Brownian Motion and Chemical Dynamics on Solid Surfaces

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The complexity of chemical forces makes the theory of even the simplest chemical processes elaborate. Indeed, a full quantum calculation of the gas-phase exchange reaction $H + H_2 \rightarrow H_2 + H$ has only recently been achieved.[1,2] Most chemical reactions are, of course, much more complex than hydrogen exchange, and, moreover, occur in condensed phases, i.e., in solution or on solids.

The theory of even simple nonchemical phenomena in condensed phase is, however, far from easy. For example, Onsager's 40-year-old theories of the dielectric constant of a polar fluid and the conductivity of a salt solution have not yet been superseded! The difficulties, of course, arise because condensed-phase systems are composed of many interacting molecules and thus present an imposing many-body problem to the theorist. A dynamical theory of chemical phenomena in condensed phases must deal with the many-body problem, the traditional domain of statistical mechanics, and *simultaneously* with the difficulties arising from specific chemical interactions, the traditional domain of theoretical chemical dynamics. Both many-body and chemical aspects of the problem are essential. Any theory which deals unrealistically with either aspect will fail to properly describe key phenomena. Two classes of theories often employed to study gas/solid surface dynamics, cluster models[3] and perturbation theories, illustrate this point. The cluster models replace the many-body solid by one or a few representative atoms. These models thus predict residence times, τ_R, on solid surfaces to be comparable to an atom vibration period; i.e., $\tau_R \lesssim 1$ ps. Physical residence times on cold solids, however, can be greater than 1 s due to a many-body effect, gas molecule energy dissipation into the lattice.[4] Perturbation methods, unlike the cluster models, are in principal adequate to treat many-body aspects of the problem. They cannot deal adequately, however, with the harsh forces typical of chemical interaction. The pioneering work of the Lennard-Jones school on gas/solid dynamics, while a remarkable tour de force, points up the limitation of the perturbation approach. The Lennard-Jones per-

turbation calculations predict that the fundamentally important sticking probability of a gas molecule on a solid surface *increases* with solid temperature. This result contradicts both intuition and experiment! Thus it is clear that any realistic treatment of chemical phenomena in condensed phases must involve a fully democratic marriage of statistical and chemical dynamical theory.

For the problem of chemistry in liquid solutions, this marriage has not yet been accomplished. For chemistry on solid surfaces,[5] however, significant progress has been made. New techniques based on a fusion of gas-phase collision methodology with ideas borrowed from modern nonequilibrium statistical mechanics, in particular the theory of generalized Brownian motion, are now available.[6] The new methods are yielding valuable results about elementary gas/solid energy-transfer processes. Furthermore, these methods have opened the way to studies of such basic surface processes as adsorption/desorption, diffusion, and heterogeneous chemical reactions.

The physical fact underlying the new approach is that the gas molecules whose dynamics are of interest interact strongly (i.e., through the short-range repulsive part of the gas/solid potential) with only a few solid surface atoms at any given time. This is illustrated schematically in Figure 1 for the simplest case of a single impinging gas atom colliding with a single surface atom. We call the gas molecule and the few surface atoms with which they strongly interact the primary zone particles (see Figure 1). We call the remainder of the solid the heat bath.

The new approach is based on the following three ideas:

(1) The specific chemical processes are intrinsically complex and must be dealt with in detail. Primary zone dynamics, in other words, must be treated at the same level of detail as a gas-phase collision problem. This usually implies a full computer simulation of the primary zone dynamics; such a simulation is feasible since

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(1) G. Schatz and A. Kupperman, *J. Chem. Phys.*, **65**, 4668 (1976).

(2) A. B. Elkowitz and R. E. Wyatt, *J. Chem. Phys.*, **62**, 2504 (1975).

