Brownian motion model of the interactions between chemical species and metallic electrons: Bootstrap derivation and parameter evaluation*

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We develop a Brownian motion model of the interaction between reacting chemicals on metal surfaces and the substrate electrons. The basic equation of such a model is the transport equation for the description of the chemicals' kinetics. We assume here that this equation has the functional form of the classical Fokker-Planck equation. The parameters of this equation—the average force and the friction coefficient—are determined by a bootstrap procedure, which requires that equilibrium and linear-response properties of the solution of the Fokker-Planck equation be identical to those calculated from the full quantum-mechanical equations. This derivation has the advantage that there is no need to explicitly require the electron-adparticle mass ratio to be small. We show further that our general expressions for the parameters reduce to those derived previously for systems in which the electron-adparticle mass ratio is formally made to tend to zero. These small mass-ratio expressions for the average force and the friction coefficient are then evaluated for several model metal plus adparticles systems. Simple systems and/or approximations are used in order to clarify the physical magnitude and dependences of these parameters.

I. INTRODUCTION

As described in an earlier publication, [1] there is strong evidence that the speed of a heterogeneously catalyzed reaction is quite sensitive to variations in the fluctuation characteristics of the solid substrate. For example, near a phase transition of the substrate, fluctuations in the appropriate substrate degrees of freedom are enhanced, and substantial anomalies occur in certain reaction rates around the transition temperature. A similar effect is noted when the fluctuation (or equally well the response) characteristics of the substrate are changed by alloying. Yet in some cases, the activation energy for the reaction (to which any thermally activated rate will be most sensitive) does not change materially. For a partial listing of the available experimental evidence, the reader is referred to Ref. 1.

Any thermally activated process takes place at a rate

$$\kappa = \nu e^{-F_B/k_BT} , \tag{1}$$

where T is the temperature and k_B is Boltzmann's constant. F_B is a barrier free energy, and ν is a "successful-attempt" frequency. Very crudely, one may say that F_B is obtained in a calculation of the systematic energetics of the reagents as a function of their position, while ν is determined by the dissipative part of the interaction between the reagents and the degrees of freedom of the heat bath (the substrate in the present case) responsible for activation of the reaction.

In order to expand on these statements, we need to use the Born-Oppenheimer conceptual scheme for describing electron-nuclear problems. [2] Within this scheme various chemical compounds correspond to minima in the electronic eigenenergy hypersurface in the space of the nuclear coordinates of the constituent atoms (adparticles). In many cases a chemical reaction may be viewed as a Brownian motion of the system's representative point in this space from one minimum to another. Usually, this motion is essentially classical, and we shall assume this throughout. The manner in which the prefactor ν in Eq. (1) is related within such a Brownian-motion model to the coefficients embodying the dynamics of the adparticle interaction with the heat bath or substrate has been discussed by Kramers, [3] and we begin by summarizing his results.

It is often possible to reduce the problem to motion in one dimension. For energetic reasons the statistically favored path taken by the representative point from one minimum to another hugs the line of steepest ascent and descent over the saddle point separating the two minima. This line is called the reaction path. The probability distribution for finding the representative point at a certain position $\vec{R}$, and moving with momentum $\vec{P}$ (where each of these are $3N$-component vectors, if there are N participating atoms) approximately factors into a function of the coordinate and momentum along the reaction path f, say, and a function of coordinate and momenta along suitable coordinates orthogonal to this path. This latter function may be taken to be a Boltzmann factor. The conditions for the validity of this factorization are (i) the principal curvature, as well as the higher "torsions" of the reaction path must vary sufficiently slowly along the path and (ii) the reaction must proceed sufficiently slowly so that quasiequilibrium has time to set in at each point along the path, with respect to the trans-

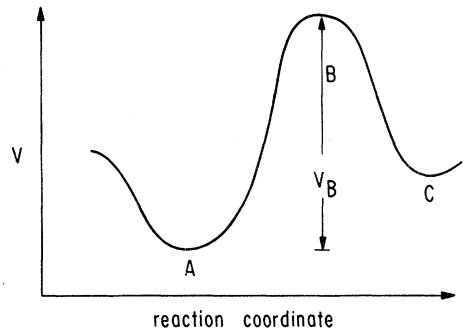

FIG. 1. Plot of typical effective adparticle potential energy V vs reaction coordinate in one dimension. The activation energy V_B for a reaction from A to C is marked.

verse coordinates.

Assuming this factorization, it is easy to show that the Boltzmann factor only contributes the entropy portion of F_B in formula (1). We shall not mention it further. The energy part of F_B is the height V_B of the saddle point above the minimum (A in Fig. 1), if the reaction goes in the direction from A to a neighboring minimum C (Fig. 1).

The first factor f in the probability distribution obeys a transport equation for one-dimensional motion along the reaction path, which in lowest approximation is identical to that of a single adparticle. When one can regard as small the momentum changes of the adparticles in collisions with the bath, this transport equation plausibly takes Fokker-Planck form. Since in this paper we shall emphasize the influence of the electronic degrees of freedom of the substrate, this assumption is reasonable because of the small electron mass m to adparticle mass M ratio. Thus, f obeys the equation

$$\frac{\partial f}{\partial t}+\frac{P}{M}\frac{\partial f}{\partial R}+\langle F\rangle\frac{\partial f}{\partial P}=\eta\frac{\partial}{\partial P}\left(Pf+Mk_BT\frac{\partial f}{\partial P}\right). \qquad (2)$$

Here $\langle F\rangle=-\partial V/\partial R$ is the systematic force along the reaction path and η is the friction coefficient which embodies the "random" interactions with the substrate degrees of freedom. Corrections to M arising from the average transverse deviation of the "adparticle" from the curved reaction path can be neglected if we assume that such a deviation is very small with respect to the radius of curvature of the path.

A general solution of Eq. (2) is still not known. However, Kramers[3] discusses it in the limits of small and large η and presents strong evidence that for intermediate values of η the purely kinematic theory of Eyring, known as the absolute-rate theory[4] (ART) must apply. He shows that (for the configuration in Fig. 1), the formulas in the three regions are $[\beta=(k_BT)^{-1}]$,

$$\kappa\sim\eta\beta V_B\,e^{-\beta V_B}\,, \qquad \eta<\omega_A k_B T/V_B\,, \qquad (3a)$$

$$\kappa\sim\omega_A\,e^{-\beta V_B}\,, \qquad \omega_A k_B T/V_B<\eta<\omega_B\,, \qquad (3b)$$

$$\kappa\sim(\omega_A\omega_B/\eta)\,e^{-\beta V_B}\,, \qquad \eta>\omega_B\,. \qquad (3c)$$

Here $\omega_{A,B}^2=(2/M)\,|\partial^2V/\partial R^2|_{A,B}$. The physical reasons for these differences are roughly the following: On the grounds of pure kinematics, one would simply count the number of particles in the Maxwellian tail about A with sufficient velocity to surmount the barrier. Such an argument assumes that there is an inexhaustible Maxwell distribution in well A, and the result then does not involve η. However, the thermal agitation of which η is a measure, must be adequate to replenish the tail, otherwise the reaction would cease. Thus for small η, the rate may be expected to be proportional to η. Once η is large enough to replenish the tail fully, no further dependence of κ on η will result and the ART applies until η becomes so large that the friction between adparticles and bath (of which η is likewise a measure) begins to inhibit the motion. Then the rate falls off. In this region (in which the Fokker-Planck equation reduces to the Smoluchowski equation) κ falls off as $1/\eta$. (For an extension of Kramers calculation to higher order in η and $1/\eta$, the reader is referred to Ref. 1.)

The basic motivation of this paper is that in some catalytic reactions ART may not apply. One of the standard explanations for the role of the catalyst in bringing about a larger rate is that it lowers V_B. At the same time, a lowering of V_B is plausibly accompanied by a reduction in ω_B. Hence, the interval of validity of ART, $\omega_A k_B T/V_B$ to ω_B, evidently shrinks, and a strong η dependence of κ might occur, if η falls outside this reduced interval. Such a hypothesis would explain why the reaction rate can change drastically without significant change in V_B as, for example, alloying changes the substrate fluctuations and thereby η (as we shall see). As a first step towards the understanding of such phenomena, we develop in this paper prescriptions for the evaluation of η and $\langle F\rangle$ and give several model results for η. This approach of expressing the parameters of the Fokker-Planck equation in terms of substrate properties is one way that solid state physics may be able to contribute to the science of catalysis.

A satisfactory procedure from the standpoint of rigor would be, for example, to begin with the Liouville equation for the density matrix of the whole system, adparticles plus substrate, and to extract from it, by suitable tracing operations and assumptions about the approximate thermal distribution of the substrate, an equation of motion for the reduced density matrix of the adparticles alone. Finally, since quantum effects in the motion of the latter are expected to be small, a "classical"

transformation (e.g., that of Wigner[5] or Husimi[6]) should reduce that equation to the classical Fokker-Planck form, Eq. (2), with the parameters η and $\langle F\rangle$ being defined *inter alia*.

Such a procedure in various forms has in fact been carried out several times previously (see Dagonnier's[7] review article) for systems with homogeneous heat baths and has recently been extended to treat the inhomogeneous case by one of the authors.[8] These derivations however are formally valid only to lowest order in some small parameter which may be for instance m/M or $\hbar\omega_A/k_BT$. The latter case in particular is a source of puzzlement since this ratio can easily be greater than unity in practical cases, supposedly signifying the complete breakdown of classical mechanics. On the other hand, from the success of the classical viewpoint of reaction kinetics one can conclude with some confidence that these difficulties are to a certain extent only formal, and that a classical transport equation for the adparticles is, in fact, a reasonable representation of their motion. That this equation must take Fokker-Planck form would appear to be dictated by simple symmetry and detailed balance considerations, once it is agreed that the unsystematic part of the bath-adparticle interaction causes a succession of very small momentum changes in the adparticles.[9] As noted above, this last assumption is reasonable for the electronic baths we consider. Hence we shall in this paper derive expressions for η and $\langle F\rangle$ of Eq. (2) through a "bootstrap" procedure, based on the presumed validity of (2).

This is described in detail in Sec. II. There we also show how our general expressions reduce to those of the formal derivations[7,8] in the limit of all small parameters forced to zero. In Sec. III we give several model calculations of η, attempting to elucidate its magnitude and physical dependences. Finally, there are several Appendixes dealing with subsidiary material that is perhaps too detailed for the general reader. Appendix A gives an alternate bootstrap procedure to that of Sec. II that nicely generalizes work by Kubo[10] but unfortunately seems only applicable to an harmonically bound adparticle. In Appendix B we show how the bootstrap procedure of Sec. II, which is done for an effective single adparticle moving in one dimension, may be carried through for an arbitrary number of adparticles in three dimensions. More of the details of one of the model calculations of η are described in Appendix C since this involved an application of multiple scattering theory that is not generally known. Lastly in Appendix D we give a model calculation of η for a system in which phonons are the source of the random forces in a Fokker-Planck equation. This allows one to compare the relative efficiencies of the two kinds (electronic or vibrational) of thermal reservoir.

II. BOOTSTRAP

In this section we develop a bootstrap procedure for calculating the parameters of the Fokker-Planck equation. Such an approach is not completely new, for it has been variously applied to other phenomenological equations,[11] but its use in connection with the Fokker-Planck equation is original. The basic assumption of the method is that use of the classical distribution function, f, determined by a kinetic equation of Fokker-Planck form, gives an adequate description of the system. This assumption can only be expected to hold true on a certain limited time scale, for a certain range of temperature and mass, and for a limited rapidity of variation of the potential along the reaction path. Estimates of these limitations may be obtained from the formal derivations of the Fokker-Planck equation; but, as we argued in the introduction, these estimates will be more stringent than necessary. The Fokker-Planck equation is expected to simulate closely the actual motion of the heavy particle for most cases of practical interest. The various possible exceptions to this conclusion have been discussed elsewhere.[8,12]

Once we accept the Fokker-Planck equation as the appropriate phenomenological equation, the coefficients in the equation should be obtainable by the following method: (i) Calculate certain physical quantities on the basis of the Fokker-Planck equation; (ii) calculate the same quantities on the basis of rigorous formulas using the full Hamiltonian of the system; (iii) equate the two sets of results. Then since the results of step (i) are functions of the parameters of the Fokker-Planck equation, step (iii) will yield equations for these parameters. Evidently the potential V, which serves to define $\langle F\rangle$ through $\langle F\rangle = -\partial V/\partial R$, should be obtainable from the equilibrium situation; whereas η, describing dissipation, requires consideration of at least small deviations from equilibrium. We shall carry out the formal determination of these parameters here based on Eq. (2) and reserve for Appendix B the general case of many particles in three dimensions.

To determine V we note that the equilibrium solution of (2) is

$$f_{eq} \sim \exp[-\beta(P^2/2M + V(R)]\,, \tag{4}$$

and hence the density in configuration space ρ_{eq} is

$$\rho_{eq}(R) \sim e^{-\beta V(R)}\,. \tag{5}$$

On the other hand, in terms of the full Hamiltonian operator $\hat{H}$ (adparticle plus substrate), it is also proportional to

$$\mathrm{Tr}[e^{-\beta\hat{H}}\delta(R-\hat{R})]\,, \tag{6}$$

where $\hat{R}$ is the position operator. Thus equating these two results we find

$$V(R) = -k_B T \ln \mathrm{Tr}[e^{-\beta\hat{H}}\delta(R-\hat{R})] + \text{const.} \tag{7}$$

so the force is

$$\langle F(R)\rangle = +\mathrm{Tr}\left(e^{-\beta\hat{H}}\frac{\partial}{\partial R}\delta(R-\hat{R})\right)\Big/\beta\,\mathrm{Tr}[e^{-\beta\hat{H}}\delta(R-\hat{R})]\ . \tag{8}$$

The friction coefficient η may be determined by calculating the response of the adparticle to an infinitesimal slowly varying applied field according to the Fokker-Planck equation, calculating the same response according to exact formulas of the type given by Kubo,[13] and finally equating the two responses. The validity of this method is restricted to low frequencies, since the Fokker-Planck equation as it stands can only yield a basically Lorentzian response, whereas it it known[14] that the true response must fall off faster than any inverse power of the frequency at high frequencies. A more accurate theory would have to take account of non-Markovian retardation effects resulting from elimination of the bath degrees of freedom that would make η, and presumably also the effective force $\langle F\rangle$, frequency dependent.

We imagine a small disturbance $V_1 = -F_1 R e^{-i\omega t}$ applied to the heavy particle alone. The solution of the Fokker-Planck equation will then have the form $f = f_{eq} + f_1 e^{-i\omega t}$, with f_1 of order F_1, and one can linearize the full equation, yielding an equation for f_1. However, the effective potential is not obviously $V + V_1$, since the bath degrees of freedom presumably also react to the disturbance, though indirectly, so that a reaction field might arise that should be added to V_1. We neglect the possibility of such effects here, which is in the spirit of the usual approach to the Pauli rate equation[15] that the transition probabilities occurring therein are given by their equilibrium values, even though the equation supposedly describes the course of deviations from equilibrium.

The linearized equation for f_1 is

$$-i\omega f_1 + \frac{P}{M}\frac{\partial f_1}{\partial R} + \langle F\rangle\frac{\partial f_1}{\partial P} + F_1\frac{\partial f_{eq}}{\partial P} = \eta\frac{\partial}{\partial P}\left(Pf_1 + Mk_B T\frac{\partial f_1}{\partial P}\right)\ . \tag{9}$$

Multiplying by P and integrating over P we find the following relation between the linear increments in density $\rho_1 = \int f_1\,dP$, current density $j_1 = \int (P/M) f_1\,dP$, and kinetic energy density $K_1 = \int (P^2/2M) f_1\,dP$:

$$j_1 M(\eta - i\omega) = \left(F_1\rho_{eq} + \langle F\rangle\rho_1 - 2\frac{\partial K_1}{\partial R}\right)\ , \tag{10}$$

where ρ_{eq} is the (normalized) equilibrium density [see Eq. (5)].

