_i \sum_{j=1}^{N_i} \left( \frac{\mu_0}{4\pi} \right)^2 q_i^2 Q^2(r_{ij}, z_{ij}; r_0) c_i |\Delta\Omega_{ij}| \\ &= \left( \frac{\mu_0}{4\pi} \right)^2 \rho_i q_i^2 c_i \sum_{j=1}^{N_i} Q^2(r_{ij}, z_{ij}; r_0) |\Delta\Omega_{ij}| \\ c'_i &= \left( \frac{\mu_0}{4\pi} \right)^2 \rho_i q_i^2 c_i \int \int \int_{\Omega} Q^2(r, z; r_0) \, dx dy dz. \end{aligned} \quad (3.7)$$

The second line of Eqs. (3.7) follows from Eqs. (3.1) and (3.5), and the last line is justified by noting that since the

subvolumes  $|\Delta\Omega_{ij}|$  are so small, then any sum over those subvolumes can be accurately evaluated as a volume integral over  $\Omega$ .

The form of Eq. (3.7) suggests that we define the *geometry factor*

$$G(\Omega; r_0) \equiv \int \int \int_{\Omega} Q^2(r, z; r_0) \, dx dy dz, \quad (3.8)$$

where  $r \equiv (x^2 + y^2)^{1/2}$ . Taking account of the shape and location of  $\Omega$ , as shown in Fig. 1, we can write  $G$  more explicitly as an integral over cylindrical coordinates. Since the integrand is independent of the azimuthal variable, we get

$$\begin{aligned} G(\Omega; r_0) &= G(a, h, R_0; r_0) \\ &= 2\pi \int_{-(a+h)}^{-a} dz \int_0^{R_0} dr r Q^2(r, z; r_0). \end{aligned} \quad (3.9)$$

We conclude that  $\Phi_i(t)$  is an OU process whose relaxation time  $\tau_i$  and diffusion constant  $c'_i$  are

$$\tau_i = \frac{D_i m_i'}{kT}, \quad (3.10a)$$

$$c'_i = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{2\rho_i q_i^2}{D_i m_i'^2} (kT)^2 G(a, h, R_0; r_0). \quad (3.10b)$$

#### IV. THE GEOMETRY FACTOR G

In Appendix B, we prove that the factor  $G$  in Eq. (3.10b), which is defined through Eq. (3.9) and the two alternative formulas for  $Q$  in Eqs. (A2), can be written in either of the following two explicit quadrature forms: First,

$$\begin{aligned} G(a, h, R_0; r_0) & \\ & \equiv 8\pi r_0^3 \int_{-(a+h)/r_0}^{-a/r_0} du_1 \int_0^{R_0/r_0} du_2 \int_{-1}^1 dv \int_{-1}^1 dv' \\ & \quad \times u_2 F_1(u_1, u_2, v) F_1(u_1, u_2, v'), \end{aligned} \quad (4.1)$$

where  $F_1$  is defined by

$$F_1(u_1, u_2, v) \equiv \frac{(u_2 - v)(1 - v^2)^{1/2}}{(u_1^2 + (u_2 - v)^2)(1 + u_1^2 + u_2^2 - 2u_2v)^{1/2}}; \quad (4.2)$$

and second,

$$\begin{aligned} G(a, h, R_0; r_0) & \\ & \equiv 8\pi r_0^3 \int_{-(a+h)/r_0}^{-a/r_0} du_1 \int_0^{R_0/r_0} du_2 \int_0^1 dw \int_0^1 dw' \\ & \quad \times u_2 F_2(u_1, u_2, w) F_2(u_1, u_2, w'), \end{aligned} \quad (4.3)$$

where  $F_2$  is defined by

$$\begin{aligned} F_2(u_1, u_2, w) & \equiv [1 + u_1^2 + u_2^2 - 2u_2(1 - w^2)^{1/2}]^{-1/2} \\ & \quad - [1 + u_1^2 + u_2^2 + 2u_2(1 - w^2)^{1/2}]^{-1/2}. \end{aligned} \quad (4.4)$$

Several comments on these formulas should be made. First, they show that  $G$  has dimensions of *volume*. Second, they show that, except in the trivially uninteresting case in which either  $h$  or  $R_0$  is zero,  $G$  will always be positive; this fact is also clear from Eq. (3.8). Third, since it seems un-

likely that either of the above two integral formulas for  $G$  can be computed analytically, then a *numerical computation* will probably be necessary. That of course will require that we specify definite numerical values for the four variables  $a$ ,  $h$ ,  $R_0$ , and  $r_0$ , which collectively define the *geometry* of the loop-ion system.

One numerical method for evaluating  $G$  is the Monte Carlo method.<sup>10</sup> In connection with that procedure, it is worth noting that Eq. (4.3) might well yield a more accurate result than Eq. (4.1). The reason is that the integrand in Eq. (4.3) is always positive, whereas the integrand in Eq. (4.1) sometimes goes negative (doing so whenever  $u_2$  is smaller than either, but not both, of  $v$  and  $v'$ ). This suggests, since the value of the integral itself is positive, that the integrand in Eq. (4.1) will exhibit a larger variance over its integration domain than will the integrand in Eq. (4.3), in which case a Monte Carlo evaluation of  $G$  using Eq. (4.1) would have a larger uncertainty than a Monte Carlo evaluation using Eq. (4.3). But in any case, the circumstance of having two different integral formulas for  $G$  allows one to check any numerical result by making two independent computations.