(3) See, for example, R. M. Logan and J. C. Keck, *J. Chem. Phys.*, **49**, 680 (1968); J. Lorenzen and L. M. Raff, *ibid.*, **49**, 1165 (1968); J. D. McClure, *ibid.*, **57**, 2810 (1972).
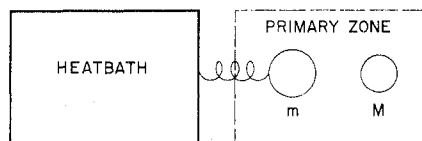
(4) Diffusion-controlled reactions can, of course, be treated, but for these cases chemical dynamics is unimportant.

(5) For a recent review of gas-surface/solid-surface theories and experiments, see W. H. Weinberg, *Adv. Colloid Interface Sci.*, **4**, 301 (1975).

(6) S. A. Adelman and J. D. Doll, *J. Chem. Phys.*, **61**, 4242 (1974); **64**, 2375 (1976); J. D. Doll, L. E. Myers, and S. A. Adelman, *ibid.*, **63**, 4908 (1975). For earlier, related work see R. Zwanzig, *ibid.*, **32**, 1173 (1960), and F. O. Goodman, *J. Phys. Chem. Solids*, **23**, 1269, 1491 (1962). For an alternative approach to many-body problems in gas/solid dynamics see K. Kitahara, H. Metiu, J. Ross, and R. Silbey, *J. Chem. Phys.*, **65**, 2871 (1976).

Figure 1. Shown schematically is the breakdown of the gas/solid system into a primary zone, containing the gas and those lattice atoms with which it strongly interacts, and the remainder of the lattice, which functions as a heat bath for the primary lattice.

the number of primary zone particles is limited.

(2) Heat-bath motion need not be followed in detail since only the *influence* of this motion on the chemical phenomena is observable. Inclusion of this influence is, however, essential; for example, if heat bath influence on adsorption–desorption processes is ignored, computed residence times as mentioned above will often be unphysically short.[7]

(3) The heat-bath influence on the chemical process depends only on rather gross features of the heat-bath's complex dynamics and thus may be simply, but realistically, modeled.[8]

Thus, we solve the many-body problem in gas/solid dynamics by simulating the heat-bath's influence rather than following its detailed motion.

This represents a radical break with traditional chemical dynamical theory. Conventional collisional calculations, whether classical,[9] quantum,[10] or semi-classical,[11] involve computer simulation of the motion of *all* particles in the system. Such methods have thus been limited to small systems; the computer work rapidly increases with the number of particles explicitly treated. The new methods can handle systems with unlimited number of particles because only a few are followed in detail.

We deal here with a classical mechanical formulation of these ideas. Extension to quantum phenomena are given elsewhere.[12] The major quantum effects in atom/solid scattering arise from diffractive interference and solid zero-point motion. We expect these quantum effects will only be important at relatively low solid temperature. Quantum oscillations of the type familiar in gas-phase collisions are obliterated by averaging[13] and thus will be unobservable in gas/solid dynamics.

To implement the above ideas, we transform the original many-body gas/solid classical dynamical equations to effective few-body equations which govern the motion of only the primary zone particles (eq 1). The effective equations of motion involve only the coordinates of the primary zone particles; they include many-body terms, however, which exactly account for the heat-bath influence. The effective few-body equations, being formally exact, are probably no easier to solve exactly than the original many-body problem. Fortunately, the many-body terms in the effective equations may be efficiently modeled. With modeling, numerical solution of the effective equations becomes

comparable in labor to solving a gas-phase collision problem.

The significance of this development is clear. Molecular collision theory has been liberated from the gas phase. We believe that our work represents the infancy of an important new field within chemical dynamics and that new theoretical advances as well as many new applications are possible. Application of our approach to vibrational relaxation of a molecule in a solid, for example, has recently been accomplished.[14] Extension of the approach to liquid-state dynamics appears possible. In the short run, the road is now open to detailed theoretical study of a wide class of fundamental heterogeneous processes.