Now consider the operators

$$\hat{\rho}(R) = \hat{\delta}(R) = \delta(R-\hat{R})\ , \tag{11}$$

$$\hat{j}(R) = (\hat{P}\hat{\delta} + \hat{\delta}\hat{P})/2M\ , \tag{12}$$

$$\hat{K}(R) = (\hat{P}^2\hat{\delta} + 2\hat{P}\hat{\delta}\hat{P} + \hat{\delta}\hat{P}^2)/8M\ , \tag{13}$$

$$\hat{F}(R)\hat{\delta}(R) = \hat{F}\hat{\rho}\ , \tag{14}$$

where $\hat{P} = -i\hbar(\partial/\partial\hat{R})$ and $\hat{F} = -\partial\hat{H}/\partial\hat{R}$ is the total force on the adparticle. These operators satisfy a Heisenberg equation of motion

$$M\frac{\partial\hat{j}}{\partial t} + 2\frac{\partial\hat{K}}{\partial R} - \hat{F}\hat{\rho} = 0\ . \tag{15}$$

The traces of these operators over *all* variables, weighted by the statistical operator of the whole system, satisfy the same equation and so do the linear increments in these traces produced by the external field V_1. Denoting such an increment in the trace of an operator by braces $\{\ \}$ and a subscript 1, we have in the presence of V_1,

$$-i\omega M\{j\}_1 + 2\frac{\partial}{\partial R}\{K\}_1 - \{(F+F_1)\rho\}_1 = 0$$

or

$$-i\omega M\{j\}_1 + 2\frac{\partial}{\partial R}\{K\}_1 - \{F\rho\}_1 - F_1\{\rho\}_{eq} = 0\ . \tag{16}$$

The essence of the bootstrap procedure now comes in making the identifications $\rho_1 = \{\rho\}_1$, $j_1 = \{j\}_1$, and $K_1 = \{K\}_1$. We also use the identification $\rho_{eq} = \{\rho\}_{eq}$, which earlier served to define $\langle F\rangle$, Eq. (7). Note that these various identifications refer only to adparticle responses: we cannot so treat $\{F\rho\}_1$, the linear increment in the average force density, since the force operator depends on both the adparticle's and bath particles's coordinates and hence its average may not be computed merely from a solution of the Fokker-Planck equation.[16] We can now combine (10) and (16) to find

$$M\eta(R) = -(\{F\rho\}_1 - \langle F\rangle\{\rho\}_1)/\{j\}_1\ . \tag{17}$$

The quantities on the right-hand side are now evaluated by the Kubo formalism. They will all be functions of frequency, and the expression for η will in general not be frequency independent. However if it is sensibly flat over a frequency range from zero to well above the time rates of variation of interest in the solution of the Fokker-Planck equation the use of a frequency independent η is justified, and we require only the zero frequency limit of the right hand side. [Similar results apply if V_1 is allowed to vary sinusoidally in space. The Fokker-Planck equation with a purely local η is then justified if the right-hand side of (17) is not significantly wave-number dependent at low wave number.]

For a disturbance $-F_1\hat{R}e^{-i\omega\tau}$, the relevant Kubo formula[13] giving the increment in the expectation value of an operator $\hat{A}$ is

$$\bar{A}_1 = \frac{F_1}{M}\int_0^\infty d\tau\, e^{i\omega\tau}\int_0^\beta d\lambda\,\langle \hat{P}(-\tau - i\lambda\hbar)\hat{A}\rangle\ . \tag{18}$$

Here $\langle \ldots \rangle$ means $\mathrm{Tr}(e^{-\beta\hat{H}}\ldots)/\mathrm{Tr}(e^{-\beta\hat{H}})$ and $\hat{P}(\tau)$ is the Heisenberg operator $\hat{P}$ after evolution over a time τ under the Hamiltonian $\hat{H}$. Thus (17) becomes

$$M\eta(R) = -\int_0^\infty d\tau\, e^{i\omega\tau}\int_0^\beta d\lambda\,\langle \hat{P}(-\tau - i\lambda\hbar)(\hat{F}\hat{\delta} - F_{\mathrm{eq}}\hat{\delta})\rangle \times\left(\int_0^\infty d\tau\, e^{i\omega\tau}\int_0^\beta d\lambda\,\langle \hat{P}(-\tau - i\lambda\hbar)\frac{1}{2M}(\hat{P}\hat{\delta} + \hat{\delta}\hat{P})\rangle\right)^{-1}, \tag{19}$$

where the right-hand side is to be evaluated at $\omega = 0$ and the symbol F_{eq} has been introduced for the expression of Eq. (8) in order to avoid confusion. Integrating the numerator by parts with respect to τ, recalling that $i\hbar\hat{P} = [\hat{R}, \hat{H}]$ and $i\hbar\hat{F} = [\hat{P}, \hat{H}]$, and applying the Kubo identity[13] for any operator $\hat{A}$,

$$[e^{-\beta\hat{H}}, \hat{A}] = \int_0^\beta d\lambda\, e^{-\beta\hat{H}}[\hat{A}(-i\lambda\hbar), H]\ , \tag{20}$$

we may alternatively write

$$M\eta(R) = \int_0^\infty d\tau\, e^{i\omega\tau}\int_0^\beta d\lambda\,\langle \hat{F}(-\tau - i\lambda\hbar)(\hat{F} - F_{\mathrm{eq}})\hat{\delta}\rangle \times\left(-i\omega\int_0^\infty d\tau\, e^{i\omega\tau}\int_0^\beta d\lambda\langle \hat{P}\,(-\tau - i\lambda\hbar)\,\frac{1}{2M}(\hat{P}\hat{\delta} + \hat{\delta}\hat{P})\rangle\right)^{-1}. \tag{21}$$

Either Eq. (19) or (21) is our most general result, subject only to the presumed validity of the Fokker-Planck equation. It is important to verify that these expressions agree with the result of the formal derivations of the Fokker-Planck equation, that, as $M \to \infty$, η should be proportional to the correlation of the fluctuating force on the (static) adparticle. We proceed to prove this in the limit M tends to infinity first and ω tends to zero afterwards. That the opposite sequence of limits gives the same result is implicit in the formal derivations.[7,8]

To carry out the limiting process we first rewrite (21) as $M\eta(R) = N/D$, where

$$N = \lim_{\omega\to 0}\lim_{M\to\infty}\mathrm{Tr}_A\,\mathrm{Tr}_B\left(e^{-\beta\hat{H}}\int_0^\infty d\tau\, e^{i\omega\tau} \times\int_0^\beta d\lambda\,\hat{F}(-\tau - i\lambda\hbar)(\hat{F} - F_{\mathrm{eq}})\hat{\delta}\right), \tag{22}$$

$$D = \lim_{\omega\to 0}\lim_{M\to\infty}\mathrm{Tr}_A\,\mathrm{Tr}_B\left(e^{-\beta\hat{H}}\int_0^\infty d\tau\, e^{i\omega\tau}(-i\omega) \times\int_0^\beta d\lambda\,\hat{P}(-\tau - i\lambda\hbar)\frac{1}{2M}(\hat{P}\hat{\delta} + \hat{\delta}\hat{P})\right), \tag{23}$$

with Tr_A and Tr_B denoting traces over the degrees of freedom of the adparticle and the bath, respectively. To perform Tr_A we use a plane-wave basis. We neglect all commutators involving $\hat{P}^2/2M$ and effectively treat $\hat{P}$ as a c number except when it acts on a plane-wave state. Such a procedure becomes exact if $M \to \infty$ first.[17] We see that in this limit $\hat{P}$ in (23) loses its time dependence while $\hat{F}$ in (22) retains only a time dependence due to the adiabatic Hamiltonian $\hat{H}^{\mathrm{ad}} = \hat{H} - \hat{P}^2/2M$. For both equations the traces are of the form

$$\mathrm{Tr}[e^{-\beta\hat{H}}g(\hat{R}, \hat{P}, \{\hat{B}\})\delta(R - \hat{R})] = \int\frac{dk}{2\pi}\langle k|\,\mathrm{Tr}_B[e^{-\beta\hat{H}}g(\hat{R}, \hat{P}, \{\hat{B}\})\delta(R - \hat{R})]\,|k\rangle\ , \tag{24}$$

where $\{\hat{B}\}$ represents the collection of bath operators and k labels the plane-wave basis. In the limit $M \to \infty$, (24) becomes

$$\int\frac{dk}{2\pi}\int d\bar{R}\exp\left(-\frac{\beta\hbar^2k^2}{2M}\right) \times\mathrm{Tr}_B[e^{-\beta H^{\mathrm{ad}}(\bar{R},\{\hat{B}\})}g(\bar{R}, \hbar k, \{\hat{B}\})\delta(R - \bar{R})] \tag{24'}$$

or

$$\int\frac{dk}{2\pi}\exp\left(-\frac{\beta\hbar^2k^2}{2M}\right)\mathrm{Tr}_B[e^{-\beta H^{\mathrm{ad}}(R,\{\hat{B}\})}g(R, \hbar k, \{\hat{B}\})]\ .$$

Now in Eq. (22) the g function is independent of k while in (23) it varies quadratically with k; hence in both cases the k integration is trivial. We find for the ratio N/D,

$$M\eta(R) = \mathrm{Tr}_{\mathrm{bath}}\Big(e^{-\beta H^{\mathrm{ad}}(R,\{\hat{B}\})} \times\int_0^\infty d\tau\int_0^\beta d\lambda\, F_0(-\tau - i\lambda\hbar, R, \{\hat{B}\}) \times[F(R, \{\hat{B}\}) - F_{\mathrm{eq}}(R)]\Big)[\mathrm{Tr}_{\mathrm{bath}}(e^{-\beta H^{\mathrm{ad}}(R,\{\hat{B}\})})]^{-1} = \left\langle\int_0^\infty d\tau\int_0^\beta d\lambda\,\hat{F}_0(-\tau - i\lambda\hbar)(\hat{F} - F_{\mathrm{eq}})\right\rangle_{0,R}\ . \tag{25}$$

Here the subscript 0 on F denotes that the only time dependence comes from $\hat{H}^{\mathrm{ad}}$; similarly the thermal average is only over the bath degrees of freedom and is weighted with the adiabatic thermal factor. Equation (25) is evaluated with the adparticle immobile at R. We may reduce (25) to its more familiar form if we note that the limiting procedure above reduces F_{eq}, (8), to $\langle\hat{F}\rangle_{0,R}$ in the notation of Eq. (25). Then we can define the fluctuating force on the immobile adparticle at R as

$$\mathfrak{F}(R, \{\hat{B}\}) = F(R, \{\hat{B}\}) - \langle\hat{F}\rangle_{0,R}\ , \tag{26}$$

with $\langle\mathfrak{F}\rangle_{0,R} = 0$. Furthermore we can eliminate the λ integration in (25) if we take the real part of the time integral. We find then

$$M\eta(R) = \mathrm{Re}\beta\int_0^\infty d\tau\,\langle\hat{\mathfrak{F}}\hat{\mathfrak{F}}_0(\tau)\rangle_{0,R}\ , \tag{27}$$

which is the result of the formal derivations. Note that this limiting expression implies that η becomes basically just an electronic property with its only dependence on the adparticles being through their instantaneous configuration.

Thus our general expressions, (19) or (21), have

the appropriate limiting form. Furthermore, they hopefully represent a meaningful extrapolation away from that limit, though we shall not examine carefully this point here.

III. MODEL CALCULATIONS

In this section we evaluate the large mass limit expression for the friction, Eq. (27) or the analogous expressions of Appendix B, for several model systems. Our aim is to clarify the physical dependences of η, allowing one in the future to make reasonable approximations on more complex systems. Therefore we choose very simple systems to consider here for two reasons: First, we want the evaluation of η to be straightforward; and second, we want to see clearly how the physics of the model determines η. In all, we discuss six different models below and in addition give a phonon model estimate of η in Appendix D.

A. Charge-response model

We consider first the friction on a heavy particle in an otherwise homogeneous interacting electron gas. Assuming that the heavy particle has a single positive charge, we can write the force operator of Eq. (26), suitably generalized to three dimensions, as

$$\hat{\mathcal{F}}(\vec{R}) = -\nabla_{\vec{R}} \int d\vec{r}\, V(|\vec{R}-\vec{r}|)\delta\hat{n}(\vec{r},\vec{R})\,, \tag{28}$$

where $V(R) = -e^2/R$ and $\delta\hat{n}(\vec{r}) = \hat{n}(\vec{r}) - \langle\hat{n}(\vec{r})\rangle_{0,\vec{R}}$ is the (fluctuating) density operator of the electron gas. For such a model system the friction is diagonal in its Cartesian indices and all components are equal. Furthermore, it is independent of $\vec{R}$. Thus, we can write η [$=\eta_{xx}(\vec{R})$, say] as

$$\eta = \frac{1}{3Mk_BT}\lim_{\omega\to 0}\lim_{\vec{R}\to 0,\vec{R}'\to 0} \mathrm{Re}\int_0^\infty e^{i\omega\tau}d\tau\,\nabla_{\vec{R}}\cdot\nabla_{\vec{R}'} \times\iint d\vec{r}\,d\vec{r}'\,V(|\vec{R}-\vec{r}|)V(|\vec{R}'-\vec{r}'|)c_1(\vec{r},\vec{r}',\tau), \tag{29}$$

where

$$c_1(\vec{r},\vec{r}',\tau) = \langle\delta\hat{n}(\vec{r})\delta\hat{n}_0(\vec{r}',\tau)\rangle_{0,\vec{R}=0}\,. \tag{30}$$

This correlation function c_1 may be reworked into the form of a charge response function of the system; and because one takes the real part in (29), only the "lossy" part of the response survives. To make this more explicit we apply the further approximation here of neglecting the presence of the heavy particle in the evaluation of c_1. This amounts to evaluating η to lowest order in the forces coupling the heavy particle motion to the electron bath. The validity of such a perturbation approach will be examined below for more tractable single-particle models. We find from Eq. (29), noting that a Fourier representation of (30) is now appropriate,

$$\eta = \frac{4\pi e^2}{3M}\int\frac{d^3q}{(2\pi)^3}\lim_{\omega\to 0}\mathrm{Im}[-\omega\epsilon(\vec{q},\omega)]^{-1}\,, \tag{31}$$

where the dielectric constant $\epsilon(\vec{q},\omega)$ is given by

$$\epsilon^{-1}(\vec{q},\omega) = 1 - V(q)\frac{i}{\hbar\Omega} \times\int_0^\infty d\tau\, e^{i\omega\tau}\langle[\hat{n}_0^0(\vec{q},\tau),\hat{n}(-\vec{q})]\rangle_0^0\,, \tag{32}$$

with $\hat{n}(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\hat{n}(\vec{r})$, $V(q) = 4\pi e^2/q^2$, and Ω is the volume of the system. The zero subscript in (32) is a reminder to neglect the heavy particle in evaluating both the time dependence and the bath average. To proceed further we use the random-phase approximation (RPA) for $\epsilon(\vec{q},\omega)$ (Ref. 18)

$$\lim_{\omega\to 0}\mathrm{Im}[-\omega\epsilon^{\mathrm{RPA}}(q,\omega)]^{-1} = \begin{cases}\left(\frac{\pi}{4}\frac{\hbar}{E_F}\frac{k_s^2}{q^2}\frac{k_F}{q}\right)\left[1+\frac{k_s^2}{2q^2}\left(1+\frac{1-(q/2k_F)^2}{q/k_F}\ln\left|\frac{1+q/2k_F}{1-q/2k_F}\right|\right)\right]^{-2}, & q<2k_F\\ 0\,, & q>2k_F\end{cases} \tag{33}$$

and in addition take the Thomas-Fermi approximation for the real part of $\epsilon(\vec{q},\omega)$, replacing the denominator in (33) with $(1+k_s^2/q^2)^2$. Here k_F is Fermi momentum, $E_F = \hbar^2k_F^2/2M$ is the Fermi energy, and $k_s = (4k_F/\pi a_0)^{1/2}$ the Thomas-Fermi screening wave vector, where a_0 is the Bohr radius. We now have

$$\eta = \frac{4}{3\pi}\frac{m}{M}\frac{e^2/a_0}{\hbar}\int_0^{2k_F}\frac{q\,dq}{k_s^2}\frac{k_s^2/q^2}{(1+k_s^2/q^2)^2} = \frac{4}{3\pi}\frac{m}{M}\frac{e^2/2a_0}{\hbar}\left(\ln(1+\pi k_Fa_0) - \frac{\pi k_Fa_0}{1+\pi k_Fa_0}\right). \tag{34}$$

For reasonable values of k_F the expression in the brackets is of order unity and we see that η is roughly the mass ratio times a typical electron frequency. The various approximations that we have made for ϵ do not affect this conclusion.