### V. DYNAMICAL EQUATIONS FOR THE CURRENT IN THE LOOP

We know that if the ionic solution were *not* present, then the electrical current  $I(t)$  in the wire loop would be governed by the circuit equation (2.12), wherein the Johnson emf  $V(t)$  is  $(2kTR)^{1/2}$  times Gaussian white noise. We shall now argue that, in the *presence* of the ionic solution, the potential terms on the left side of Eq. (2.12) will, to a good approximation, just be additively augmented by the Faraday emfs that are induced by the temporally changing magnetic fluxes arising from the thermally moving ions; i.e., the current  $I(t)$  in the wire loop above the ionic solution should obey, to a good approximation, the equation

$$-\frac{d[LI(t)]}{dt} + [-RI(t) + (2kTR)^{1/2}\Gamma_0(t)] - \sum_{i=1}^K \frac{d\Phi_i(t)}{dt} = 0, \tag{5.1}$$

where  $\Gamma_0(t)$  is statistically independent Gaussian white noise, and  $\Phi_i(t)$  is the ion species- $i$  magnetic flux calculated in Sec. III.

The correctness of Eq. (5.1) evidently hinges on *two assumptions*: (i) the fluctuating electromagnetic field arising from the thermally moving ions inside  $\Omega$  does not alter either the resistance  $R$  of the loop or the Johnson emf in the loop; and (ii) the fluctuating current in the loop does not alter the ionic motions inside  $\Omega$  that give rise to the magnetic fluxes  $\Phi_i(t)$ . We shall claim that assumption (i) is *exactly* true, and assumption (ii) will be *approximately* true in nearly all cases of practical interest.

The basis for assumptions (i) and (ii) lies in the analysis given in Ref. 11 of the thermal currents in two inductively coupled  $R$ - $L$  loops. The relevance of that exactly solvable loop-loop problem to our present loop-ion problem stems from the fact that, so far as the current in an  $R$ - $L$  loop is

concerned, it should make no difference whether the externally produced Faraday emf arises from thermally moving ions in a nearby ionic solution, or from the thermally fluctuating current in a nearby wire loop. The analysis of the loop-loop problem in Ref. 11 showed that the magnetic flux produced by the current in one loop does not change the other loop's resistance, nor its Johnson emf formula (2.15), nor its Nyquist formula (2.16), nor its conductance formula (2.19). That result for the loop-loop problem is the basis for our assumption (i) here.

Of course, in the two-loop problem, the current in one loop will usually have an effect on the current in the other loop, and sometimes a quite dramatic effect. But it is shown in Ref. 11 that there is one case in which this effect turns out to be practically negligible: If the  $L/R$  relaxation time of one loop is very much smaller than that of the other loop, and if the inductive coupling between the two loops is weak, then the current in the loop with the *smaller* relaxation time will be practically unaffected by the current in the loop with the larger relaxation time (but not vice-versa). This result is relevant to our loop-ion problem because the relaxation times of the magnetic fluxes  $\Phi_i(t)$ , namely the times  $\tau_i$  in Eq. (3.10a), will typically be on the order of  $10^{-13}$  s, and that is generally orders of magnitude smaller than the relaxation times  $L/R$  of commonly encountered wire loops. Furthermore, in most practical situations the coupling between the wire loop and the ionic solution will be weak. In such cases, the fluctuating current in the wire loop should have no sensible effect on the much more rapidly fluctuating ionic movements that produce the magnetic fluxes  $\Phi_i(t)$ .

The condition that the relaxation time of the current in the wire loop be much larger than the largest relaxation time of the ions in  $\Omega$  is, by Eqs. (2.14) and (3.10a),

$$\tau^* \equiv \text{Max}_{i=1}^K \left\{ \frac{D_i m_i}{kT} \right\} \ll \frac{L}{R}. \tag{5.2a}$$

And, as will be shown at the end of this section, the condition that the inductive coupling between the loop and the ionic solution be "weak" is

$$\Delta \equiv \left( \frac{\mu_0}{4\pi} \right)^2 \frac{G(a, h, R_0; r_0)}{L} \sum_{i=1}^K \frac{\rho_i q_i^2}{m_i} \ll 1. \tag{5.2b}$$

These conditions should suffice to ensure the validity of Eq. (5.1). We shall henceforth assume that conditions (5.2) are satisfied, as they in fact will be in most practical situations.

We found in Sec. III that the  $\Phi_i(t)$  are statistically independent OU processes with relaxation times  $\tau_i$  and diffusion constants  $c_i'$ , as given in Eqs. (3.10); therefore, the  $\Phi_i(t)$  will satisfy the OU Langevin equations [see Eq. (2.2b)]

$$\frac{d\Phi_i(t)}{dt} = -\frac{1}{\tau_i} \Phi_i(t) + c_i'^{1/2} \Gamma_i(t) \quad (i = 1, \dots, K), \tag{5.3}$$

where  $\Gamma_1(t), \dots, \Gamma_K(t)$  are statistically independent Gaussian white noise processes. By substituting Eq. (5.3) into Eq. (5.1) and then solving for  $dI(t)/dt$ , we get

$$\begin{aligned} \frac{dI(t)}{dt} = & -\frac{R}{L} I(t) + \sum_{i=1}^K \frac{1}{L\tau_i} \Phi_i(t) \\ & + \frac{(2kTR)^{1/2}}{L} \Gamma_0(t) - \sum_{i=1}^K \frac{c_i'^{1/2}}{L} \Gamma_i(t). \end{aligned} \quad (5.4)$$

The  $K+1$  equations (5.3) and (5.4) completely define the dynamics of our loop-ion system. Technically speaking,<sup>12</sup> Eqs. (5.3) and (5.4) constitute a multivariate Langevin equation for the  $(K+1)$ -variate continuous Markov process  $[\Phi_1(t), \dots, \Phi_K(t), I(t)]$ . The  $K$  processes  $\Phi_1(t), \dots, \Phi_K(t)$  are *individually* Markovian, each being in fact a statistically independent OU process, but the process  $I(t)$  is *not* by itself Markovian.