Langevin Representation

The effective equations of motion for the primary zone particles are similar in form to the generalized Langevin equation (GLE) of modern Brownian motion theory.[15] Thus we call our approach the generalized Langevin method. Our GLE may be derived for arbitrary numbers of primary zone particles of arbitrary chemical species coupled to an arbitrary heat bath. It is not even necessary that the primary zone be spatially continuous; i.e., heat-bath atoms may separate noncontiguous primary zone patches. For the simplest case of a single gas atom (mass M and coordinate R) and a single surface atom (mass m and coordinate r) in the primary zone (Figure 1), the GLE of motion is[6] (we suppress vector notation)

$$M\ddot{R}(t) = -\frac{\partial W(r,R)}{\partial R} \tag{1a}$$

$$m\ddot{r}(t) = -\frac{\partial}{\partial r}[V(r) + W(r,R)]$$
$$- \int_0^t m\beta(t-\tau)\dot{r}(\tau)d\tau + R_\beta(t)$$
$$+ \text{transient term} \tag{1b}$$

Note that $W(r,R)$ is the gas/solid potential-energy function and $V(r)$ is the (generally anharmonic) effective potential which binds the primary zone solid atom to the heat bath.

The GLE requires several comments:

(i) The basic assumption in the theory is that the gas/solid potential depends on the *instantaneous* positions of only the primary zone particles [e.g., $W(r,R)$ in eq 1 depends only on the single solid coordinate r]. It may, however, depend on the *equilibrium* positions of an arbitrary number of heat-bath particles. The idea is that the gas atom is only sensitive (on the average) to position fluctuations in the solid atoms with which it interacts strongly. This basic assumption can be made arbitrarily precise by expanding the number of atoms in the primary zone.

(ii) The GLE is derived in the following manner. The trajectories of the heat-bath atoms are found as functionals of the primary zone solid-atom trajectories. The heat-bath trajectories are then used to eliminate heat-bath degrees of freedom from the primary zone classical equations of motion. This elimination may be carried through exactly for harmonic heat baths linearly coupled to the primary zone solid atoms. This is be-

(7) For example, if an Einstein (uncoupled oscillator) solid model is adapted, residence times will be roughly a vibrational period; desorption will occur via dynamics analogous to the motion of two coupled pendulums.

(8) S. A. Adelman and B. J. Garrison, *J. Chem. Phys.*, **65**, 3751 (1976).

(9) For a recent review, see R. N. Porter, *Annu. Rev. Phys. Chem.*, **25**, 317 (1974).

(10) For a recent review, see T. F. George and J. Ross, *Annu. Rev. Phys. Chem.*, **24**, 263 (1973).

(11) For a recent review, see W. H. Miller, *Adv. Chem. Phys.*, **25**, 69 (1974).

(12) S. A. Adelman, *Chem. Phys. Lett.*, **40**, 495 (1976).

(13) See, for example, W. H. Miller, *J. Chem. Phys.*, **54**, 5386 (1971).

(14) J. Tully, private communication.

(15) H. Mori, *Prog. Theoret. Phys.*, **33**, 423 (1965); R. Kubo, *Rep. Prog. Theoret. Phys.*, **29**, 255 (1966).

cause solving for the heat-bath trajectories for this harmonic case amounts to solving a driven harmonic oscillator problem. For the case of anharmonic heat baths, the reaction of the bath to the motion of the primary zone must be treated in the linear response approximation.[16]

(iii) A connection can be made between eq 2.1 for the case that the gas atom is absent [$W(r,R) = 0$] and the phenomenological Langevin equation[17] for a harmonic oscillator of frequency ω undergoing Brownian motion in a solvent. The phenomenological equation is

$$m\ddot{r}(t) = -m\omega^2 r(t) - m\beta\dot{r}(t) + R_B(t) \qquad (2)$$

For the special case that the solid is harmonic and that

$$\beta(t) = 2\beta\delta(t) \qquad (3)$$

[where $\delta(t)$ is the Dirac δ function], eq 1b with $W(r,R) = 0$ and eq 2 are identical.