Note that the $\omega\to 0$ limit in (31) removes any plasmon contribution to η.

B. Spin-response model

Now let us consider the evaluation of the friction if we imagine a switch from a direct Coulomb interaction to an exchange interaction. Such a situation would arise if an electron remains more or less localized on the heavy particle. We would then

write the force operator of Eq. (26) as

$$\hat{\mathcal{F}}(\vec{R}) = -\nabla_{\vec{R}} \int d\vec{r}\, J(\vec{R}, \vec{r}) \hat{S} \circ \hat{s}(\vec{r}) , \tag{35}$$

where $\hat{S}$ is the local spin operator, $\hat{s}(\vec{r})$ the electron-spin density operator, and $J(\vec{R}, \vec{r})$ a measure of the exchange interaction strength. We have assumed for simplicity here that $\langle \hat{S} \rangle_0 = \langle \hat{s} \rangle_0 = 0$. If we specialize to an otherwise homogeneous medium, we may reduce the friction expression as in Sec. III A,

$$\eta = \frac{1}{3Mk_BT} \lim_{\omega \to 0} \lim_{\vec{R} \to 0, \vec{R}' \to 0} \mathrm{Re} \int_0^\infty e^{i\omega\tau} d\tau \, \nabla_{\vec{R}} \cdot \nabla_{\vec{R}'} \times \int d\vec{r}\, d\vec{r}\,' J(|\vec{R} - \vec{r}|) J(|\vec{R}' - \vec{r}\,'|) c_2(\vec{r}, \vec{r}\,', \tau) , \tag{36}$$

where

$$c_2(\vec{r}, \vec{r}\,', \tau) = \langle \hat{S} \circ \hat{s}(\vec{r}) \hat{S}(\tau) \cdot \hat{s}(\vec{r}\,', \tau) \rangle_{0,R} = 0 . \tag{37}$$

Now we again apply a perturbation treatment with respect to the interaction between the bath and the heavy particle. To lowest order in J we find

$$c_2(\vec{r}, \vec{r}\,', \tau) = S(S+1) \langle \hat{s}_z(\vec{r}) \hat{s}^0_{z,0}(\vec{r}\,', \tau) \rangle^0_0 \tag{38}$$

and

$$\eta = \frac{S(S+1)}{3M} \int \frac{d^3q}{(2\pi)^3} q^2 J^2(q) \lim_{\omega \to 0} \mathrm{Im}\left(-\frac{1}{\omega} \chi(\vec{q}, \omega) \right), \tag{39}$$

where

$$\chi(\vec{q}, \omega) = -\frac{i}{\hbar\Omega} \int_0^\infty d\tau\, e^{i\omega\tau} \langle [\hat{s}^0_{z,0}(\vec{q}, \tau), \hat{s}_z(-\vec{q})] \rangle^0_0 . \tag{40}$$

The zero superscript means that J is set to zero in the evaluation of (38) or (40). Note that our use of perturbation theory for η yields an expression similar to that previously derived from the "Golden Rule."[19] An interesting result for η is obtained if we use the paramagnetic form of the response function $\chi(\vec{q}, \omega)$ (Ref. 20):

$$\lim_{\omega \to 0} \mathrm{Im}\left(-\frac{1}{\omega} \chi(q, \omega) \right) \approx \begin{cases} \dfrac{mk_F}{\pi^2\hbar^2} \dfrac{1/qv_F}{(1 - \bar{I} + \bar{I}q^2/12k_F^2)^2}, & q < 2k_F \\ 0 , & q > 2k_F \end{cases} \tag{41}$$

where v_F is the Fermi velocity and $\bar{I}$ is a measure of the exchange interaction between the bath electrons, $0 < \bar{I} < 1$. Substituting (41) into (39), we find, neglecting the q dependence of J,

$$\eta = 24 \frac{m}{M} \frac{S(S+1)}{\bar{I}^2} \left(J(q=0) \frac{mk_F}{\pi^2\hbar^2} \right)^2 \times \frac{E_F}{\hbar} \left[\ln\left(\frac{1 - \frac{2}{3}\bar{I}}{1 - \bar{I}} \right) + \frac{1 - \bar{I}}{1 - \frac{2}{3}\bar{I}} - 1 \right] . \tag{42}$$

The limiting values of the square brackets are

$$1/\bar{I}^2[\ ] \xrightarrow[\bar{I} \to 0]{} \tfrac{1}{24} \xrightarrow[\bar{I} \to 1]{} \ln[\tfrac{1}{3}/(1 - \bar{I})] - 1 . \tag{43}$$

Thus we see that though η diverges as $\bar{I}$ goes to 1, the divergence is much slower than that of the susceptibility, which is proportional to $(1 - \bar{I})^{-1}$.[20]

C. Phase-shift model

Next we turn to single-particle models. For independent electrons in an arbitrary potential we can reduce Eq. (B16) to

$$\eta_{\alpha\beta} = \frac{\pi\hbar}{M} \int d\epsilon \left(-\frac{\partial n}{\partial \epsilon} \right) \sum_{n,m} \langle n | \hat{F}_\alpha | m \rangle \langle m | \hat{F}_\beta | n \rangle \times \delta(\epsilon - \epsilon_n) \delta(\epsilon - \epsilon_m) \tag{44a}$$

$$= \frac{\pi\hbar}{M} \int d\epsilon \left(-\frac{\partial n}{\partial \epsilon} \right) \mathrm{Tr}_{\{r\}} [\hat{F}_\alpha \delta(\epsilon - \hat{h}^{\mathrm{ad}}) \hat{F}_\beta \delta(\epsilon - \hat{h}^{\mathrm{ad}})] , \tag{44b}$$

where $\partial n/\partial\epsilon$ is the energy derivative of the electron Fermi-distribution function. Since we shall always consider the electron bath to be degenerate we retain below only the zero-temperature limit of n,

$$-\frac{\partial n}{\partial \epsilon} = \delta(\epsilon - \mu) , \tag{45}$$

where μ $(= E_F)$ is the chemical potential of the electron bath, governed by $\hat{H}^{\mathrm{ad}}$. Note that the eigenstates and eigenenergies in (44a) are for single electrons and that the trace in (44b) is to be done in the Hilbert space of one electron. Also the single-particle Hamiltonia $\hat{h}^{\mathrm{ad}}$ is defined by

$$\hat{H}^{\mathrm{ad}} = \sum_i \hat{h}^{\mathrm{ad}}_i , \tag{46}$$

where the summation is over all the bath particles.

The careful reader will perhaps wonder why there is no restriction on $n \neq m$ in (44a). This omission is negligible for all but one dimensional systems, and even there the problem is only formal. If we consider the friction to be defined by

$$\eta = \lim_{\omega \to 0} \frac{\beta}{M} \int_0^\infty e^{i\omega\tau} d\tau \, \langle \hat{\mathcal{F}} \hat{\mathcal{F}}_0(\tau) \rangle_{0,R} , \tag{47}$$

rather than Eq. (27), and take the limit $\omega \to 0$ only after inserting complete sets of states of the infinite medium, we obtain (44a). In other words, to get the physical result we must take the ω limit after the thermodynamic limit.

Equation (44) is as far as we can proceed without introducing a specific $\hat{h}^{\mathrm{ad}}$. The simplest case to consider is when the heavy particle is the only inhomogeneity in the electron gas, the single particle analogue of the model of Sec. III A. The only forces in the problem then are between the electrons and the heavy particle, which we describe by a potential V. We assume V has a finite range—specifically we assume it is not Coulombic—but otherwise arbitrary. The reduction of (44a) proceeds most

easily if we use some formal operator manipulation.[21] To this end we introduce the t matrix:

$$\hat{t}^{\pm} = \hat{V} + \hat{V}\hat{G}_0^{\pm}\hat{t}^{\pm} , \tag{48}$$

where

$$\hat{G}_0^{\pm} = (\mu - \hat{p}^2/2m \pm i0^+)^{-1} \tag{49}$$

and $\hat{p}$ is an electronic momentum operator.

Noting that $\hat{F} = (i/\hbar)[\hat{p}, \hat{V}]$ is the force on the ad-particle and that $[\hat{p}, \hat{G}_0^{\pm}] = 0$, we deduce

$$(i/\hbar)[\hat{p}, \hat{t}^{\pm}] = (1 + \hat{t}^{\pm}\hat{G}_0^{\pm})\hat{F}(1 + \hat{G}_0^{\pm}\hat{t}^{\pm}) . \tag{50}$$

Taking matrix elements of this equation with plane waves $|\vec{k}\rangle$ and $|\vec{k}'\rangle$, and recalling that the scattering wave states, $|\psi_{\vec{k}}^{\pm}\rangle$ are related to plane wave states by

$$|\psi_{\vec{k}}^{\pm}\rangle = (1 + \hat{G}_0^{\pm}\hat{t}^{\pm})|\vec{k}\rangle \tag{51}$$

yields

$$(i/\hbar)\langle\vec{k}'|[\hat{p}, \hat{t}^{\pm}]|\vec{k}\rangle = \langle\psi_{\vec{k}'}^{\mp}|\hat{F}|\psi_{\vec{k}}^{\pm}\rangle . \tag{52}$$

Now to rewrite (44a), we simply use $|\psi_{\vec{k}}^{+}\rangle$ for $|n\rangle$ and $|\psi_{\vec{k}'}^{-}\rangle$ for $|m\rangle$ plus Eq. (52). We find

$$\eta_{\alpha\beta} = \frac{\pi\hbar}{M}\int d\epsilon\left(-\frac{\partial n}{\partial\epsilon}\right)\sum_{\vec{k},\vec{k}'}\sum_{\sigma,\sigma'}|\langle\vec{k}'\sigma'|\hat{t}^{+}|\vec{k}\sigma\rangle|^2 \times (k_\alpha - k'_\alpha)(k_\beta - k'_\beta)\delta\left(\epsilon - \frac{\hbar^2k^2}{2m}\right)\delta\left(\epsilon - \frac{\hbar^2k'^2}{2m}\right), \tag{53}$$

where we have included summations over spin eigenstates $|\sigma\rangle$ and $|\sigma'\rangle$, which until now were only implicit. If we now assume that V is spherically symmetric, or at least that we may average out the non spherically symmetric portion of the square of the t matrix element,[22] then we can rewrite (53) as

$$\eta = \eta_{\alpha\alpha} = \frac{m}{M}n\frac{2\pi}{\hbar}\sum_{\sigma'}\int\frac{d^3k'}{(2\pi)^3}\int\frac{d^2k_F}{4\pi}|\Omega\langle\vec{k}'\sigma'|\hat{t}^{+}|\vec{k}_F\sigma\rangle|^2 \times (1 - \cos\theta_{\vec{k}',\vec{k}_F})\delta\left(\mu - \frac{\hbar^2k'^2}{2m}\right), \tag{54}$$

where $\vec{k}_F$ is a vector of magnitude k_F and whose orientation is averaged over, $|\sigma\rangle$ is a spin eigenstate of $\hat{s}_Z$, $\theta_{\vec{k}',\vec{k}_F}$ is the angle between $\vec{k}'$ and $\vec{k}_F$, and $n = k_F^3/3\pi^2$ is the average density of electrons. Such an expression for η was first derived by Davis and Dagonnier by another method.[23] Equation (54) may be directly compared to the transport time τ of impurity resistance $\rho = m/ne^2\tau$ in the low-density and zero-temperature limit

$$\eta = (m/M)(n/n_i)1/\tau , \quad \text{as } n_i \to 0 , \tag{55}$$

where n_i is the density of impurities. The direct relationship between η and ρ can be understood physically as a consequence of Newton's third law. The forces that slow a drifting heavy particle are equal but oppositely directed to the forces that impede the flow of electrons.

If we assume that V is a spherically symmetric spin-independent potential, then a phase shift representation of t is appropriate[24]

$$\Omega\langle\vec{k}'\sigma'|t^{+}|\vec{k}_F\sigma\rangle = \delta_{\sigma,\sigma'}4\pi\sum_l(2l+1) \times\left(-\frac{\hbar^2}{2mk_F}e^{i\delta_l}\sin\delta_l\right)P_l(\cos\theta_{\vec{k}',\vec{k}_F}) , \tag{56}$$

where δ_l is the phase shift of the lth partial wave and the P_l are Legendre polynominals.[25] Substituting (56) in (54) we obtain[26]

$$\eta = \frac{8}{3\pi}\frac{m}{M}\frac{E_F}{\hbar}\sum(l+1)\sin^2(\delta_l - \delta_{l+1}) \tag{57}$$

which again confirms the order of magnitude conclusion of Sec. III A.

We close this section with a brief discussion of a "proof" that η vanishes identically for the model considered here. The argument is as follows: If the only forces are between the electrons and the heavy particle, one may write the force on the heavy particle as

$$\hat{F} = (i/\hbar)[\hat{p}, \hat{h}^{\text{ad}}] . \tag{58}$$

Then, since in Eq. (44a) the friction is related to matrix elements of $\vec{F}$ between states of equal energy, one deduces

$$\langle n|\hat{F}|m\rangle = (i/\hbar)\langle n|(\hat{p}\hat{h}^{\text{ad}} - \hat{h}^{\text{ad}}\hat{p})|m\rangle = (i/\hbar)(\epsilon_m - \epsilon_n)\langle n|\hat{p}|m\rangle = 0 \text{ since } \epsilon_n = \epsilon_m , \tag{59}$$

and hence $\eta = 0$. This conclusion is false. The error in the "proof" lies in the step between the first and second line of (59). One assumed there that $\hat{h}^{\text{ad}}$ is Hermitian, which it is not when acting between states that are not square integrable. The culprit is the kinetic energy, whose anomalous properties in this regard are well known.[27] Furthermore the "proof" cannot be repaired by working in a large box in order to give the electron states a finite norm. The walls of the box will contribute to the forces in (58). Thus, though one can then prove that the equal energy matrix elements of the total force must vanish, this is not relevant for the force only on the heavy particle.

D. Two-particle phase-shift model

We now generalize the model of Sec. III C to include two heavy particles in an otherwise homogeneous electron bath. Each heavy particle is assumed to interact with the electrons through a local central spin-independent potential and furthermore these potentials are presumed not to overlap. This muffin-tin model of the potential will allow us to solve the electronic multiple-scattering problem in closed form. Our evaluation proceeds from (44b) and its generalization from Appendix B. We write

$$\langle\vec{r}|\delta(\mu - \hat{h}^{\text{ad}})|\vec{r}'\rangle = -(1/\pi)\text{Im}\langle\vec{r}|G^{+}|\vec{r}'\rangle , \tag{60}$$

where Im denotes imaginary part and

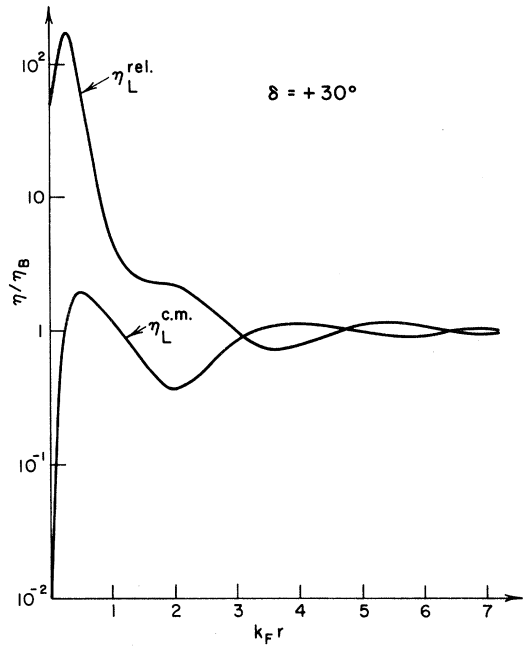

FIG. 2. Center-of-mass and relative friction in the longitudinal L direction versus the separation r of the two muffin-tin spheres. The single s-wave phase shift of either sphere at the Fermi energy is $+30°$. The infinite separation limit of the friction is η_B.

$$G^+ = (\mu - \hat{h}^{ad} + i0^+)^{-1} ; \tag{61}$$

note that we only need to know $\langle \vec{r}\,|G^+|\,\vec{r}\,'\rangle$ for $\vec{r}$, $\vec{r}\,'$ in one or the other of the two muffin tins, since only there is the force nonzero. The solution of this problem for G^+ requires a straightforward application of multiple scattering theory. However, the relevant formulas are rather cumbersome so we relegate to Appendix C an explicit listing of the results we use. The final expressions depend only on the separation r of the two muffin tins and the phase shifts of the separate potentials. For simplicity, we assume the two potentials are identical and have only an s-wave phase shift δ. Since the requirement that the potentials not overlap is only implicit in the formulas, we shall take the view that the phase shift is produced by a model potential of arbitrarily short range[28] and shall evaluate our results for all values of r.