The ‘‘white-noise form’’ Langevin equations (5.3) and (5.4) are not especially convenient for analysis. We shall use instead the corresponding ‘‘standard-form’’ Langevin equations,<sup>13</sup>

$$\begin{aligned} I(t+dt) = & I(t) - \frac{R}{L} I(t)dt + \sum_{i=1}^K \frac{1}{L\tau_i} \Phi_i(t)dt \\ & + \frac{(2kTR)^{1/2}}{L} N_0(t)(dt)^{1/2} \\ & - \sum_{i=1}^K \frac{c_i'^{1/2}}{L} N_i(t)(dt)^{1/2}, \end{aligned} \quad (5.5)$$

$$\begin{aligned} \Phi_i(t+dt) = & \Phi_i(t) - \frac{1}{\tau_i} \Phi_i(t)dt + c_i'^{1/2} N_i(t)(dt)^{1/2} \\ & (i=1, \dots, K). \end{aligned} \quad (5.6)$$

In these equations,  $dt$  is a non-negative infinitesimal variable, and  $N_0(t), \dots, N_K(t)$  are temporally uncorrelated, statistically independent unit normal random variables.

One immediate consequence of Eqs. (5.5) and (5.6) is that, if the value of the current  $I$  is specified at some initial time  $t_0$ , then  $I(t)$  for  $t > t_0$  will be a *normal* random variable. This follows from a theorem in random variable theory which says that any linear combination of normal random variables, whether or not they are statistically independent, will itself be normal.<sup>14</sup> So, taking  $t=t_0$  in Eq. (5.5), and recalling from Eq. (2.3) that any OU process is normal, we see that  $I(t_0+dt)$  is expressed as a linear combination of normal random variables, and thus is itself normal. The normality of  $I(t)$  for *all*  $t > t_0$  then follows by a simple induction argument. But of course, we expect  $I(t)$  to be correlated with the  $\Phi_i(t)$ .

In order to calculate the spectral density function of  $I(t)$ , we must first calculate the three asymptotic moments  $\langle I(\infty) \rangle, \langle I(\infty)\Phi_i(\infty) \rangle$  and  $\langle I^2(\infty) \rangle$ . To that end, we begin by deriving from Eqs. (5.5) and (5.6) three moment-evolution equations. The first is obtained by averaging Eq. (5.5), using the fact that  $\langle N_i(t) \rangle = 0$ , and then passing to the limit  $dt \rightarrow 0$ . We get

$$\frac{d}{dt} \langle I(t) \rangle = -\frac{R}{L} \langle I(t) \rangle + \sum_{i=1}^K \frac{1}{L\tau_i} \langle \Phi_i(t) \rangle. \quad (5.7)$$

To obtain the second moment-evolution equation, we first take the product of Eqs. (5.5) and (5.6). Upon averaging the

result, using the facts that  $\langle \Phi_j(t)N_i(t) \rangle = 0$  and  $\langle \Phi_i(t)\Phi_{j \neq i}(t) \rangle = \langle \Phi_i(t) \rangle \langle \Phi_j(t) \rangle$ , and then passing to the limit  $dt \rightarrow 0$ , we get

$$\begin{aligned} \frac{d}{dt} \langle I(t)\Phi_i(t) \rangle = & -\left(\frac{1}{\tau_i} + \frac{R}{L}\right) \langle I(t)\Phi_i(t) \rangle - \frac{c_i'}{L} + \frac{1}{L\tau_i} \langle \Phi_i^2(t) \rangle \\ & + \sum_{\substack{j=1 \\ j \neq i}}^K \frac{1}{L\tau_j} \langle \Phi_j(t) \rangle \langle \Phi_i(t) \rangle. \end{aligned} \quad (5.8)$$

It is tempting to use condition (5.2a) to approximate the coefficient of the first term in Eq. (5.8) by  $1/\tau_i$ , but we must refrain from making such approximations until much later. Our third moment-evolution equation is obtained by first squaring Eq. (5.5). Upon averaging the result, using  $\langle N_i^2(t) \rangle = 1$  and the statistical independence of the  $N_i(t)$ 's, and then letting  $dt \rightarrow 0$ , we get

$$\begin{aligned} \frac{d}{dt} \langle I^2(t) \rangle = & -2\frac{R}{L} \langle I^2(t) \rangle + \frac{1}{L^2} \left( 2kTR + \sum_{i=1}^K c_i' \right) \\ & + 2\sum_{i=1}^K \frac{1}{L\tau_i} \langle I(t)\Phi_i(t) \rangle. \end{aligned} \quad (5.9)$$

Since  $\Phi_i(t)$  is an OU process with relaxation time  $\tau_i$  and diffusion constant  $c_i'$ , then explicit formulas for  $\langle \Phi_i(t) \rangle$  and  $\langle \Phi_i^2(t) \rangle$  can be read off from Eq. (2.3), and Eqs. (5.7)–(5.9) can then be solved in succession for  $\langle I(t) \rangle, \langle I(t)\Phi_i(t) \rangle$ , and  $\langle I^2(t) \rangle$ . However, we require here only the  $t \rightarrow \infty$  values of those three moments, and they can be deduced most easily by first taking the  $t \rightarrow \infty$  limits of Eqs. (5.7)–(5.9):

$$0 = -\frac{R}{L} \langle I(\infty) \rangle + \sum_{i=1}^K \frac{1}{L\tau_i} \langle \Phi_i(\infty) \rangle, \quad (5.10a)$$

$$\begin{aligned} 0 = & -\left(\frac{1}{\tau_i} + \frac{R}{L}\right) \langle I(\infty)\Phi_i(\infty) \rangle - \frac{c_i'}{L} + \frac{1}{L\tau_i} \langle \Phi_i^2(\infty) \rangle \\ & + \sum_{\substack{j=1 \\ j \neq i}}^K \frac{1}{L\tau_j} \langle \Phi_j(\infty) \rangle \langle \Phi_i(\infty) \rangle, \end{aligned} \quad (5.10b)$$

$$\begin{aligned} 0 = & -2\frac{R}{L} \langle I^2(\infty) \rangle + \frac{1}{L^2} \left( 2kTR + \sum_{i=1}^K c_i' \right) \\ & + 2\sum_{i=1}^K \frac{1}{L\tau_i} \langle I(\infty)\Phi_i(\infty) \rangle. \end{aligned} \quad (5.10c)$$