(iv) Many-body dynamics (heat-bath influence) enters the GLE (eq 1) in two distinct ways: through $R_\beta(t)$ and through the history-dependent (memory) term linear in the heat-bath response function $\beta(t)$. If these terms are artificially suppressed, eq 1 describes atom scattering off a gas-phase anharmonic oscillator.

(v) The memory term accounts for systematic dissipation of primary zone energy into the thermal bath. It thus functions analogously to the friction term in eq 2, which describes viscous damping of the Brownian oscillator energy by the solvent.

There is, however, an important difference between the effects produced by a GLE memory term (eq 1b) and those produced by the viscous term in (2). Since the viscous term involves only the instantaneous oscillator velocity, the frictional term alters the oscillator's response in a manner independent of the frequency of the applied force. Specifically, the Fourier transform of the memory kernel is frequency independent. For disturbances whose characteristic frequency exceeds that of the thermal bath (e.g., a collision whose time scale is short compared with the response time of the background lattice) we can see that the phenomenological model will be inadequate. For such situations the frequency independence associated with the simple viscous term in (2) will not allow the oscillator to respond in a correct (undamped) fashion. Thus, while the phenomenological equation and its associated assumption of instantaneous solvent response may be useful for the classical problem of Brownian motion, it is too crude for gas/solid phenomena (see below).

(vi) $R_\beta(t)$ is an *external* force on the primary zone due to the heat-bath's random thermal motion. Each set of heat-bath initial conditions generates a unique $R_\beta(t)$. Since these initial conditions are not set experimentally (only the solid's temperature, T_s, is subject to the experimentalist's control), the $R_\beta(t)$ influencing a particular dynamical event is known only probabilistically. Thus, we call $R_\beta(t)$ a random force. It is analogous to the stochastic force $R_B(t)$ appearing in the phenomenological Langevin equation (eq 2). This stochastic force describes the chaotic nature of Brownian trajectories and is analogous to the Johnson noise voltage put out by a thermal resistor.

(vii) The dissipative part of the heat-bath influence

(16) S. A. Adelman, manuscript in preparation.
(17) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).

[$\beta(t)$] leads (on the average) to energy flow out of the primary zone; the random part [$R_\beta(t)$] leads to two-way flow between heat bath and primary zone. Thus, the effects of $R_\beta(t)$ and $\beta(t)$ must be in balance if the primary zone and bath are to remain in thermal equilibrium. The quantitative expression of this balance is the fluctuation–dissipation theorem[6,15]

$$\beta(t) = \frac{\langle R_\beta(t)R_\beta(0)\rangle}{3mk_\beta T} \qquad (4)$$

where k_B is Boltzmann's constant, and where $\langle\rangle$ denotes a thermal average.

(viii) All relevant, i.e., statistical, information about $R_\beta(t)$ is contained in its autocorrelation function $\langle R_\beta(t)R_\beta(0)\rangle$ which (eq 4) depends on $\beta(t)$. This demonstrates the important result that *all* many-body information relevant to the chemical phenomena may be compressed into a single response function $\beta(t)$.

This result gives a clean separation between collisional and many-body aspects of gas/solid phenomena. The response function is computed once for a given solid in a statistical mechanical calculation. It may then be repeatedly employed in a variety of dynamical studies based on the GLE (eq 1). Thus, the GLE (eq 1) may be regarded as a "storage device" for many-body information.

For harmonic solids, $\beta(t)$ may be computed if the normal mode spectrum of the solid is known.[6] Standard methods are available for computing such spectra. For anharmonic solids, the analogous spectral information is unavailable. The response function, however, can be "measured" in a molecular dynamics simulation of the anharmonic solid. Thus, while large-scale calculations may be needed to compute the responses, they can be indefinitely "reused" in small-scale Langevin calculations. The contrast with a conventional trajectory study of scattering off a truncated set of coupled oscillators is striking. There the lattice dynamics is, in effect, recomputed during each trajectory.