Before presenting the results of our calculation we need to discuss the form that the friction tensor takes.[29] By the symmetry of the problem η is diagonal in the Cartesian indices but has different values in the directions parallel or perpendicular to the heavy particle separation vector $\vec{r}$. We label these two values longitudinal and transverse, respectively. Furthermore, the friction is nondiagonal in the heavy particle indices. If we label the two heavy particles 1 and 2, the appropriate Fokker-Planck equation is

$$\frac{\partial f}{\partial t} + \sum_{j=1}^{2}\sum_{\alpha=1}^{3}\left(\frac{1}{M}P_\alpha^j \frac{\partial}{\partial R_\alpha^j} + \langle F_\alpha^j\rangle \frac{\partial}{\partial P_\alpha^j}\right) f = \sum_{\substack{j=1\\ j'=1}}^{2}\sum_{\alpha=1}^{3} \eta_{\alpha\alpha}^{jj'} \frac{\partial}{\partial P_\alpha^j}\left(P_\alpha^{j'} + Mk_BT\frac{\partial}{\partial P_\alpha^{j'}}\right) f , \tag{62}$$

where we have assumed the two particles have the same mass M. This equation is more clearly written for this simple model if we use the center of mass and relative coordinate

$$\vec{R} = \tfrac{1}{2}(\vec{R}_1 + \vec{R}_2), \quad \vec{r} = \vec{R}_1 - \vec{R}_2 \tag{63}$$

and their conjugate momenta

$$\vec{P} = \vec{P}_1 + \vec{P}_2 , \quad \vec{p} = \tfrac{1}{2}(\vec{p}_1 - \vec{p}_2) . \tag{64}$$

In terms of these new variables (62) is

$$\frac{\partial f}{\partial t} + \sum_{\alpha=1}^{3}\frac{1}{2M}P_\alpha\frac{\partial}{\partial R_\alpha} f + \sum_{\alpha=1}^{3}\left(\frac{1}{M/2}p_\alpha\frac{\partial}{\partial r_\alpha} + \langle F_\alpha\rangle\frac{\partial}{\partial p_\alpha}\right) f = \sum_{\alpha=1}^{3}\eta_{\alpha\alpha}^{c.m.}\frac{\partial}{\partial P_\alpha}\left(P_\alpha + 2Mk_BT\frac{\partial}{\partial P_\alpha}\right) f + \sum_{\alpha=1}^{3}\eta_{\alpha\alpha}^{rel}\frac{\partial}{\partial p_\alpha}\left(p_\alpha + \frac{M}{2}k_BT\frac{\partial}{\partial p_\alpha}\right) f , \tag{65}$$

where $\langle F_\alpha\rangle = \langle F_\alpha^1\rangle = -\langle F_\alpha^2\rangle$ is the average force on particle 1 and

$$\eta_{\alpha\alpha}^{c.m.} = \eta_{\alpha\alpha}^{11} + \eta_{\alpha\alpha}^{12} , \tag{66}$$

$$\eta_{\alpha\alpha}^{rel} = \eta_{\alpha\alpha}^{11} - \eta_{\alpha\alpha}^{12} . \tag{67}$$

We have used the symmetry here that $\eta^{11} = \eta^{22}$ and $\eta^{12} = \eta^{21}$. It is the pair of equations (66) and (67) for the center-of-mass and relative friction coefficients that we calculate.

Figures 2–4 show some typical results. Due to its considerable variation we have plotted the logarithm of η/η_B vs $k_F r$, where η_B is the bulk value of the friction for a single adparticle [Eq. (57)]. Only the value of the phase shift at E_F enters the formula for η/η_B; we choose this to be $\pm 30°$ here. The large difference between these two cases is a consequence of the multiple scattering. As one can easily see from the expressions of Appendix C, the basic manifestation of the multiple scattering between the two heavy particles is through the factor

$$[1 - e^{2i\delta}\sin^2\delta\, e^{2ik_Fr}/(k_Fr)^2]^{-1} , \tag{68}$$

which represents the sum of all the electron scattering back and forth between the two. For $k_Fr \approx -\delta$ with $0 < -\delta \ll \frac{1}{2}\pi$, this factor nearly diverges, while for positive δ there is no strong structure as r varies. This accounts for the presence or absence of the spike in η near $k_Fr \approx 0.5$ in Figs. 2–4. Note that this feature would be lost if we were to use a perturbative evaluation of η as we did in Secs. III A and III B, for the factor (68) would be set equal to unity. Thus, perturbation theory could only be used here for a rough estimate of η. Some further illustration of this point is contained in Appendix C.

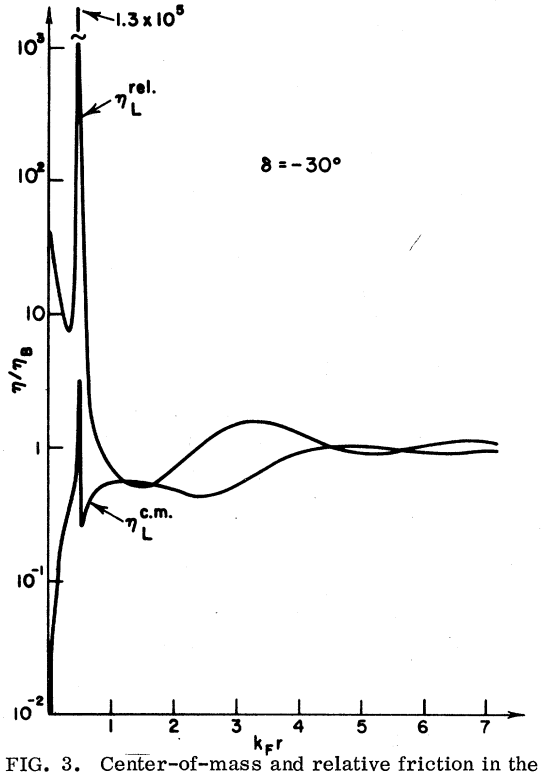

FIG. 3. Center-of-mass and relative friction in the longitudinal, L, direction versus the separation, r, of the two muffin tin spheres. The single s-wave phase shift of either sphere at the Fermi energy is $-30°$. The infinite separation limit of the friction is η_B.

However, we note that as $k_F r$ becomes large the multiple-scattering effects between the two heavy particles become small. This feature alleviates concern that the electron gas may not rapidly equilibrate for large r.[29,8] A local equilibrium about each heavy particle would then be sufficient to essentially determine η.

Since the solutions of the Fokker-Planck equation seems to depend critically on the relative magnitude of the friction and the curvature in $V(r)$,[3] we have also calculated a $V(r)$ for this model. We take as V the binding energy ΔE of the two heavy particles due to their indirect interaction through the electron gas. This is the appropriate result for V to yield the average force $\langle F \rangle$ of either Eq. (B3) or (B21) in the limit of large M. For simplicity we evaluate ΔE at zero electronic temperature. To do such a calculation one needs to know the phase shift as a function of energy. For this purpose we use the scattering length formula[30]

$$\tan(\delta(E)) = -ka\,, \quad k = (2mE/\hbar)^{1/2}\,, \tag{69}$$

with the scattering length a chosen so that $\delta(E_F)$ is the value used to compute η. The formula for the binding energy is[31]

$$\Delta E(r) = \int_{-\infty}^{E_F} dE\,(E - E_F)\Delta\rho_r(E)\,, \tag{70}$$

where we have omitted a factor of 2 for spin. The factor $\Delta\rho_r(E)$ is the change in the density of states at energy E when the two heavy particles are separated by r from when they were at infinite separation. This quantity can also be computed from G^+, Eq. (61); we give further details in Appendix C. We only remark here that one must carefully follow the motion in energy of all bound states (with $E<0$) as well as the resonances in the continuous density of states for $E>0$ in order to find a ΔE continuous in r, as required by the Kohn-Majumdar theorem.[32]

We plot in Fig. 5 the binding energy for $\delta(E_F)$ equal to minus or plus 30°. Again there is a considerable difference between the two cases which can be understood in terms of the multiple scattering. The divergence of ΔE as $k_F r$ goes to zero is an artifact of this model, in particular the approximation (69). Equation (69), when extended to negative energies gives a poor representation of $\delta(E)$ as E goes to minus infinity. Furthermore if we had used realistic potentials in the model they would overlap before r became very small and thereby violate the conditions for our solution of G^+. At the

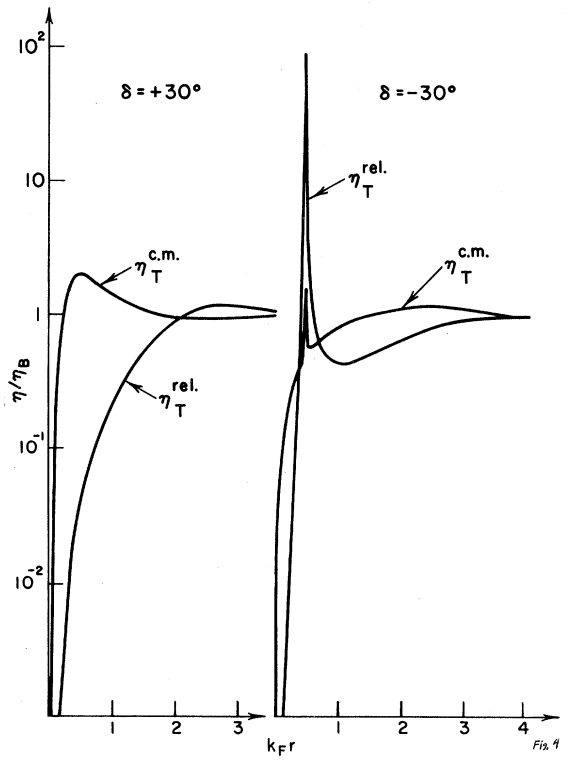

FIG. 4. Center-of-mass and relative friction in the transverse T direction versus the separation r of the two muffin-tin spheres. The single s-wave phase shift of either sphere at the Fermi energy is $\pm 30°$. The infinite separation limit of the friction is η_B.

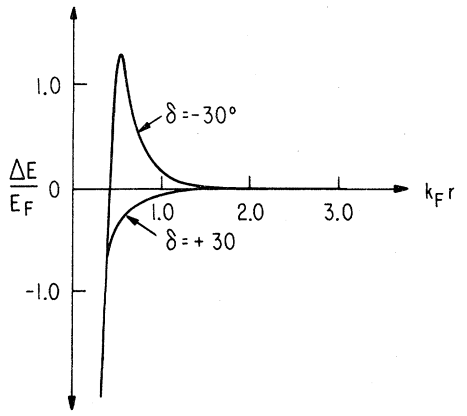

FIG. 5. Binding energy ΔE of two-muffin-tin scatterer model vs the separation r of the two-muffin-tin spheres. The single s-wave phase shift of either sphere δ at the Fermi energy E_F is $\pm 30°$. As normalized, the figure is independent of the specific value of E_F.

other limit in r, we remark that the expected Friedel oscillations in ΔE are present, roughly beyond $k_F r \approx 2$; but that they are at greatest of magnitude 0.01 in the units of the figure.

E. One-dimensional-surface model

Let us now consider a model which has a surface, albeit one dimensional. The model is defined by the potential energy of $\hat{h}^{ad}$ and is shown schematically in Fig. 6. There is a semi-infinite well of depth V_0, which represents the metal potential energy. To the left of this a distance x_1 (>0) is a square well of depth V and width $2a$, representing the adparticle potential energy. The zero of energy is taken at the bottom of the metal band. If we write for the electronic eigenstates with energy $E = \hbar^2 k^2/2m$

$$\Psi_k(x) = A \sin(kx + \delta) \quad \text{for } x > 0 , \tag{71}$$

and match this wave function at each discontinuity in the potential energy until we have only a decaying wave as $x \to -\infty$ (for $E < V_0$), we obtain the complete wave function and an expression for $\delta [= \delta(x_1, E)]$:

$$\delta = \tan^{-1}\{(k/\beta)[(1+\gamma)/(1-\gamma)]\} , \tag{72}$$

where

$$\hbar^2\beta^2/2m = V_0 - E , \tag{73}$$

$$\gamma = e^{-2\beta x_1} \sin(2k'a)/\sin(2\varphi - 2k'a) , \tag{74}$$

with

$$\hbar^2 k'^2/2m = E + V - V_0 , \tag{75}$$

$$\varphi = \tan^{-1}(\beta/k') . \tag{76}$$

We note in passing that the poles in γ occur at the bound state energies of the isolated square well.[33] The choice $A = 2$ in Eq. (71) ensures that the states have a δ-function normalization: $\langle k | k' \rangle = \delta(k - k')$.

As in the previous model we compute both the friction and the binding energy as a function of the adparticle position, here measured by x_1. From Eq. (44a) and the simple dispersion relation of this model we can write

$$\eta = \frac{1}{8\pi} \frac{m}{M} \frac{1}{E_F} \frac{1}{\hbar} |\langle \Psi_{k_F} | F | \Psi_{k_F} \rangle|^2 , \tag{77}$$

where we again omit a factor of two for spin. The matrix element of the force from the square well is simply written

$$\langle \Psi_{k_F} | F | \Psi_{k_F} \rangle = V[\Psi^2_{k_F}(-x_1 - 2a) - \Psi^2_{k_F}(-x_1)] . \tag{78}$$

From (78) we see that η will vanish whenever the wave-function magnitudes are equal on both sides of the square well. This happens when $E = E_B$, a bound state energy of the isolated square well. This vanishing of η at E_B is a general result in one dimension as long as the adparticle and metal potential energies do not overlap. One need merely note that at E_B the eigenfunction outside the range of the metal potential energy is proportional to the eigenstate of the isolated adparticle Hamiltonian. Since the matrix element of F is identically zero in the isolated adparticle eigenstate, by the Hellmann-Feynman theorem, our assertion is proved. This result would appear to be an artifact of one dimension though as we show in Sec. III F its analog can occur in three dimensions in a (too) simple model.

For the binding energy we again use (70). The change in the density of states due to the adparticle being at x_1, rather than at infinity, is given here by

$$\Delta\rho_{x_1}(E) = \frac{1}{\pi} \frac{d}{dE} [\delta(x_1 E) - \delta(\infty, E)] . \tag{79}$$

Since we include no repulsive interaction between the adparticle and the metal, we only compute $\Delta E(x_1)$ down to $x_1 = 0$.

Some typical results are shown in Figs. 7 and 8. We have chosen here $V_0 = 26.9$ eV, to simulate the high-electron density of a transition metal and $V = 27.2$ eV and $a = 0.37$ Å to place E_B—there is only

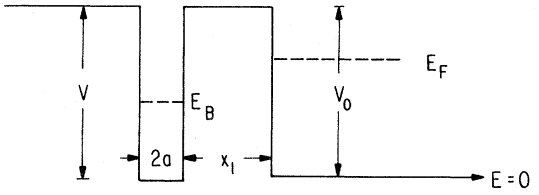

FIG. 6. Electronic potential energy versus position for a one-dimensional model of metal plus adparticle. The position of the Fermi level E_F and of the bound state energy E_B of the adparticle (if isolated) are marked and the parameters of the model, V_0, V, x_1 and $2a$, are defined.