Next we note from the general OU result (2.3) that  $\langle \Phi_i(\infty) \rangle = 0$  and  $\langle \Phi_i^2(\infty) \rangle = c_i' \tau_i / 2$ . Substituting into Eqs. (5.10) and then successively solving those three equations for  $\langle I(\infty) \rangle, \langle I(\infty)\Phi_i(\infty) \rangle$ , and  $\langle I^2(\infty) \rangle$ , we find after a bit of algebra the following results:

$$\langle I(\infty) \rangle = 0, \quad (5.11)$$

$$\langle I(\infty)\Phi_i(\infty) \rangle = -\frac{kT\lambda_i}{L + R\tau_i}, \quad (5.12)$$

$$\langle I^2(\infty) \rangle = \frac{kT}{L} \left( 1 + \sum_{i=1}^K \frac{\lambda_i}{L + R\tau_i} \right), \tag{5.13}$$

where

$$\lambda_i \equiv \frac{c_i' \tau_i}{2kT} = \left( \frac{\mu_0}{4\pi} \right)^2 G(a, h, R_0; r_0) \frac{\rho_i q_i^2}{m_i'}. \tag{5.14}$$

We shall make use of the results (5.11)–(5.13) in the next section, when we compute the spectral density function of the equilibrium loop current. But first we note from Eq. (5.13), after invoking the fact that  $\tau_i \ll L/R$  [condition (5.2a)], that the mean equilibrium energy of the current in the wire loop is approximately

$$\langle \frac{1}{2} L I^2(\infty) \rangle \approx \frac{1}{2} kT (1 + \Delta), \tag{5.15}$$

where

$$\Delta \equiv \sum_{i=1}^K \frac{\lambda_i}{L} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{G(a, h, R_0; r_0)}{L} \sum_{i=1}^K \frac{\rho_i q_i^2}{m_i'}. \tag{5.16}$$

Evidently, the ionic solution increases the mean equilibrium energy of the current in the loop by (approximately) the factor  $(1 + \Delta)$ . The condition that the coupling between the loop and the solution be “weak” can therefore be expressed as in Eq. (5.2b).

### VI. SPECTRAL DENSITY FUNCTION OF THE EQUILIBRIUM CURRENT

The previously established normality of the loop current, coupled with the asymptotic results (5.11) and (5.13), implies that the asymptotic or equilibrium current in the loop is

$$\begin{aligned} I^*(t) &\equiv \lim_{t_0 \rightarrow -\infty} I(t) \\ &= I(\infty) \\ &= \mathbf{N} \left( 0, \frac{kT}{L} \left( 1 + \sum_{i=1}^K \frac{\lambda_i}{L + R\tau_i} \right) \right). \end{aligned} \tag{6.1}$$

As was discussed in connection with Eq. (2.4),  $I^*$  will have an autocovariance function,

$$\begin{aligned} C_I(t') &\equiv z_0(t') \equiv \langle I^*(t) I^*(t+t') \rangle \\ &= \lim_{t_0 \rightarrow -\infty} \langle I(t) I(t+t') \rangle \quad (t' \geq 0), \end{aligned} \tag{6.2}$$

from which one can compute the spectral density function of  $I^*$ :

$$S_{I^*}(\nu) = 4 \int_0^\infty z_0(t') \cos(2\pi\nu t') dt' \quad (\nu \geq 0). \tag{6.3}$$

That computation will be our goal in this section.

To compute  $z_0(t')$ , we begin by replacing in Eqs. (5.5) and (5.6)  $t$  by  $t+t'$  ( $t' > 0$ ) and  $dt$  by  $dt'$ . We then multiply both equations through by  $I(t)$ , and average the resulting equations using the fact that  $\langle I(t') N_i(t) \rangle = 0$  for all  $t' \leq t$ . Passage to the limit  $dt' \rightarrow 0$  then gives

$$\begin{aligned} \frac{d}{dt'} \langle I(t) I(t+t') \rangle &= -\frac{R}{L} \langle I(t) I(t+t') \rangle \\ &\quad + \sum_{i=1}^K \frac{1}{L\tau_i} \langle I(t) \Phi_i(t+t') \rangle, \end{aligned} \tag{6.4a}$$

$$\frac{d}{dt'} \langle I(t) \Phi_i(t+t') \rangle = -\frac{1}{\tau_i} \langle I(t) \Phi_i(t+t') \rangle. \tag{6.4b}$$

We now define, for  $i = 1$  to  $K$ ,

$$z_i(t') \equiv \lim_{t_0 \rightarrow -\infty} \langle I(t) \Phi_i(t+t') \rangle = \langle I^*(t) \Phi_i^*(t+t') \rangle \quad (t' \geq 0), \tag{6.5}$$

where, by the general OU result (2.5),  $\Phi_i^*(t) = \Phi_i(\infty) = \mathbf{N}(0, c_i' \tau_i/2)$ . Then by simply taking the limit  $t_0 \rightarrow -\infty$  of Eqs. (6.4), we obtain

$$\frac{d}{dt'} z_0(t') = -\frac{R}{L} z_0(t') + \sum_{i=1}^K \frac{1}{L\tau_i} z_i(t'), \tag{6.6a}$$

$$\frac{d}{dt'} z_i(t') = -\frac{1}{\tau_i} z_i(t') \quad (i = 1, \dots, K). \tag{6.6b}$$