Dynamical Solid Models

The generalized Langevin theory described above provides a general framework upon which physically motivated and rapidly convergent approximation schemes may be developed. The idea is that, even though the dynamics of the heat bath is complex, its influence on the primary zone is qualitatively simple. The bath merely serves as an energy source and sink for the primary zone.

The Langevin theory allows us to exploit this simplification by modeling the response function $\beta(t)$. This function is qualitatively simple because of the underlying simple nature of the heat-bath effect.

Mathematically, the advantage of modeling $\beta(t)$ is that it permits reduction of the integro-differential GLE to tractable purely differential first-order equations. These may be solved by algorithms employed in conventional classical trajectory calculations.

We plot out $\Theta(t) \equiv -\dot{\beta}(t)$ in Figure 2 for the Debye solid. [Our theory is actually most conveniently formulated in terms of $\Theta(t)$; we have employed $\beta(t)$ here since it facilitates comparison with Brownian motion theory.[17]] Note that $\Theta(t)$ has a pronounced peak at $t \simeq 0.3\tau_D$ [$\tau_D \equiv 2\pi\omega_D^{-1}$, $\omega_D =$ Debye cutoff frequency] and displays damped oscillatory behavior at longer
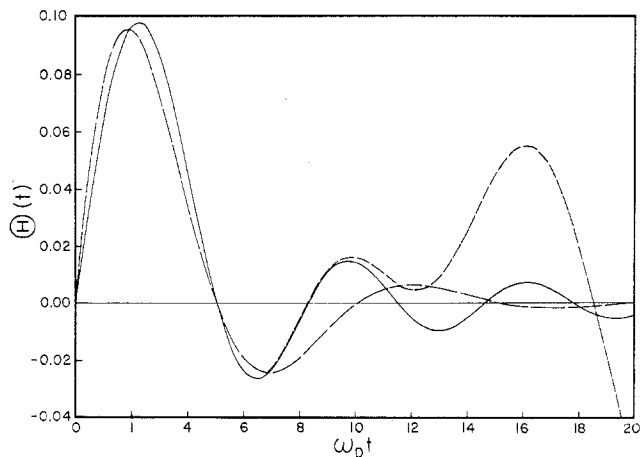
Figure 2. Memory kernel $\Theta(t)$ vs. $\omega_D t$ for the Debye model. Exact Debye model results (—); one-term damped oscillator approximant, eq 5 (— —); approximant obtained by modeling the heat bath by four undamped oscillators (- - - -). Damped oscillator approximant is adequate in the important short-time regime and properly decays asymptotically; undamped oscillator approximant displays unphysical behavior for $\omega_D t > \sim 10$; such behavior causes spuriously short residence times.

times. Response functions for real solids display similar qualitative behavior. We expect that the decaying oscillatory part of $\Theta(t)$ should not contribute in an essential way to trajectory averaged heat-bath influence; the peak should determine the physically important efficiency of heat-bath–primary-zone energy exchange.

Thus we may replace the exact heat-bath response by a model response which faithfully reproduces the peak in $\Theta(t)$ and which displays oscillatory decay at longer times. These features are obtained if we expand $\Theta(t)$ as a *convergent* series of damped sine functions; i.e.,

$$\Theta(t) = \sum_{\lambda=1}^{N} C_\lambda e^{-\gamma_\lambda t} \sin(\tilde{\omega}_\lambda t - \delta_\lambda) \tag{5}$$

The parameters C_λ, γ_λ, δ_λ, and $\tilde{\omega}_\lambda$ are chosen via a numerical contour integration method[8] to optimally reproduce the exact $\Theta(t)$. The point is that truncating the sum in eq 5 at N terms allows one to reduce the GLE to an $(N + 2)$-particle classical trajectory problem for the simplest case of gas atom scattering off a single primary-zone solid atom.