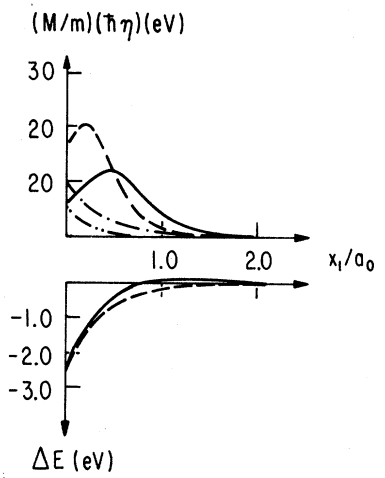

FIG. 7. Friction η and binding energy ΔE of one-dimensional model vs adparticle distance from the metal surface x_1 for various values of the Fermi-level position E_F: solid line, $E_F = 19$ eV, dashed line, $E_F = 9.5$ eV. Also drawn are the perturbation estimates of η for $E_F = 19$ eV, dot-dashed line and $E_F = 9.5$ eV, dot-dot dashed line. The parameter a_0 is the Bohr radius; the value of the other parameters of the model are given in the text.

one value—at 14.5 eV. In our computation we varied both x_1 and E_F. Qualitatively, the behavior is as follows: For the friction there is a maximum at small x_1 for E_F well above E_B. As E_F decreases to E_B this maximum moves to larger x_1 and decreases in magnitude. As noted above η vanishes for all $x_1 > 0$ when $E_F = E_B$. When E_F falls below E_B the reverse behavior is seen. A maximum moves in from infinite x_1 and grows in magnitude, but the detailed structure is naturally not completely symmetric with $E_F > E_B$. The behavior of the binding energy is simpler. For E_F moving towards E_B, ΔE decreases for all x_1. The binding energy is maximum for $E_F = E_B$ since this is the optimum position of the Fermi level to take advantage of the adparticle induced resonance in the electronic density of states, lowering the most electrons in energy consistent with raising the fewest and conserving the total number of electrons below E_F.[31]

We have also plotted in Fig. 7 a perturbative estimate of η. This was found by using eigenfunctions of the metal potential alone to compute $\langle \Psi^0_{k_F} | F | \Psi^0_{k_F} \rangle$. As expected η exponentially decays with x_1. Furthermore, there is no significant change as E_F is varied; all trace of the nodes of Fig. 8 is lost. Again we conclude that perturbation theory, though satisfactory for a rough estimate of η, may completely miss certain detailed structure.

F. Tight-binding model

Finally we examine a model which allows a straightforward extension to three dimensions. For simplicity we present only its one dimensional form. The transition to three dimensions is easy but, as we shall argue below, does not seem to possess any new features. We write the adiabatic Hamiltonian in single-particle tight-binding form, retaining only nearest-neighbor coupling

$$\hat{h}^{\mathrm{ad}} = \hat{h}_0 + \hat{v} , \tag{80}$$

$$\hat{h}_0 = \sum_{n=1}^{\infty} [\,|n\rangle E_0 \langle n| + |n\rangle \times t \langle n+1| + |n+1\rangle t \langle n|\,] + |a\rangle E_a \langle a| , \tag{81}$$

$$\hat{v} = |1\rangle \bar{t} \langle a| + |a\rangle \bar{t} \langle 1| . \tag{82}$$

The orbitals of the metal are labeled from one to infinity and the single orbital of the adparticle is labeled a. The only dependence in $\hat{h}^{\mathrm{ad}}$ on the position of the adparticle is assumed to be in the parameter $\bar{t}$. Hence

$$\hat{F} = |a\rangle \left(-\frac{\partial \bar{t}}{\partial R}\right) \langle 1| + |1\rangle \left(-\frac{\partial \bar{t}}{\partial R}\right) \langle a| . \tag{83}$$

This result greatly simplifies the reduction of (44b), for we only need determine the following matrix elements of G^+, Eqs. (60) and (61):

$$\langle a | G^+ | a \rangle = g_a / (1 - \bar{t} g_1 \bar{t} g_a) , \tag{84}$$

$$\langle 1 | G^+ | 1 \rangle = g_1 / (1 - \bar{t} g_a \bar{t} g_1) , \tag{85}$$

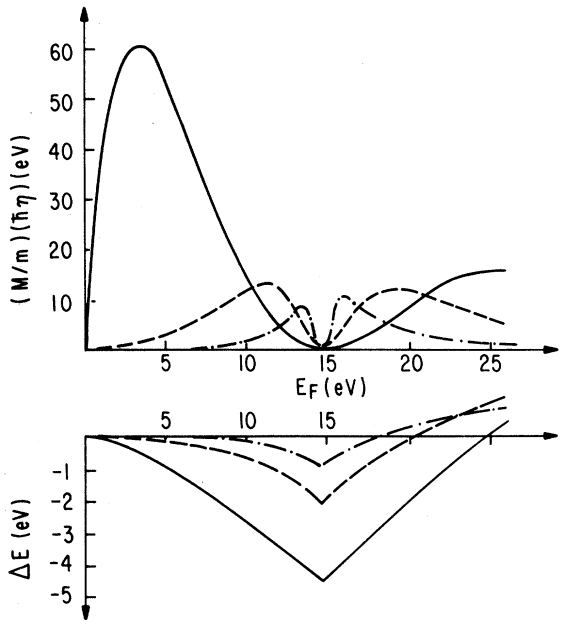

FIG. 8. Friction η and binding energy ΔE of one-dimensional model vs Fermi level position E_F for various values of the adparticle distance from the metal surface, x_1, measured in Bohr radii a_0: solid line, $x_1/a_0 = 10^{-4}$; dashed line, $x_1/a_0 = 0.5$; and dot-dashed line, $x_1/a_0 = 1$. The values of the other parameters of the model are given in the text.

$$\langle a|G^+|1\rangle = g_a \bar{t} g_1/(1-\bar{t} g_a \bar{t} g_1)\,, \tag{86}$$

$$\langle 1|G^+|a\rangle = g_1 \bar{t} g_a/(1-\bar{t} g_1 \bar{t} g_a)\,, \tag{87}$$

where $g_a = \langle a|g^+|a\rangle$ and $g_1 = \langle 1|g^+|1\rangle$ with

$$g^+ = (\mu - \hat{h}_0 + i0^+)^{-1}\,. \tag{88}$$

In particular, $g_a = 1/(\mu - E_a + i0^+)$ so that when $\mu(=E_F)$ is equal to E_a, g_a is infinite. As a consequence $\langle 1|G^+|1\rangle$ vanishes and $\langle a|G^+|1\rangle$ and $\langle 1|G^+|a\rangle$ are both real quantities at this special value of the Fermi level and these results in turn imply that the friction vanishes. Thus, as in the previous model, $\eta = 0$ when $E_F = E_a$. This peculiar effect cannot always be removed by working in a system of higher dimension. For even if we generalize $\hat{h}_0$ to higher dimension with more than nearest-neighbor coupling, Eqs. (84)–(87) remain formally valid; only the value of g_1 changes. However, if we allow $\hat{v}$ to couple $|a\rangle$ to more than just its nearest neighbor or if we allow an R dependence in E_a, then we can no longer prove that η is zero when g_a diverges. The persistence of the node in η in this model is probably an artifact of the tight-binding representation of $\hat{h}^{\rm ad}$, which too severely restricts the eigenfunctions of the whole system at E_a. Rather than attempt to analyze a more-complex tight-binding model, it would appear more useful to develop a less restricted representation of $\hat{h}^{\rm ad}$. Such work is currently in progress.

To conclude this section we remark that for comparison with the electronic models that we have considered here, we have in Appendix D examined the predicted η of a phonon model, wherein the dominant energy transfer mechanism between an adparticle and the substrate is presumed to arise from atomic (or molecular) collisions.

APPENDIX A

We give here an application of our linear response method of determining the friction coefficient to the well known problem of a harmonically bound Brownian particle in one dimension. Although the spirit of the approach is entirely similar to that of Sec. II, this special model allows the fruitful application of certain alternate methods.

The Fokker-Planck equation in this case has the form

$$\frac{\partial f}{\partial t} + u\frac{\partial f}{\partial x} - \omega_0^2 x \frac{\partial f}{\partial u} = \eta \frac{\partial}{\partial u}\left(uf + \frac{k_B T}{M}\frac{\partial f}{\partial u}\right), \tag{A1}$$

where x, u and M are position, velocity, and mass of the Brownian particle, ω_0 is the frequency of oscillation in the harmonic well, and η is the friction, which is assumed here to be position independent.

If a small, uniform force $F_1 e^{-i\omega t}$ is applied to the Brownian particle, Eq. (A1) becomes

$$\frac{\partial f}{\partial t} + u\frac{\partial f}{\partial x} - \omega_0^2 x \frac{\partial f}{\partial u} + \frac{F_1 e^{-i\omega t}}{M}\frac{\partial f}{\partial u} = \eta \frac{\partial}{\partial u}\left(uf + \frac{k_B T}{M}\frac{\partial f}{\partial u}\right). \tag{A2}$$

We seek now a solution of (A2) that describes a small displacement of f from equilibrium, due to the external disturbance

$$f = f^{\rm eq} + f_1(x, u, \omega)e^{-i\omega t}\,, \tag{A3}$$

where

$$f^{\rm eq}(x, u) = e^{-\beta H(x,u)} \Big/ \int dx\, du\, e^{-\beta H(x,u)}$$

is the Boltzmann distribution and $H = \frac{1}{2}Mu^2 + \frac{1}{2}M\omega_0^2 x^2$. Putting (A3) back into (A2), and retaining only terms linear in the external force, we obtain

$$-i\omega f_1 + u\frac{\partial f_1}{\partial x} - \omega_0^2 x \frac{\partial f_1}{\partial u} + \frac{F_1}{M}\frac{\partial f^{\rm eq}}{\partial u} = \eta \frac{\partial}{\partial u}\left(u + \frac{k_B T}{M}\frac{\partial}{\partial u}\right) f_1\,, \tag{A4}$$

where we have used the obvious results

$$\left(u\frac{\partial}{\partial x} - \omega_0^2 x \frac{\partial}{\partial u}\right) f^{\rm eq} = \eta \frac{\partial}{\partial u}\left(u + \frac{k_B T}{M}\frac{\partial}{\partial u}\right) f^{\rm eq} = 0\,.$$

From now on we will slightly generalize Eq. (A4), including the possibility that η be frequency dependent. Integration over u of Eq. (A4) gives the "continuity-equation" result

$$-i\omega \int_{-\infty}^{+\infty} du\, f_1(x, u) + \frac{\partial}{\partial x}\int_{-\infty}^{+\infty} du\, u f_1(x, u) = 0 \tag{A5}$$

or

$$-i\omega \rho^{(1)}(x, \omega) + \frac{\partial}{\partial x} j^{(1)}(x, \omega) = 0\,,$$

where we have introduced density and current density responses in the usual way. On the other hand, multiplying Eq. (A4) by u, and integrating over u again, we find

$$-i\omega j^{(1)}(x, \omega) + \frac{\partial}{\partial x}\int du\, u^2 f_1(x, u) + \omega_0^2 x \rho^{(1)}(x, \omega) - \frac{F_1 \rho^{\rm eq}}{M}(x) = -\eta(\omega) j^{(1)}(x, \omega)\,. \tag{A6}$$

Integration of Eq. (A6) over x gives

$$-i\omega j^{(1)}(\omega) + \omega_0^2 \int_{-\infty}^{+\infty} dx\, x \rho^{(1)}(x, \omega) - \frac{F_1}{M}\int_{-\infty}^{+\infty} dx\, \rho^{\rm eq}(x) = -\eta(\omega) j^{(1)}(\omega)\,, \tag{A7}$$

where $j^{(1)}(\omega) = \int_{-\infty}^{+\infty} dx\, j^{(1)}(x, \omega)$ is the over-all current response. Using Eq. (A5), we obtain from Eq. (A7)

$$j^{(1)}(\omega) = -\frac{F_1}{M}\left(i\omega - \frac{i\omega_0^2}{\omega} - \eta(\omega)\right)^{-1}\,. \tag{A8}$$

Equation (A8) divided by F_1 gives the spatial average mobility of the Brownian particle

$$\mu(\omega)=\frac{1}{M}\frac{i\omega}{\omega^2-\omega_0^2+i\omega\eta(\omega)}, \tag{A9}$$

which is related to the velocity-velocity correlation function by the fluctuation-dissipation theorem

$$\mu(\omega)=\frac{1}{k_BT}\int_0^\infty dt\, e^{i\omega t}\langle u(t_0)u(t_0+t)\rangle . \tag{A10}$$

Equation (A10) in our case is proved as follows: Setting

$$C(\omega)=\int_0^\infty dt\, e^{i\omega t}\langle u(t_0)u(t_0+t)\rangle ,$$

we have

$$C(\omega)=\int_{-\infty}^{+\infty}dx_0\int_{-\infty}^{+\infty}du_0\,u_0 f^{eq}(x_0u_0)A(x_0,u_0,\omega), \tag{A11}$$

where

$$A(x_0,u_0,\omega)=\int_0^\infty dt\, e^{i\omega t}\times\int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}du\,uF(x,u,x_0,u_0,t_0+t) \tag{A12}$$

and $F(x,u,x_0,u_0,t_0+t)$ is a solution of Eq. (A1) subject to the initial condition $F(x,u,x_0,u_0,t_0)=\delta(x-x_0)\times\delta(u-u_0)$. On the other hand, taking the Fourier-Laplace transform of Eq. (A1) and following the same steps as we did in deriving Eqs. (A5) and (A7), we obtain

$$-i\omega\rho(x,\omega)-\rho(x,t=t_0)+\frac{\partial}{\partial x}j(x,\omega)=0 , \tag{A13}$$

$$[-i\omega+\eta(\omega)]A(x_0,u_0,\omega)-u_0+\omega_0^2\int_{-\infty}^{+\infty}dx\,x\rho(x,\omega)=0 , \tag{A14}$$

where

$$\rho(x,\omega)=\int_0^\infty e^{i\omega t}\rho(x,t_0+t)$$

and

$$j(x,\omega)=\int_0^\infty dt\, e^{i\omega t}j(x,t_0+t)$$

are the Fourier-Laplace transforms of the density and of the current density. We also have

$$A(x_0,u_0,\omega)=\int_{-\infty}^{+\infty}dx\,j(x,\omega) . \tag{A15}$$

Inserting the expression for $\rho(x,\omega)$ from Eq. (A13) into Eq. (A14), we obtain, after having done integration over x by parts, and having used Eq. (A15),

$$A(x_0,u_0,\omega)=\frac{i\omega u_0+\omega_0^2x_0}{\omega^2+i\omega\eta(\omega)-\omega_0^2} . \tag{A16}$$

Finally, substitution of Eq. (A16) back into Eq. (A11) gives Eq. (A10).

We would like now to calculate the friction coefficient η, at least in the dc limit (i.e., at $\omega=0$): as we can see from Eqs. (A9) and (A10), η is related to the velocity-fluctuation spectrum of the system; another relation of this kind can be derived, if we assume that the Fokker-Planck equation (A1) holds together with a generalized (i.e., non-Markovian) Langevin equation: If $R(t)$ denotes the random force in the Langevin equation, we find

$$\eta(\omega)=\frac{1}{Mk_BT}\int_0^\infty dt\, e^{i\omega t}\langle R(t_0)R(t_0+t)\rangle . \tag{A17}$$

Equation (A17), which is essentially the Nyquist theorem, can be easily proved, using a straightforward generalization of the analogous proof given by Kubo[10] for the case of a "free" Brownian particle.

In the present case the Nyquist theorem has a somewhat different meaning, since the left-hand side is not simply the inverse mobility; the last is infinite in the dc limit, as immediately follows from Eq. (A9), while η is in general finite at $\omega=0$.