The definition (6.5) shows that  $z_i(0) = \langle I^*(t) \Phi_i^*(t) \rangle = \langle I(\infty) \Phi_i(\infty) \rangle$ , a quantity that we computed earlier in Eq. (5.12). Upon solving Eq. (6.6b) for that initial condition and then substituting the result into Eq. (6.6a), we obtain the following closed differential equation for  $z_0(t')$ :

$$\frac{d}{dt'} z_0(t') = -\frac{R}{L} z_0(t') - \frac{kT}{L} \sum_{i=1}^K \frac{\lambda_i / \tau_i}{L + R\tau_i} e^{-t'/\tau_i}. \tag{6.7}$$

The initial condition for this differential equation is, by the definition (6.2),  $z_0(0) = \langle I^*(t) I^*(t) \rangle = \langle I^2(\infty) \rangle$ , a quantity that we computed earlier in Eq. (5.13). As can easily be checked, the solution to the differential equation (6.7) for that initial condition is

$$\begin{aligned} z_0(t') &= \frac{kT}{L} \left\{ e^{-Rt'/L} + \sum_{i=1}^K \frac{\lambda_i}{L^2 - (R\tau_i)^2} \right. \\ &\quad \left. \times [L e^{-t'/\tau_i} - (R\tau_i) e^{-Rt'/L}] \right\}. \end{aligned} \tag{6.8}$$

We now substitute the result (6.8) into Eq. (6.3) and integrate over  $t'$ . The integration is straightforward, and subsequent algebraic manipulation will bring the result into the form

$$\begin{aligned} S_{I^*}(\nu) &= \frac{4kT}{R} \left( \frac{1}{1 + (2\pi L\nu/R)^2} \right) \\ &\quad \times \left\{ 1 + \frac{(2\pi\nu)^2}{R} \sum_{i=1}^K \frac{\lambda_i \tau_i}{1 + (2\pi\tau_i\nu)^2} \right\} \quad (\nu \geq 0). \end{aligned} \tag{6.9}$$

Comparing this with the isolated  $R$ - $L$  spectral density formula (2.18), we see that the ionic solution increases the spectral density function of the equilibrium loop current by the factor in curly brackets. Now, we normally will be concerned with cycle frequencies  $\nu$  that are very small compared

to  $1/\tau_i = kT/D_i m_i'$  (which for typical ions will be on the order of  $10^{13}$  Hz). In that low-to-moderate frequency regime, Eq. (6.9) evidently predicts a *quadratic enhancement effect*,

$$S_{I^*}(\nu) \approx \frac{4kT}{R} \left( \frac{1}{1 + (2\pi L\nu/R)^2} \right) \{1 + \alpha \nu^2\} \left( \nu \ll \text{Min}_{i=1}^K \left\{ \frac{kT}{D_i m_i'} \right\} \right), \quad (6.10)$$

where the constant  $\alpha$  is, recalling Eqs. (5.14) and (3.10a),

$$\alpha \equiv \frac{(2\pi)^2}{R} \sum_{i=1}^K \lambda_i \tau_i = 4\pi^2 \left( \frac{\mu_0}{4\pi} \right)^2 \frac{G(a, h, R_0; r_0)}{kTR} \sum_{i=1}^K \rho_i q_i^2 D_i. \quad (6.11)$$

Note that the enhancement coefficient  $\alpha$  is independent of  $L$ , but inversely proportional to  $R$ . That  $\alpha$  should be an increasing function of  $\rho_i$ ,  $q_i$ , and  $D_i$  seems quite reasonable; however, that  $\alpha$  should be independent of the ionic masses is perhaps a bit surprising.

The quadratic enhancement effect predicted by Eq. (6.10) does not continue for arbitrarily high frequencies; indeed, one sees from Eq. (6.9) that

$$S_{I^*}(\nu) \approx \frac{4kT}{R} \left( \frac{1}{1 + (2\pi L\nu/R)^2} \right) \left\{ 1 + \frac{1}{R} \sum_{i=1}^K \frac{\lambda_i}{\tau_i} \right\} \left( \nu \gg \max\{1/\tau_1, \dots, 1/\tau_K\} \right). \quad (6.12)$$

But it is questionable whether this result has much practical significance, since quantum effects will invalidate our classical theory at very high frequencies.

### VII. THE ENHANCED JOHNSON EMF

There is another way of looking at the effect of ionic noise on the current in the wire loop that is interesting, not only because of what it implies, but also because of what it does *not*.

We have seen that  $\Phi_i(t)$  is an OU process with relaxation time  $\tau_i$  and diffusion constant  $c_i'$ . But  $\tau_i$  is typically ‘‘very small,’’ so it follows from the zero-tau limit theorem for OU processes<sup>15</sup> that, at least on time scales large compared to  $\tau_i$ , we can approximate  $\Phi_i(t)$  as

$$\Phi_i(t) \approx \tau_i c_i'^{1/2} \Gamma_i^*(t), \quad (7.1)$$

where  $\Gamma_i^*(t)$  is Gaussian white noise. Multiplying Eq. (7.1) through by  $dt$  and using the fact that  $dt\mathbf{N}(0,1/dt) = (dt)^{1/2}\mathbf{N}(0,1)$  [cf. Eqs. (2.2a) and (2.2b)], we get

$$\Phi_i(t)dt \approx \tau_i c_i'^{1/2} N_i^*(t)(dt)^{1/2}, \quad (7.2)$$

where  $N_i^*(t)$  is a temporally uncorrelated unit normal. Substituting this into Eq. (5.5) gives

$$I(t+dt) \approx I(t) - \frac{R}{L} I(t)dt + \frac{(dt)^{1/2}}{L} \left\{ (2kTR)^{1/2} N_0(t) + \sum_{i=1}^K \left[ c_i'^{1/2} N_i^*(t) - c_i'^{1/2} N_i(t) \right] \right\}. \quad (7.3)$$