To calculate η, we need therefore a more detailed microscopic description of the system, to be linked with our statistical approach. In order to do this, let us first write

$$M\mu(\omega)=-1/i\omega+\varphi(\omega)/\omega^2 . \tag{A18}$$

This equation simply defines the function $\varphi(\omega)$; if a Langevin equation is assumed together with Eq. (A1), one has

$$\varphi(\omega)=\frac{1}{Mk_BT}\int_0^\infty dt\, e^{i\omega t}\langle F_t(t_0)F_t(t_0+t)\rangle , \tag{A19}$$

where $F_t(t)=-M\omega_0^2x(t)-\eta Mu(t)+R(t)$ denotes the total force on the Brownian particle; Eq. (A19) can be proved using the same argument as Kubo[10] did for the force-free case.

We now proceed in two steps: first, we relate $\eta(\omega=0)$ to $\varphi(\omega)$ using Eqs. (A18) and (A9); this gives

$$\varphi(\omega)=i\omega\frac{\omega_0^2-i\omega\eta(\omega)}{\omega^2-\omega_0^2+i\omega\eta(\omega)} . \tag{A20}$$

Expanding $\varphi(\omega)$ in a Taylor series around $\omega=0$ we have

$$\varphi(\omega)=-i\omega-\frac{i\omega^3}{\omega_0^2}+\frac{\eta_0}{\omega_0^4}\omega^4+\cdots , \tag{A21}$$

where $\eta_0=\eta(\omega=0)$.

Both coefficients of zero and second powers of ω are zero here, since $\mu(\omega)\to 0$ when $\omega\to 0$.

We also note that the expansion (A21) in the force free case becomes

$$\varphi^{(free)}=-i\omega+\omega^2/\eta_0+\cdots , \tag{A22}$$

since in this case $\mu(\omega)\to 1/M\eta_0$ when $\omega\to 0$.

The second step of our procedure consists in deriving an expression for $\varphi(\omega)$ in terms of microscopic or "Hamiltonian" parameters; Eq. (A21) will

be then the link for relating η_0 and, as we can notice now, ω_0, to those same parameters.

The basic assumption here is that the mobility of the Brownian particle calculated using quantum mechanics is equal to the expression (A9) calculated from the Fokker-Planck equation. We may notice that this assumption implies much less than the validity of the Fokker-Planck equation itself; as a matter of fact the last can be rigorously proved[8] only for $M \to \infty$; it is not the scope of this calculation to prove the validity of the Fokker-Planck equation in a less restrictive hypothesis, but only to calculate the average driving force of the oscillator and the friction coefficient even for cases where we do not make such a restriction. Our assumption is that such a procedure is reasonable. This is the essence of the bootstrap.

The microscopic model we use is very simple: An Einstein oscillator interacting with a quantum bath, so that the Hamiltonian is given by

$$\hat{H} = \hat{H}_B(\{\hat{x}_i\}, \{\hat{p}_i\}) + \frac{\hat{P}^2}{2M} + \frac{M\Omega^2}{2}\hat{X}^2 + V(\hat{X}, \{x_i\}) , \qquad \text{(A23)}$$

where $\{\hat{x}_i\}$, $\{\hat{p}_i\}$ and $\hat{X}$, $\hat{P}$ stand for position and momentum operators for the bath particles and for the oscillator, respectively; $\hat{H}_B$ is the bath Hamiltonian, given by

$$\hat{H}_B = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} v(|\hat{x}_i - \hat{x}_j|) \qquad \text{(A24)}$$

and v is the interaction energy between oscillator and bath. Ω is the microscopic frequency of the Einstein oscillator which is in general different from the ω_0 appearing in Eq. (A1).

If a small, uniform external force $F_1 e^{-i\omega t}$ is applied to the oscillator, the Hamiltonian becomes

$$\hat{H}_t = \hat{H} + \hat{H}_1 , \qquad \text{(A25)}$$

where

$$\hat{H}_1 = -\hat{X} F_1 e^{-i\omega t} . \qquad \text{(A26)}$$

The velocity response of the oscillator is given by Kubo's[13] linear-response formula

$$u^{(1)}(\omega) = \frac{F_1}{i\hbar M}\int_0^\infty dt\, e^{i\omega t}\langle[\hat{X}, \hat{P}(t)]\rangle , \qquad \text{(A27)}$$

where $\langle \cdots \rangle$ means $\mathrm{Tr}(e^{-\beta\hat{H}} \cdots)/\mathrm{Tr}(e^{-\beta\hat{H}})$, the bracket $[\ ,\ ]$ indicates a commutator and $\hat{P}(t) = e^{i\hat{H}t/\hbar}\hat{P}e^{-i\hat{H}t/\hbar}$.

Equation (A27) gives a "microscopic" expression for the spatial average mobility of the Brownian particle

$$\mu(\omega) = \frac{u^{(1)}(\omega)}{F_1} = \frac{1}{i\hbar M}\int_0^\infty dt\, e^{i\omega t}\langle[\hat{X}, \hat{P}(t)]\rangle . \qquad \text{(A28)}$$

If we introduce the quantum-mechanical analog $\varphi^{Q.M.}(\omega)$ of the function $\varphi(\omega)$ defined in Eq. (A18), by writing

$$M\mu(\omega) = -1/i\omega + \varphi^{Q.M.}(\omega)/\omega^2 , \qquad \text{(A29)}$$

we find, after two integrations by parts of Eq. (A28) in which we neglect the end point corrections at $t = +\infty$ (this is justified, for example, if we suppose adiabatic switching of the external force),

$$\varphi^{Q.M.}(\omega) = \int_0^\infty dt\, e^{i\omega t}\frac{d^2\chi(t)}{dt^2} , \qquad \text{(A30)}$$

where

$$\chi(t) = (i/\hbar)\langle[\hat{X}, \hat{P}(t)]\rangle , \qquad \text{(A31)}$$

so that

$$\frac{d^2\chi}{dt^2} = \frac{i}{\hbar}\left\langle\left[\frac{\hat{P}}{M}, M\Omega^2\hat{X}(t) + \frac{\partial V}{\partial \hat{X}}(t)\right]\right\rangle . \qquad \text{(A32)}$$

If we now rework the right-hand side of this equation using the identity[13]

$$[e^{-\beta\hat{H}}, \hat{0}] = \int_0^\beta d\lambda\, e^{-\beta\hat{H}}\, e^{\lambda\hat{H}}[\hat{O}, \hat{H}]\, e^{-\lambda\hat{H}} \qquad \text{(A33)}$$

(where $\hat{O}$ is a generic operator), and substitute into Eq. (A30), we obtain

$$\varphi^{Q.M.}(\omega) = \frac{1}{Mk_B T}\int_0^\infty dt\, e^{i\omega t}\langle\hat{F}_t\,;\, \hat{F}_t(t)\rangle , \qquad \text{(A34)}$$

where we have introduced here the canonical correlation[10] between two operators $\hat{A}$ and $\hat{B}$, defined as

$$\langle\hat{A}\,;\,\hat{B}\rangle = \int_0^\beta \frac{d\lambda}{\beta}\langle e^{\lambda\hat{H}}\hat{A}e^{-\lambda\hat{H}}\hat{B}\rangle \qquad \text{(A35)}$$

and

$$\hat{F}_t = -M\Omega^2\hat{X}(t) + \hat{f}(\hat{X}, \{\hat{x}_i\}) \qquad \text{(A36)}$$

is the operator for the total force on the Brownian particle; note that $\hat{f} = -\partial V/\partial\hat{X}$ is the part of this force produced by the bath. We note now that, in order for the mobility given by Eq. (A28) to be equal to the expression (A9) from the Fokker-Planck equation, $\varphi^{Q.M.}(\omega)$ as defined in Eq. (A29) and given by Eq. (A34), must be equal to $\varphi(\omega)$ defined in Eq. (A19) and given by Eq. (A19) or (A20); therefore comparison of Eq. (A34) with Eq. (A19) shows that the classical force-force correlation function has to be interpreted as a quantum canonical correlation function; a suitable choice of $\eta(\omega)$ makes in fact the two equal. The last step of our procedure consists in expanding $\varphi^{Q.M.}(\omega)$ given by Eq. (A30) in a Taylor series around $\omega = 0$; comparison with Eq. (A21) will provide expressions for ω_0, η_0 in terms of microscopic quantities. From Eq. (A30) we obtain $\varphi(\omega = 0) = 0$, and

$$\left.\frac{\partial^n\varphi^{Q.M.}}{\partial\omega^n}\right|_{\omega=0} = -ni^n\int_0^\infty dt\, t^{n-1}\frac{d\chi(t)}{dt}, \quad n \geq 1 \qquad \text{(A37)}$$

so that[34]

$$\left.\frac{\partial \varphi^{\text{Q.M.}}}{\partial \omega}\right|_{\omega=0} = i\chi(0) = -i, \tag{A38}$$

$$\left.\frac{\partial^2 \varphi^{\text{Q.M.}}}{\partial \omega^2}\right|_{\omega=0} = 2\int_0^\infty dt\, t\frac{d\chi(t)}{dt} = -2\int_0^\infty dt\,\chi(t)$$

$$= -\frac{2iM}{\hbar}\int_0^\infty dt \frac{d}{dt}\langle[\hat{X}, \hat{X}(t)]\rangle = 0. \tag{A39}$$

From this we see that the first two coefficients of the Taylor expansion of $\varphi(\omega)$ are in agreement with Eq. (A21). To find the next two coefficients we proceed as follows:

$$\left.\frac{\partial^3 \varphi^{\text{Q.M.}}}{\partial \omega^3}\right|_{\omega=0} = 3i\int_0^\infty dt\, t^2 \frac{d\chi(t)}{dt}$$

$$= -\frac{6M}{\hbar}\int_0^\infty dt\,\langle[\hat{X}, \hat{X}(t)]\rangle . \tag{A40}$$

Comparison with Eq. (A21) gives

$$\frac{1}{\omega_0^2} = -\frac{iM}{\hbar}\int_0^\infty dt\langle[\hat{X}, \hat{X}(t)]\rangle . \tag{A41}$$

Noting that

$$\frac{i}{\hbar}\langle[\hat{X}, \hat{X}(t)]\rangle = \beta\frac{d}{dt}\langle X; \hat{X}(t)\rangle , \tag{A42}$$

we obtain, from Eq. (A41),

$$\omega_0^2 = (kT/M)1/\langle X; \hat{X}\rangle . \tag{A43}$$

Note that ω_0^2, and not Ω^2, appears in the left-hand side of this "equipartition law"; Eq. (A43) should be compared with the similar result

$$\langle \hat{P}; \hat{P}\rangle = MkT \tag{A44}$$

already proved by Kubo[10] for a "free" Brownian particle, and still valid here.

Since we would like to compare ω_0 with Ω, we prefer to rewrite the compact result of Eq. (A43) in a different way. Noting that

$$\frac{d\hat{P}(t)}{dt} = -M\Omega^2\hat{X}(t) + \hat{f}(t) \tag{A45}$$

from which

$$\hat{X}(t) = -\frac{1}{M\Omega^2}\left(\frac{d\hat{P}(t)}{dt} - \hat{f}(t)\right) , \tag{A46}$$

we obtain, from Eq. (A41),

$$\frac{1}{\omega_0^2} = \frac{1}{\Omega^2} - \frac{i}{\hbar}\frac{1}{\Omega^2}\int_0^\infty dt\,\langle[\hat{X}, \hat{f}(t)]\rangle . \tag{A47}$$

On the other hand, using again Eq. (A46), we have

$$\int_0^\infty dt\,\langle[\hat{X}, \hat{f}(t)]\rangle$$

$$= \frac{1}{M\Omega^2}\left(\int_0^\infty dt\frac{d}{dt}\langle[\hat{P}, \hat{f}(t)]\rangle + \int_0^\infty dt\,\langle[\hat{f}, \hat{f}(t)]\rangle\right), \tag{A48}$$

so that Eq. (A47) becomes

$$\frac{1}{\omega_0^2} = \frac{1}{\Omega^2}\left(1 + \frac{1}{M\Omega^2}\left\langle\frac{\partial \hat{f}}{\partial \hat{X}}\right\rangle - \frac{i}{\hbar}\frac{1}{M\Omega^2}\int_0^\infty dt\,\langle[\hat{f}, \hat{f}(t)]\rangle\right). \tag{A49}$$

If we finally note that

$$\frac{i}{\hbar}\langle[\hat{f}, \hat{f}(t)]\rangle = \beta\frac{d}{dt}\langle\hat{f}; \hat{f}(t)\rangle , \tag{A50}$$

we obtain, from Eq. (A49),

$$\omega_0^2 = \Omega^2\Big/\left(1 + \frac{1}{M\Omega^2}\left\langle\frac{\partial \hat{f}}{\partial \hat{X}}\right\rangle + \frac{1}{\Omega^2 Mk_BT}\langle\hat{f}; \hat{f}\rangle\right) . \tag{A51}$$

Note that if $\langle\partial\hat{f}/\partial\hat{X}\rangle = 0$ one has $\omega_0^2 \le \Omega^2$, since $\langle\hat{f}; \hat{f}\rangle \ge 0$ (the canonical autocorrelation of an Hermitian operator being positive). In the general case we can note that the denominator in the right-hand side of Eq. (A51) is always positive, because of Eq. (A43). For calculating the friction we need to go to the next order,

$$\frac{1}{4!}\left.\frac{\partial^4 \varphi}{\partial \omega^4}\right|_{\omega=0} = -\frac{1}{4!}\times 4\int_0^\infty dt\, t^3\frac{d\chi}{dt}$$

$$= -\frac{Mi}{\hbar}\int_0^\infty dt\, t\langle[\hat{X}, \hat{X}(t)]\rangle , \tag{A52}$$

so that comparison with Eq. (A21) gives

$$\frac{\eta_0}{\omega_0^4} = -\frac{Mi}{\hbar}\int_0^\infty dt\, t\langle[\hat{X}, \hat{X}(t)]\rangle . \tag{A53}$$

On the other hand, using Eq. (A46) we easily find

$$\int_0^\infty dt\, t\langle[\hat{X}, \hat{X}(t)]\rangle = \frac{1}{M\Omega^2}\int_0^\infty dt\, t\langle[\hat{X}, \hat{f}(t)]\rangle \tag{A54}$$

and

$$\int_0^\infty dt\, t\langle[\hat{X}, \hat{f}(t)]\rangle = \frac{1}{M\Omega^2}\int_0^\infty dt\, t\langle[\hat{f}, \hat{f}(t)]\rangle , \tag{A55}$$

since $[\hat{X}, \hat{f}(t=0)] = 0$, so that Eq. (A53) becomes

$$\frac{\eta_0}{\omega_0^4} = -\frac{i}{\hbar}\frac{1}{M\Omega^4}\int_0^\infty dt\, t\langle[\hat{f}, \hat{f}(t)]\rangle . \tag{A56}$$

Using Eq. (A50) this gives

$$\frac{\eta_0}{\omega_0^4} = \frac{1}{\Omega^4}\frac{1}{Mk_BT}\int_0^\infty dt\langle\hat{f}; \hat{f}(t)\rangle . \tag{A57}$$

Setting

$$\gamma(t) = (1/Mk_BT)\langle\hat{f}; \hat{f}(t)\rangle \tag{A58}$$

and using Eq. (A51) again, we finally obtain

$$\eta_0 = \int_0^\infty dt\,\gamma(t)\Big/\left(1 + \frac{1}{\Omega^2}\gamma(0) + \frac{1}{M\Omega^2}\left\langle\frac{\partial \hat{f}}{\partial \hat{X}}\right\rangle\right)^2 , \tag{A59}$$

together with

$$\omega_0^2 = \Omega^2\Big/\left(1 + \frac{1}{\Omega^2}\gamma(0) + \frac{1}{M\Omega^2}\left\langle\frac{\partial \hat{f}}{\partial \hat{X}}\right\rangle\right) . \tag{A60}$$

As a final remark, we like to point out a close relation between the friction η_0 and the scattering rate of the bath particles in presence of a spatially random array of oscillators, each with frequency

Ω, and coupled to the bath as in (A23). More specifically, if we suppose that the bath particles are electrons, and if we write, following a procedure due to Zwanzig,[35] the electrical conductivity of the system in the form

$$\sigma(\omega)=(ne^2/m)[-i\omega+1/\tau(\omega,n_I)]^{-1}\,, \tag{A61}$$

where n is the average electron density and, in the dilute limit,

$$\frac{1}{\tau(\omega,n_I)}=\frac{1}{\tau(\omega)}n_I+O(n_I^2)\,, \tag{A62}$$

n_I being the density of oscillators, we find

$$\begin{aligned}\frac{1}{\tau(\omega=0)}&=\lim_{\omega\to 0}\lim_{n_I\to 0}\frac{1}{n_I}\left(\frac{m\sigma(\omega)}{ne^2}-\frac{i}{\omega}\right)\omega^2\\&=\frac{1}{n}\frac{1}{mkT}\int_0^\infty dt\langle\hat{f};\hat{f}(t)\rangle\,,\end{aligned} \tag{A63}$$

where the last equality can be established by the same arguments used by Götze and Wolfle[36] in their conductivity calculation. We conclude that, at lowest order in n_I,

$$\begin{aligned}\frac{1}{\tau(\omega=0,n_I)}&=\frac{n_I}{n}\frac{M}{m}\frac{1}{MkT}\int_0^\infty dt\langle\hat{f};\hat{f}(t)\rangle\\&=\frac{n_I}{n}\frac{M}{m}\int_0^\infty dt\gamma(t)\end{aligned} \tag{A64}$$

or substituting Eq. (A64) into Eq. (A59),

$$\eta_0=\frac{m}{M}\frac{n}{n_I}\frac{1}{\tau}\left(1+\frac{\gamma(0)}{\Omega^2}+\frac{1}{M\Omega^2}\left\langle\frac{\partial\hat{f}}{\partial\hat{X}}\right\rangle\right)^{-2}. \tag{A65}$$

This result has not the simple form of the one derived in Sec. III C for a dilute concentration of scatterers with no internal degrees of freedom in the adiabatic approximation [i.e., $\eta=(m/M)(n_i/n)1/\tau$], though it is close to it. Note that Eq. (A65) does *not* reduce to this result, even for $m/M\to 0$. This is due to the intrinsic difference between the present model, where the Brownian particle is presumed harmonically bound to some equilibrium position, and the simpler model treated previously where the medium surrounding the Brownian particle had been supposed completely uniform.

APPENDIX B

In this appendix we show that the bootstrap procedure of Sec. II may be extended in a straightforward fashion to treat many adparticles moving in three dimensions. We first consider the case when all the adparticles are distinguishable. The Fokker-Planck equation for such a system is

$$\begin{aligned}&\frac{\partial f}{\partial t}+\sum_{i=1}^{n}\sum_{\alpha=1}^{3}\left(\frac{P_\alpha^i}{M^i}\frac{\partial}{\partial R_\alpha^i}+\langle F_\alpha^i\rangle\frac{\partial}{\partial P_\alpha^i}\right)f\\&\quad=\sum_{\substack{i=1\\j=1}}^{n}\sum_{\substack{\alpha=1\\\beta=1}}^{3}\frac{\partial}{\partial P_\alpha^i}\eta_{\alpha\beta}^{ij}\left(P_\beta^j+M^jk_BT\frac{\partial}{\partial P_\beta^j}\right)f\,,\end{aligned} \tag{B1}$$

where the superscripts distinguish the various particles of which there are n in total and the subscripts denote vector components. Note that the distribution function f here describes all the degrees of freedom of the adparticles. There has been no reduction to variables only along the reaction path. The assumption of (B1) requires no new assumption beyond those for Eq. (2). One might worry that there would now be more stringent requirements on the bath relaxation rate due to the time required for the relative motion of the adparticle to be internally communicated through the bath.[8,29] However, the calculations of Sec. III D indicate that for well separated adparticles, the mutual indirect interaction through the electron gas is essentially negligible.

To find first expressions for the $\langle F_\alpha^i\rangle$ we examine the equilibrium solution of (B1):

$$f_{eq}\sim\exp\left[-\beta\left(\sum_{i=1}^{n}\sum_{\alpha=1}^{3}\frac{1}{2M^i}(P_\alpha^i)^2+V(\{\vec{\mathrm{R}}\})\right)\right]\,, \tag{B2}$$

where $\langle F_\alpha^i\rangle=-\partial V/\partial R_\alpha^i$ and $\{\vec{\mathrm{R}}\}$ denotes the collection of coordinates, $\{\vec{\mathrm{R}}^1,\vec{\mathrm{R}}^2,\ldots,\vec{\mathrm{R}}^n\}$, which describes where each particle is. Now we require that the equilibrium joint density,

$$\rho_{eq}=\int\prod_{k=1}^{n}d\vec{\mathrm{P}}^k f_{eq}\,,$$

computed from (B2) be equal to the exact equilibrium joint density computed from

$$\{\rho\}_{eq}=\mathrm{Tr}\left(e^{-\beta\hat{H}}\prod_{k=1}^{n}\delta(\vec{\mathrm{R}}^k-\hat{R}^k)\right)\Big/\mathrm{Tr}(e^{-\beta\hat{H}})\,.$$

This yields the analogue of Eq. (8),

$$\langle F_\alpha^i\rangle=k_BT\frac{\partial}{\partial R_\alpha^i}\ln\mathrm{Tr}\left(e^{-\beta\hat{H}}\prod_{k=1}^{n}\delta(\vec{\mathrm{R}}^k-\hat{R}^k)\right)\,. \tag{B3}$$

To carry out the bootstrap for η we need to define operators analogous to those of Eqs. (11)–(14). These are

$$\hat{\rho}(\{\vec{\mathrm{R}}\})=\prod_{i=1}^{n}\delta(\vec{\mathrm{R}}^i-\hat{R}^i)=\prod_i\hat{\delta}^i\,, \tag{B4}$$

$$\begin{aligned}\hat{J}_\alpha^i(\{\vec{\mathrm{R}}\})&=\frac{1}{2M^i}(\hat{P}_\alpha^i\hat{\delta}^i+\hat{\delta}^i\hat{P}_\alpha^i)\prod_{k\neq i}\hat{\delta}^k\\&=\hat{j}_\alpha^i\prod_{k\neq i}\hat{\delta}^k\,,\end{aligned} \tag{B5}$$

$$\hat{K}_{\alpha\beta}^{ij}(\{\vec{\mathrm{R}}\})=\tfrac{1}{2}(M^iM^j)^{1/2}\hat{j}_\alpha^i\hat{j}_\beta^j\prod_{k\neq i,j}\hat{\delta}^k\,, \tag{B6}$$

$$\hat{F}_\alpha^i\hat{\rho}=-\frac{\partial\hat{H}}{\partial\hat{R}_\alpha^i}\hat{\rho}\,. \tag{B7}$$

We next require a relation between the linear increments of the traces of these operators when we apply a uniform field in one direction, β, to one of the adparticles, j; i.e.,

$$\hat{V}_1^{(j,\beta)} = -F_1 \hat{R}_\beta^j e^{-i\omega\tau} . \tag{B8}$$

We derive such a relation from the Heisenberg equation of motion of $\hat{J}$. In the notation of (16) the result is

$$-i\omega M^i \{J_\alpha^i\}_1^{(j,\beta)} + 2\sum_{k=1}^{n}\sum_{\gamma=1}^{3} \frac{\partial}{\partial R_\gamma^k} \{K_{\alpha\gamma}^{ik}\}_1^{(j,\beta)} \left(\frac{M^i}{M^k}\right)^{1/2} - \{F_\alpha^i \rho\}_1^{(j,\beta)} - F_1 \delta_{i,j}\delta_{\alpha,\beta}\{\rho\}_{eq} = 0 , \tag{B9}$$

which is the analog of (16). On the other hand, the classical equation corresponding to (10) is obtained by multiplying (B1) by P_α^i and integrating over all momenta:

$$-i\omega M^i (J_\alpha^i)_1^{(j,\beta)} + 2\sum_{k=1}^{n}\sum_{\gamma=1}^{3} \frac{\partial}{\partial R_\gamma^k} (K_{\alpha\gamma}^{ik})_1^{(j,\beta)} \left(\frac{M^i}{M^k}\right)^{1/2} - \langle F_\alpha^i \rangle \times (\rho)_1^{(j,\beta)} - F_1 \delta_{i,j}\delta_{\alpha,\beta}\rho_{eq} = -\sum_{k=1}^{n}\sum_{\gamma=1}^{3} \eta_{\alpha\gamma}^{ik} M^k (J_\gamma^k)_1^{(j,\beta)} , \tag{B10}$$

where

$$(J_\alpha^i)^{(j,\beta)} = \int \prod_{k=1}^{n} d\vec{P}^n P_\alpha^i \frac{1}{M^i} f_1^{(j,\beta)} , \tag{B11}$$

$$(K_{\alpha\gamma}^{ik})_1^{(j,\beta)} = \frac{1}{2}\int \prod_{l=1}^{n} d\vec{P}^l P_\alpha^i P_\gamma^k (M^i M^k)^{-1/2} f_1^{(j,\beta)}, \tag{B12}$$

$$(\rho)_1^{(j,\beta)} = \int \prod_{k=1}^{n} d\vec{P}^k f_1^{(j,\beta)} , \tag{B13}$$

$$\rho_{eq} = \int \prod_{k=1}^{n} d\vec{P}^k f_{eq} , \tag{B14}$$

and $f_1^{(j,\beta)}$ is the linear deviation of f from f_{eq} resulting from the application of $V_1^{(j,\beta)}$. As in Sec. II the bootstrap is effected by equating the various (purely) adparticle responses and then combining Eqs. (B9) and (B10):

$$\sum_{k=1}^{n}\sum_{\gamma=1}^{3} \eta_{\alpha\gamma}^{ik} M^k \{J_\gamma^k\}_1^{(j,\beta)} = -\{F_\alpha^i \rho\}_1^{(j,\beta)} + \langle F_\alpha^i \rangle \{\rho\}_1^{(j,\beta)} . \tag{B15}$$

Thus η is defined by a matrix equation involving the various responses.

Again it is important to show that this result reduces to that of the formal derivations in the limit that all M^k tend to infinity. This limit may be easily worked out if, as before, it is taken before the limit $\omega \to 0$ implicit in (B15). We do not present the intermediate steps since the expressions are notationally clumsy, but merely note that the J response matrix of (B15) becomes diagonal in both particles and components so that the limiting expression for η may be written

$$k_B T M^j \eta_{\alpha\beta}^{ij}(\{\vec{R}\}) = \mathrm{Re}\left\langle \hat{\mathfrak{F}}_\beta^j \int_0^\infty d\tau\, \hat{\mathfrak{F}}_{0\alpha}^i(\tau) \right\rangle_{0,\{\vec{R}\}} , \tag{B16}$$

where $\hat{\mathfrak{F}}_\beta^j = \hat{F}_\beta^j - \langle \hat{F}_\beta^j \rangle_{0,\{\vec{R}\}}$ and the extra subscript notation is defined in Sec. II.

Next we consider the case when all the adparticles ($=n$ in number) are indistinguishable. Formally, our arguments above would still hold, but in the evaluation of (B15) we would be forced to consider Kubo formulas that were not symmetric under permutations of the adparticle identities. To avoid this situation we must reinterpret the many-adparticle Fokker-Planck equation. We now view $f(=f_s)$ as a symmetrized n-fold joint distribution function so that $f_s(\{\vec{R}, \vec{P}\}, t)$ describes the joint distribution in which at time t one adparticle is at $(\vec{R}^{(1)}, \vec{P}^{(1)})$, another at $(\vec{R}^{(2)}, \vec{P}^{(2)})$, and so on up to $(\vec{R}^{(n)}, \vec{P}^{(n)})$. We use here, for example, the notation $\vec{R}^{(j)}$ to denote the value of the jth spatial argument in f_s. The superscript in parentheses serves only to differentiate the various arguments of f_s, not to label particles as before. Corresponding to this reinterpretation we have to make new definitions of the various joint densities. This is most simply illustrated by ρ. We now define the classical joint density by

$$\rho_s(\{\vec{R}\}, t) = \int \prod_{k=1}^{n} d\vec{P}^{(k)} f_s(\{\vec{R}, \vec{P}\}, t) \tag{B17}$$

and the quantum joint density operator by

$$\hat{\rho}_s(\{\vec{R}\}) = \left(\prod_{k=1}^{n} \delta(\vec{R}^{(k)} - \hat{R}^l)\right)_s . \tag{B18}$$

Here $\{\vec{R}\}$ denotes the collection of arguments $\{\vec{R}^{(1)}, \vec{R}^{(2)}, \ldots, \vec{R}^{(n)}\}$. The symmetrization symbol s in (B18) is defined by

$$\left(\prod_{k=1}^{n} \delta(\vec{R}^{(k)} - \hat{R}^l)\right)_s = \frac{1}{n!}\sum_{p} \prod_{k=1}^{n} \delta(\vec{R}^{(k)} - \hat{R}^l), \tag{B19}$$

where each $\hat{R}$ operator is to appear once and only once in each n-fold product on the right-hand side and the summation is over all permutations of the operator labels. To illustrate, for two indistinguishable adparticles,

$$\prod_{k=1}^{2} \delta(\vec{R}^{(k)} - \vec{R}^l)_s = \tfrac{1}{2}[\delta(\vec{R}^{(1)} - \hat{R}^1)\delta(\vec{R}^{(2)} - \hat{R}^2) + \delta(\vec{R}^{(1)} - \hat{R}^2)\delta(\vec{R}^{(2)} - \hat{R}^1)]. \tag{B20}$$

We may similarly proceed to define symmetrized versions of the other joint densities, both classical and quantum. The only formal distinction from the previous treatment is that all latin superscripts on the left-hand sides of Eqs. (B4)–(B7) and (B11)–(B14) acquire an enclosing set of parentheses to signify that these labels refer only to arguments rather than particles and the right-hand sides are symmetrized as in (B17) or (B18).

We can now carry through the bootstrap for $\langle F_\alpha^{(i)} \rangle$, the systematic force in the direction α on an adparticle at $\vec{R}^{(i)}$:

$$\langle F_\alpha^{(i)} \rangle = k_B T \frac{\partial}{\partial R_\alpha^{(i)}} \ln \mathrm{Tr}[e^{-\beta\hat{H}} \hat{\rho}_s(\{\vec{R}\})] . \tag{B21}$$

To determine η we need to change the applied perturbation from (B8). Before we applied a uni-

form field to a particular particle; now we apply a locally uniform field to any (indistinguishable) adparticle in a certain location. Thus

$$\hat{V}_{1,s}^{(j,\beta)} = -F_1 \sum_{i=1}^{n} \hat{R}_\beta^i g(\vec{\mathrm{R}}^{(j)} - \hat{R}^i) e^{-i\omega t} , \qquad \text{(B22)}$$

where $g(\vec{r})$ is a "gate" function: It equals unity for $|\vec{r}| \ll d$ and vanishes for $|\vec{r}| > d$, where d is a distance smaller than the typical interadparticle separation. The argument $\vec{\mathrm{R}}^{(j)}$ will be chosen equal successively to those in the joint densities. With (B22) the bootstrap procedure can again be carried through, we only note the final result

$$\sum_{k=1}^{n} \sum_{\gamma=1}^{3} M \eta_{\alpha\gamma}^{(i)(k)} \{J_\gamma^{(k)}\}_{1,s}^{((j),\beta)} = -\{F_\alpha^{(i)} \rho\}_{1,s}^{((j),\beta)} + \langle F_\alpha^{(i)} \rangle (\bar{\rho})_{1,s}^{((j),\beta)} , \qquad \text{(B23)}$$

where now all the responses require only symmetrized operators. In the limit $M \to \infty$ this reduces to

$$k_B T M \eta_{\alpha\beta}^{(i)(j)}(\{\vec{\mathrm{R}}\}) = \mathrm{Re} \left\langle \hat{\mathfrak{F}}_\beta^j \int_0^\infty d\tau \, \hat{\mathfrak{F}}_{0\alpha}^i(\tau) \right\rangle_{0,\{\vec{\mathrm{R}}\}} , \qquad \text{(B24)}$$

with $\hat{\mathfrak{F}}_\beta^j$ defined as below (B16).

APPENDIX C

We present here more of the detailed analysis of the two-particle phase-shift model. Since the multiple-scattering theory that we use has been extensively discussed elsewhere,[37-39,21] we shall only briefly record the specific formulas relevant to our simple model.