The unit normal random variables  $N_0(t)$ ,  $N_i(t)$ , and  $N_i^*(t)$  are all statistically independent of each other [the statistical independence of  $N_i(t)$  and  $N_i^*(t)$  follows from the facts that  $N_i(t)$  and  $\Phi_i(t)$  are statistically independent by the OU property, and  $\Phi_i(t) \propto N_i^*(t)$  by Eq. (7.2)]. Because of this statistical independence, we can use the result (2.1) to simplify the linear combination of unit normal random variables in braces in Eq. (7.3) as follows:

$$\begin{aligned} & (2kTR)^{1/2} N_0(t) + \sum_{i=1}^K \left[ c_i'^{1/2} N_i^*(t) - c_i'^{1/2} N_i(t) \right] \\ &= \mathbf{N} \left( 0, 2kTR + \sum_{i=1}^K c_i' + \sum_{i=1}^K c_i' \right) \\ &= \left( 2kTR + 2 \sum_{i=1}^K c_i' \right)^{1/2} \mathbf{N}(0,1) \\ &= \left( 1 + \sum_{i=1}^K \frac{c_i'}{kTR} \right)^{1/2} (2kTR)^{1/2} N^*(t), \end{aligned}$$

$N^*(t)$  being yet another temporally uncorrelated unit normal. So Eq. (7.3) can be written

$$I(t+dt) \approx I(t) - \frac{R}{L} I(t)dt + (1 + \beta)^{1/2} \frac{(2kTR)^{1/2}}{L} N^*(t)(dt)^{1/2}, \quad (7.4)$$

where the constant  $\beta$  is, recalling Eq. (3.10b),

$$\begin{aligned} \beta &\equiv \sum_{i=1}^K \frac{c_i'}{kTR} \\ &= 2 \left( \frac{\mu_0}{4\pi} \right)^2 \frac{kT}{R} G(a, h, R_0; r_0) \sum_{i=1}^K \frac{\rho_i q_i^2}{D_i m_i'^2}. \end{aligned} \quad (7.5)$$

If we transform Eq. (7.4) into ‘‘white noise’’ form and then multiply through by  $L$ , we get

$$- \frac{d[LI(t)]}{dt} + [-RI(t) + V^*(t)] \approx 0, \quad (7.6)$$

where

$$V^*(t) \equiv (1 + \beta)^{1/2} (2kTR)^{1/2} \Gamma^*(t), \quad (7.7)$$

$\Gamma^*(t)$  being a Gaussian white noise process. Recalling Eqs. (2.12) and (2.15), we see that Eq. (7.6) *appears* to describe the thermal current in an  $R$ - $L$  loop with an *enhanced Johnson emf*  $V^*(t)$ , which is larger than the true Johnson emf  $V(t)$  by a factor of  $(1 + \beta)^{1/2}$ . But this interpretation is severely circumscribed by several caveats.

First, unlike the isolated circuit equation (2.12), Eq. (7.6) is *not* a genuine OU Langevin equation. The reason is that the Gaussian white noise process  $\Gamma^*(t)$  that drives Eq. (7.6) is *not* statistically independent of  $I(t)$ , as it would have to be in a genuine OU Langevin equation. It follows from Eq.

(5.12) that  $I(t)$  is statistically dependent on  $\Phi_i(t)$ , and from Eq. (7.2) that  $\Phi_i(t)$  is statistically dependent on  $N_i^*(t)$ , and from Eqs. (7.4) that  $N_i^*(t)$  is statistically dependent on  $N^*(t) = \Gamma^*(t)(dt)^{1/2}$ ; indeed, by chasing through all these relations, one can prove that

$$\langle I(\infty)\Gamma^*(\infty) \rangle = -(1+\beta)^{-1/2} \left( \frac{kT}{2R} \right)^{1/2} \sum_{i=1}^K \frac{\lambda_i/\tau_i}{L+R\tau_i}. \quad (7.8)$$

The fact that this average is *not zero* demonstrates the statistical dependency of  $I(t)$  and  $\Gamma^*(t)$ .

Second, Eq. (7.7) evidently calls for a noise enhancement of  $(1+\beta)^{1/2}$  at *all* frequencies. But our result (6.9) shows that there is *no* noise enhancement at zero frequency.

Finally, one should *not* write the enhanced Johnson emf (7.7) as  $(2kTR')^{1/2}\Gamma^*(t)$ , where

$$R' = R(1+\beta) = R + \sum_{i=1}^K \frac{c_i'}{kT},$$

since that would suggest that the resistance of the loop has been increased by  $(kT)^{-1}\sum_i c_i'$ . The fallacy of that view can be seen in three different ways: First, Eq. (7.6) shows that the *dissipative* resistance of the loop is *still*  $R$ . Second, simply replacing  $R$  in the isolated loop spectral density function formula (2.18) with  $R'$  as given above will *not* yield the correct spectral density formula (6.9). And finally, it is easy to show, by explicitly integrating Eq. (6.8) over all  $t' > 0$ , that the equilibrium autocovariance of the loop current in the *presence* of the ionic solution *still* obeys the isolated loop conductance formula (2.19); this implies that the ionic solution induces no change in the conductance  $R^{-1}$  of the wire loop.