The problem we study is that of two-muffin-tin potentials separated by a distance r in an otherwise homogeneous noninteracting electron gas. The radius of the two tins is $R_{\mathrm{M.T.}}$ and only the s-wave phase shift δ is not zero. For simplicity we chose the $\hat{z}$ axis along the separation vector of the two muffin tins. The advantage of using muffin tin potentials is that one can then reduce the multiple scattering equations from integral form to matrix form in a site-angular momentum space. For the friction we need to compute $\langle \vec{r} | G^+ | \vec{r}' \rangle$ for either both $\vec{r}$, $\vec{r}'$ in the same muffin tin or each in a different muffin tin. The general formulas are

$$\langle \vec{r} | G^+ | \vec{r}' \rangle = \sum_{L_1,L_2} (4\pi)^{1/2} Y_{L_1}^*(\hat{r}) (i)^{l_1} \times [\ ]_{L_1,L_2} (4\pi)^{1/2} Y_{L_2}(\hat{r}') (-i)^{l_2} , \qquad \text{(C1)}$$

with

$$[\ ]_{L_1,L_2} = -\delta_{L_1,L_2} \frac{mk}{2\pi\hbar^2} R_{l_1}(r_<)[N_{l_1}(r_>) + iR_{l_1}(r_>)] + e^{i\delta l_1} R_{l_1}(r) \sum_{\substack{L',L \\ \beta,\gamma}} C_{L_1\mu,L'\beta} \mathcal{T}_{L'\beta,L\gamma}^{(\mu,\mu)} C_{L\gamma,L_2\mu} e^{i\delta l_2} R_{l_2}(r') \qquad \text{(C2)}$$

for $\vec{r}$, $\vec{r}'$ both in muffin-tin μ and

$$[\ ]_{L_1,L_2} = e^{i\delta l_1} R_{l_1}(r) \left(C_{L_1\mu,L_2\nu} + \sum_{\substack{L',L \\ \beta,\gamma}} C_{L_1\mu,L'\beta} \mathcal{T}_{L'\beta,L\gamma}^{(\mu,\nu)} C_{L\gamma,L_2\nu} \right) e^{i\delta l_2} R_{l_2}(r') \qquad \text{(C3)}$$

for $\vec{r}$ in muffin-tin μ and $\vec{r}'$ in muffin-tin ν, $\mu \neq \nu$. The Y_L are spherical harmonic functions[40]; L $(= l, m)$ is a general index denoting both the orbital quantum number l and the magnetic quantum number m. The function R_l is a solution of the l wave Schrödinger equation for an isolated muffin-tin potential at energy E $(= \hbar^2 k^2/2m)$ which is a regular at the origin and outside the muffin-tin varies as

$$R_l(r) = j_l(kr) \cos\delta_l + \eta_l(kr) \sin\delta_l , \quad r > R_{\mathrm{M.T.}} , \qquad \text{(C4)}$$

thereby defining the phase shift δ_l. The function $N_l(r)$ is the other linearly independent solution of the l wave Schrödinger equation at E; outside the muffin-tin potential it is defined by the variation

$$N_l(r) = \eta_l(kr) \cos\delta_l - j_l(kr) \sin\delta_l , \quad r > R_{\mathrm{M.T.}} . \qquad \text{(C5)}$$

The n_l and j_l are spherical Bessel functions.[41] The multiple-scattering aspect of G^+ is contained in the $\mathcal{T}$ functions:

$$\mathcal{T}_{L'\beta,L\gamma}^{(\mu,\nu)} = \{t_l \delta_{\beta,\gamma} \delta_{L',L} + t_{l'} [C/(1 - tC)]_{L'\beta,L\gamma} t_l\} \times (1 - \delta_{\beta,\mu})(1 - \delta_{\gamma,\nu}) , \qquad \text{(C6)}$$

where the Greek indices label the muffin-tin potentials and

$$C_{L'\alpha,L\beta} = -\frac{mk}{2\pi\hbar^2} \sum_{L_3} 4\pi (i)^{l_3} Y_{L_3}^* \left(\frac{\vec{\mathrm{R}}_\alpha - \vec{\mathrm{R}}_\beta}{|\vec{\mathrm{R}}_\alpha - \vec{\mathrm{R}}_\beta|} \right) \times h_{l_3}^+(k|\vec{\mathrm{R}}_\alpha - \vec{\mathrm{R}}_\beta|) \int d^2\hat{k} \, Y_{L_3}(\hat{k}) Y_{L'}(\hat{k}) Y_L^*(\hat{k}) , \qquad \text{(C7)}$$

$$t_l = -(2\pi\hbar^2/mk) e^{i\delta l} \sin\delta_l . \qquad \text{(C8)}$$

The integration in (C7) is over the direction of $\vec{k}$ and $h_l^+ = n_l + ij_l$.

For our model these equations simplify considerably. For instance, the $\mathcal{T}$ are given by

$$\mathcal{T}_{L'\beta,L\gamma}^{(\mu,\mu)} = (-2\pi\hbar^2/mk) \delta_{L',0} \delta_{L,0} (1 - \delta_{\beta,\mu}) \times (1 - \delta_{\gamma,\mu}) e^{i\delta} \sin\delta D \qquad \text{(C9)}$$

and

$$\mathcal{T}^{(\mu,\nu)}_{L'\beta,L\gamma} = (-2\pi\hbar^2/mk)\delta_{L',0}\delta_{L,0}(1-\delta_{\beta,\mu}) \times(1-\delta_{\gamma,\nu})e^{2i\delta}\sin^2\delta h_0^+(kr)D\,, \tag{C10}$$

where D is the factor of Eq. (68),

$$D=[1-e^{2i\delta}\sin^2\delta h_0^{+2}(kr)]^{-1}\,. \tag{C11}$$

Making use of the relations $Y_{lm}(\hat{z})=0$ for $m\neq 0$,[40] and

$$\int_0^{R_{\mathrm{M.T.}}} r^2 dr\, R_l(r)\frac{dv}{dr}R_{l+1}(r) = \frac{\hbar^2}{2m}\sin(\delta_l-\delta_{l+1}) = \left(\frac{\hbar^2}{2m}\sin\delta\right)\delta_{l,0}\,, \tag{C12}$$

where v is the muffin-tin potential,[42] greatly reduces the number of C's [Eq. (C7)], that we need to compute. Our final formula for the friction is

$$\underline{\eta}^{\mu\nu}=\frac{8}{\pi}\frac{m}{M}\frac{E_F}{\hbar}\underline{N}^{\mu\nu}\sin^2\delta\,, \tag{C13}$$

where

$$N^{\mu\mu}_{zz}=[1+\mathrm{Im}(e^{3i\delta}\sin\delta h_0^{+2}D)] \times[\tfrac{1}{3}+\mathrm{Im}(e^{i\delta}\sin\delta h_1^{+2}D)]+[\mathrm{Im}(e^{2i\delta}\sin\delta h_0^+h_1^+D)]^2\,, \tag{C14}$$

$$N^{\mu\nu}_{zz}=[\mathrm{Im}(e^{2i\delta}h_0^+D)][\mathrm{Im}(\tfrac{1}{3}h_0^+-\tfrac{2}{3}h_2^+ - e^{2i\delta}\sin^2\delta h_0^+h_1^{+2}D)]-[\mathrm{Im}(e^{i\delta}h_1^+D)]^2\,,\quad \mu\neq\nu\,, \tag{C15}$$

$$N^{\mu\mu}_{xx}=\tfrac{1}{3}[1+\mathrm{Im}(e^{3i\delta}\sin\delta h_0^{+2}D)]\,, \tag{C16}$$

$$N^{\mu\nu}_{xx}=\tfrac{1}{3}[\mathrm{Im}(h_0^++h_2^+)][\mathrm{Im}(e^{2i\delta}h_0^+D)]\,,\quad \mu\neq\nu\,. \tag{C17}$$

The argument of all the h's is k_Fr, and the y and x (transverse) components are equal.

From the form of (C13) we see how to define a perturbative estimate of η: We need merely set $\delta=0$ in computing the N's. We find then

$$N^{\mu\mu}_{zz}=N^{\mu\mu}_{xx}=\tfrac{1}{3}\ \text{for all } r\,, \tag{C18}$$

which agrees with the single muffin-tin result, Eq. (57). The results for the cross friction terms are more complicated in this limit:

$$N^{\mu\nu}_{zz}=\tfrac{1}{3}\mathrm{Im}(h_0^+)\,\mathrm{Im}(h_0^+-2h_2^+)-[\mathrm{Im}(h_1^{+2})]^2\,, \tag{C19}$$

$$N^{\mu\nu}_{xx}=\tfrac{1}{3}\mathrm{Im}(h_0^+)\,\mathrm{Im}(h_0^++h_2^+)\,, \tag{C20}$$

but both of these expressions reduce to $\frac{1}{3}$ so r goes to zero. This perturbative limit of (C18) to (C12) is in strong contrast to the exact result, obtained by expanding (C14) to (C17) as $r\to 0$,

$$N^{\mu\mu}_{zz}(r\to 0)=N^{\mu\nu}_{zz}(r\to 0)=2/\sin^2\delta\,, \tag{C21}$$

$$N^{\mu\mu}_{xx}(r\to 0)=N^{\mu\nu}_{xx}(r\to 0)=\tfrac{1}{3}(k_Fr)^2/\sin^2\delta\,, \tag{C22}$$

which illustrates the possibly strong difference between perturbative and exact results. Note that in the artificial limit $r\to 0$, only N^{rel}_{zz} remains finite. This feature is a consequence of the resonant scattering between the two potentials which, by producing bound states, effectively reduces the scattering efficiency of the pair.

Finally, we note that one can easily work out the asymptotic forms of the N's for r tending to infinity. As expected $N^{\mu\mu}$ tends to a constant while $N^{\mu\nu}$, $\mu\neq\nu$, decays to zero. A different sort of Friedel oscillation occurs for each component.

Let us now turn to the binding energy calculation. The formula for the density of states in a muffin-tin model has been derived previously[37] and has recently formed the basis of several cluster calculations.[43,44] For our model the form it takes is

$$\Delta\rho_r(E)=-\frac{d}{dE}\frac{\mathrm{Im}}{\pi}\ln\left(1-\frac{\tan^2\delta h_0^{+2}(kr)}{(1-i\tan\delta)^2}\right)\,,\quad E=\frac{\hbar^2k^2}{2m}\,, \tag{C23}$$

which, with use of the scattering length formula (69), becomes

$$\Delta\rho_r(E)=-\frac{d}{dE}\frac{\mathrm{Im}}{\pi}\ln\left(1-\frac{a^2e^{2ikr}/r^2}{(1+ika)^2}\right)\,. \tag{C24}$$

We have written (C24) for $E>0$. When $E<0$, one replaces k with $i\kappa$, $E=-\hbar^2\kappa^2/2m$. Since the argument of the logarithm then becomes a real number, we obtain a finite density of states only at the vanishing of the argument, which defines the bound states.

APPENDIX D

Here we examine the friction that results from a phonon model of the interaction between an adparticle and the substrate. The specific treatment we examine is that developed by Pagni and Keck[45] (PK). They use a "soft-cube" model[46] to describe the dynamic interaction between an adparticle of mass m_g and the surface, which is represented by a single particle of mass m_s coupled to a stationary background by a spring with constant k_s. The interaction between adparticle and the surface particle is a one dimensional harmonic repulsion with spring constant k_g, which is operative only for separations less than a critical amount, say, the point A of Fig. 1. The fundamental quantity of their theory is the one way equilibrium transition kernel, $R(E, E')$, which describes the transition rate between an adparticle state of energy E to one of E', averaged over an equilibrium distribution of the substrate degrees of freedom. The energies here are measured from the bottom of the binding potential well (Born-Oppenheimer ground state, say) of the adparticle. One calculates $R(E, E')$ by first assuming particular values for the amplitude and phase of the surface particle oscillation before the adparticle with energy E collides with the repulsive spring k_g; then following exactly the motion of the adparticle while it is in contact with k_g until it first separates, with a final energy E' and a velocity directed away from the surface; and finally averaging

the result over an equilibrium distribution of the surface particle amplitude and phase with an appropriate flux factor to represent the frequency of such collisions. Once the kernel R is determined, one has an explicit kinetic master equation for the adparticle energy distribution. In the limit that the energy transfer of each collision is small, the master equation can be approximated as a diffusion equation wherein only a single parameter Δ_2 appears. This is the mean-square energy transfer defined by

$$\Delta_2(E) = \int_{-\infty}^{\infty} (E - E')^2 R(E, E')\, dE' \ . \tag{D1}$$

It is at this point that we can make contact with our work. The form of the diffusion equation is identical to that of the Fokker-Planck equation in energy space. Hence we can make the identification of η as

$$\eta = \Delta_2(E)/2(k_B T) E N_e(E) \tag{D2}$$

in the notation of PK. The quantity $N_e(E)$ is the thermal equilibrium distribution function of the adparticle in energy space. From (D2) we see that to obtain a phonon estimate of η, we need only to calculate Δ_2 for an appropriate choice of the parameters m_g, m_s, k_s, k_g. Although PK have performed extensive calculations of Δ_2,[45,47] they did not consider the limit we have in mind. Our typical system is hydrogen atoms on tungsten, which is characterized by $k_s/k_g \sim 1$ but $m_g/m_s \ll 1$. Fortunately, in this limit one can easily calculate Δ_2 by using a perturbation expansion in m_g/m_s of the collision dynamics. In the lowest nonvanishing order, the result is independent of the value of k_s/k_g. We find

$$\eta^P = 8 \frac{\omega_g}{2\pi} \left(\frac{m_g}{m_s}\right) \left[1 + O\left(\frac{m_g}{m_s}\right) + \cdots\right] \ , \tag{D3}$$

where $\omega_g = (k_g/m_g)^{1/2}$ and we used a superscript P to denote that (D3) is a phonon estimate of η. Recall that all the models of Sec. III gave as electron estimate of η

$$\eta^e \sim (m/m_g) E_F/\hbar \ . \tag{D4}$$

Reasonable estimates of (D3) and (D4) show that η^e and η^P are of comparable magnitude. Of course particular resonance conditions could render one or the other dominant.

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$$\left.\frac{\partial^2\varphi}{\partial\omega^2}\right|_{\omega=0} = -2\int_0^\infty dt\, e^{-st}\left(\frac{i}{\hbar}\right)\langle[\hat{X},\hat{P}(t)]\rangle$$

$$= -\frac{2iM}{\hbar}\int_0^\infty dt\, e^{-st}\,\frac{d}{dt}\,\langle[\hat{X},\hat{X}(t)]\rangle$$

$$= -\frac{2iM}{\hbar}\,e^{-st}\,\langle[\hat{X},\hat{X}(t)]\rangle\Big|_0^\infty$$

$$-\frac{2iM}{\hbar}\,s\int_0^\infty dt\, e^{-st}\,\langle[\hat{X},\hat{X}(t)]\rangle.$$

The first term is still zero, but the second is not zero for a "free" Brownian particle, for which $\langle[\hat{X},\hat{X}(t)]\rangle \to$ const., when $t\to\infty$, so that $\lim_{s\to 0} s\int_0^\infty dt\, e^{-st}\langle[\hat{X},\hat{X}(t)]\rangle$ is finite. On the other hand, if $\hat{X}(t)$ is "bounded," $\langle[X,X(t)]\rangle$ becomes an oscillatory decaying function of time as $t\to\infty$, so that $\lim_{s\to 0} s\int_0^\infty dt\, e^{-st}\langle[\hat{X},\hat{X}(t)]\rangle = 0$. This is in agreement with Eq. (A22); so, for a "free" Brownian particle we have $1/\eta_0 = -(i/\hbar)M\lim_{s\to 0^+} s\int_0^\infty dt\, e^{-st}\,\langle[\hat{X},\hat{X}(t)]\rangle$, which is easily found to be equal to $(1/Mk_BT)\lim_{s\to 0+}\int_0^\infty dt\, e^{-st}\langle\hat{X},\hat{X}(t)\rangle$ as previously shown by Kubo (Ref. 10).
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