In spite of all these caveats, there is one effect that the enhanced Johnson emf (7.8) fairly describes: Equation (7.4) can legitimately be viewed as an “updating formula” for the loop current that is reasonably accurate for time increments  $dt$  that are *small* compared to  $L/R$ , but *large* compared to  $\tau_i$ . The second term on the right side of Eq. (7.4) obviously describes the deterministic component of the increment in  $I$ , while the third term describes the stochastic component. Evidently, the presence of the ions enhances the stochastic component of the increment by a factor of  $(1+\beta)^{1/2}$ . We may expect this enhancement to be manifested as a statistically fuzzy thickening, by a factor of  $(1+\beta)^{1/2}$ , of the trajectory of the loop current when plotted on a time scale that is large compared to the  $\tau_i$  but small compared to  $L/R$ . A similar stochastic thickening occurs in the loop-loop problem of Ref. 11, specifically in the trajectory of the loop 1 current when  $L_2/R_2 \ll L_1/R_1$  and the inductive coupling between the two loops is weak. Exact numerical simulations for that special case of the loop-loop problem (see Figs. 8 and 9 of Ref. 11) show that the trajectory of the loop 1 current is indeed thickened in this manner.

### VIII. SUMMARY

We have used continuous Markov process theory to analyze the electrical noise induced in an  $R$ - $L$  loop by the thermal motions of ions in a nearby solution. The geometry is

schematized in Fig. 1. The solution is comprised of  $K$  different ionic species, with the ions of species  $i$  being characterized by their charge  $q_i$ , hydrated mass  $m_i'$ ,<sup>9</sup> diffusion coefficient  $D_i$ , and number density  $\rho_i$ . Our analysis is “classical” in that it ignores any quantum or relativistic effects.

The purely geometrical parameters,  $a$ ,  $h$ ,  $R_0$ , and  $r_0$  enter our final results only through a function  $G(a, h, R_0; r_0)$ , which has dimensions of volume, and which is defined in quadrature through Eqs. (4.1)–(4.4). Those equations give  $G$  as two different but mathematically equivalent four-dimensional integrals, which apparently can be evaluated only numerically. If a Monte Carlo integration method is used, Eq. (4.3) is likely to give a more accurate result.

Our analysis is predicated on the assumption that conditions (5.2) are satisfied, as they should be in most practical situations. Condition (5.2a) stipulates that the time scale  $\tau^*$  of the thermal motions of the ions be much smaller than the relaxation time  $L/R$  of the loop. Condition (5.2b) stipulates that the coupling between the loop and the ionic solution be weak, in the sense that the fractional increase  $(1+\Delta)$  in the mean equilibrium energy of the current in the loop that is caused by the ions be only slightly larger than unity. The rationale for conditions (5.2) is drawn from an earlier analysis of thermal noise in two inductively coupled wire loops.<sup>11</sup>

The principal result of our analysis is Eq. (6.10). It predicts that the ionic solution increases the spectral density function of the equilibrium current in the loop, at least for moderate cycle frequencies  $\nu$ , by the approximate factor  $(1+\alpha\nu^2)$ , where  $\alpha$  is given by Eq. (6.11). We call this the *quadratic enhancement effect*. The constant  $\alpha$  is directly proportional to  $G$ , inversely proportional to  $R$ , and independent of  $L$ ; it is an increasing function of the charges, diffusion coefficients, and concentrations of the ions, but is independent of the ion masses.

Another result of our analysis here is the formula (7.7) for the *enhanced Johnson emf*. Its physical significance is this: If the loop current  $I(t)$  is plotted on a time scale that is comfortably between  $\tau^*$  and  $L/R$ , then the effect of the ion noise will be manifested as a “statistically fuzzy thickening” of the  $I(t)$  trajectory by a factor of approximately  $(1+\beta)^{1/2}$ , where  $\beta$  is given by Eq. (7.5). The dependence of  $\beta$  on the ion parameters is notably different from  $\alpha$ 's dependence:  $\beta$  *does* depend on the ion masses, and it depends *inversely* on the ion diffusion coefficients. The enhanced Johnson emf formula should *not* be construed to imply that the ionic solution causes any changes in the *actual* Johnson emf in the loop, or in the loop's resistance  $R$ .

This article concludes a series of four theoretical papers that began with the tutorial reviews in Refs. 8 and 12, and continued with the analysis of the two-loop system in Ref. 11. But this research program is not yet finished: Still unanswered is the question of whether or not the ionic noise enhancements predicted by formulas (6.10) and (7.7) accurately describe the results of laboratory measurements on real loop-ion systems. A critical ancillary task in any experimental test of these formulas will be the numerical evaluation of the four-dimensional integral  $G$  for each chosen set of system geometry parameter values. Future workers who carry



$$\begin{aligned}
 & \int_0^{(r_0^2 - \xi^2)^{1/2}} \frac{(r - \xi) d\eta}{[(r - \xi)^2 + \eta^2 + z^2]^{3/2}} \\
 &= \frac{(r - \xi)(r_0^2 - \xi^2)^{1/2}}{[(r - \xi)^2 + z^2][(r - \xi)^2 + z^2 + (r_0^2 - \xi^2)]^{1/2}} \\
 &= \frac{1}{r_0} F_1(u_1, u_2, v). \tag{B1}
 \end{aligned}$$

In the last step we have introduced the scaled variables

$$u_1 \equiv z/r_0, \quad u_2 \equiv r/r_0, \tag{B2}$$

and  $v \equiv \xi/r_0$ , and we have invoked the definition (4.2) of the function  $F_1$ . Substituting Eq. (B1) into Eq. (A2a), we get

$$\begin{aligned}
 Q(r, z; r_0) &= 2 \int_{-r_0}^{r_0} d\xi \frac{1}{r_0} F_1(u_1, u_2, v) \\
 &= 2 \int_{-1}^1 dv F_1(u_1, u_2, v). \tag{B3}
 \end{aligned}$$

And substituting this into Eq. (3.9), we get

$$\begin{aligned}
 G(a, h, R_0; r_0) &= 2\pi \int_{-(a+h)}^{-a} dz \int_0^{R_0} dr \\
 &\quad \times r \left( 2 \int_{-1}^1 dv F_1(u_1, u_2, v) \right) \\
 &\quad \times \left( 2 \int_{-1}^1 dv' F_1(u_1, u_2, v') \right). \tag{B4}
 \end{aligned}$$

The integration variables change  $(z, r) \rightarrow (u_1, u_2)$  of Eq. (B2) then gives the claimed result (4.1).

To derive Eq. (4.3), we begin by changing, in the inner integral of Eq. (A2b), the integration variable  $\xi$  to  $\zeta \equiv r - \xi$ , and then evaluating that inner integral analytically:

$$\begin{aligned}
 & \int_{-(r_0^2 - \eta^2)^{1/2}}^{(r_0^2 - \eta^2)^{1/2}} \frac{(r - \xi) d\xi}{[(r - \xi)^2 + \eta^2 + z^2]^{3/2}} \\
 &= \int_{r - (r_0^2 - \eta^2)^{1/2}}^{r + (r_0^2 - \eta^2)^{1/2}} \frac{\zeta d\zeta}{(\zeta^2 + \eta^2 + z^2)^{3/2}} \\
 &= [r^2 - 2r(r_0^2 - \eta^2)^{1/2} + z^2 + r_0^2]^{-1/2} \\
 &\quad - [r^2 + 2r(r_0^2 - \eta^2)^{1/2} + z^2 + r_0^2]^{-1/2} \\
 &= \frac{1}{r_0} F_2(u_1, u_2, w). \tag{B5}
 \end{aligned}$$

In the last step we have used the definitions of  $u_1$  and  $u_2$  in Eqs. (B2), the new definition  $w \equiv \eta/r_0$ , and the definition (4.4) of the function  $F_2$ . Substituting Eq. (B5) into Eq. (A2b), we get

$$\begin{aligned}
 Q(r, z; r_0) &= 2 \int_0^{r_0} d\eta \frac{1}{r_0} F_2(u_1, u_2, w) \\
 &= 2 \int_0^1 dw F_2(u_1, u_2, w). \tag{B6}
 \end{aligned}$$

And substituting this into Eq. (3.9), we get

$$\begin{aligned}
 G(a, h, R_0; r_0) &= 2\pi \int_{-(a+h)}^{-a} dz \int_0^{R_0} dr \\
 &\quad \times r \left( 2 \int_0^1 dw F_2(u_1, u_2, w) \right) \\
 &\quad \times \left( 2 \int_0^1 dw' F_2(u_1, u_2, w') \right). \tag{B7}
 \end{aligned}$$

The integration variables change  $(z, r) \rightarrow (u_1, u_2)$  of Eq. (B2) then gives the claimed result (4.3).

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<sup>2</sup>M. von Smoluchowski, *Ann. Phys. (Leipzig)* **21**, 756 (1906).  
<sup>3</sup>P. Langevin, *Comptes Rendus* **146**, 530 (1908).  
<sup>4</sup>G. E. Uhlenbeck and L. S. Ornstein, *Phys. Rev.* **36**, 823 (1930).  
<sup>5</sup>M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945).  
<sup>6</sup>J. B. Johnson, *Phys. Rev.* **32**, 97 (1928).  
<sup>7</sup>H. Nyquist, *Phys. Rev.* **32**, 110 (1928).  
<sup>8</sup>D. T. Gillespie, *Am. J. Phys.* **64**, 225 (1996).  
<sup>9</sup>An ion in solution will, because water molecules are polar or charge-separated, attract and bind to it several water molecules in its immediate vicinity. The ion thus becomes ‘‘hydrated’’; it and its retinue of bound water molecules move about more or less as a single particle, whose charge is the ion’s nominal charge  $q$ , but whose mass is the ion’s *hydrated mass*  $m'$ , the sum of the ion’s bare mass  $m$  and the masses of the bound water molecules. For  $\text{Na}^+$  and  $\text{Cl}^-$  ions, the number of hydrating water molecules is often taken to be about 6, although various measurement techniques have yielded a rather broad range of estimates. See H. Ohtaki and T. Radnal, *Chem. Rev.* **93**, 1157 (1993).  
<sup>10</sup>Monte Carlo integration techniques are discussed at length in many places; e.g., M. H. Kalos and P. A. Whitlock, *Monte Carlo Methods*, Vol. I: *Basics* (Wiley, New York, 1986), and D. T. Gillespie, *The Monte Carlo method of evaluating integrals* (Naval Weapons Center Tech. Pub. #7514, China Lake, CA, 1975) No. NWC TP7514.  
<sup>11</sup>D. T. Gillespie, *Phys. Rev. E* **55**, 2588 (1997); see particularly Sec. IV.  
<sup>12</sup>D. T. Gillespie, *Am. J. Phys.* **64**, 1246 (1996).  
<sup>13</sup>For the simple OU process, Eqs. (2.2a) and (2.2b) are, respectively, the ‘‘standard form’’ Langevin equation and the ‘‘white-noise form’’ Langevin equation. A detailed discussion of those two equivalent Langevin equation forms for a general multivariate continuous Markov process can be found in Ref. 12, Sec. II.  
<sup>14</sup>See, for instance, M. D. Springer, in *The Algebra of Random Variables* (Wiley, New York, 1979), pp. 70–75.  
<sup>15</sup>See, for instance, Ref. 8, Sec. II D.