The simplest model, $\Theta(t)$, $N = 1$, *thus reduces the original many-body problem to a three-particle classical trajectory calculation.*

Even this simplest model correctly describes all qualitative effects of heat-bath influence. Moreover, detailed collisional studies[8] show that the simplest model yields remarkably satisfactory quantitative results. Small-scale collisional calculations, based on short damped sine expansions, should thus yield high-precision results. Given the current resolution of molecular beam gas/solid scattering experiments,[5] the simplest heat-bath models should suffice to interpret measured scattering attributes.

Our modeling scheme for $\Theta(t)$ has a direct physical meaning. Truncating the expansion 5 is equivalent to replacing the heat bath by N damped, noisy, i.e., Brownian, harmonic oscillators. The parameters characterizing the fictitious oscillators are chosen to optimally mimic the true heat-bath response. The reason for the reduction of the GLE (eq 1) to an $(N +$
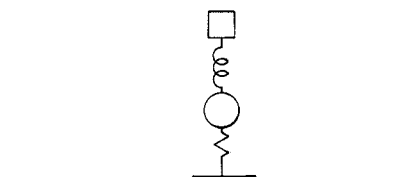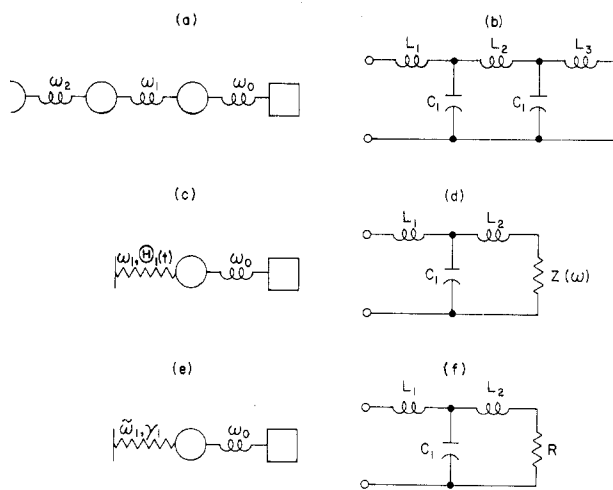

Figure 3. Schematic representation of lattice models discussed in the text. In each model a "curly" spring denotes a simple harmonic coupling, while a zigzag connection indicates harmonic coupling plus simple Brownian forces.

Figure 4. Solid-circuit analogy. (a) An infinite harmonic chain. (b) The electrical analogue as an LC transmission line. (c) Rigorous replacement of the heat bath by a single harmonic oscillator with damping characteristics $\hat{\Theta}_1(z)$. (d) Analogous replacement of the tail of transmission line by an ac impedance, $Z(\omega)$, with correct analytical structure. (e) Simplest solid model which generalizes the soft-cube model to include the many-body effect; the heat bath is approximated by a Brownian oscillator with a time-local friction constant, γ_1, and frequency $\tilde{\omega}_1$. (f) Analogous circuit, the simplest LC filter; $Z(\omega)$ is approximated by a frequency independent resistance, R.

2)-particle trajectory problem is now clear. The primary zone solid atom and the fictitious N-particle heat bath simply comprise an $(N + 1)$-particle system. (This is illustrated in Figure 3a for the single Brownian oscillator heat-bath model.) Thus simulating atom scattering off this system leads to an $(N + 2)$-particle trajectory calculation.

Our modeling procedure has an electrical as well as a mechanical analogue. It is akin to the equivalent impedance technique for simulating a complex electrical network by one or a few resistors. The electrical analogue of our modeling scheme is illustrated in Figure 4.

The models proposed are not the simplest possible. The full solid rather than the heat bath might be replaced by a Brownian oscillator. Such modeling amounts to ignoring memory effects in eq 1 by assuming eq 3 holds. The simple Brownian approximation[17] for
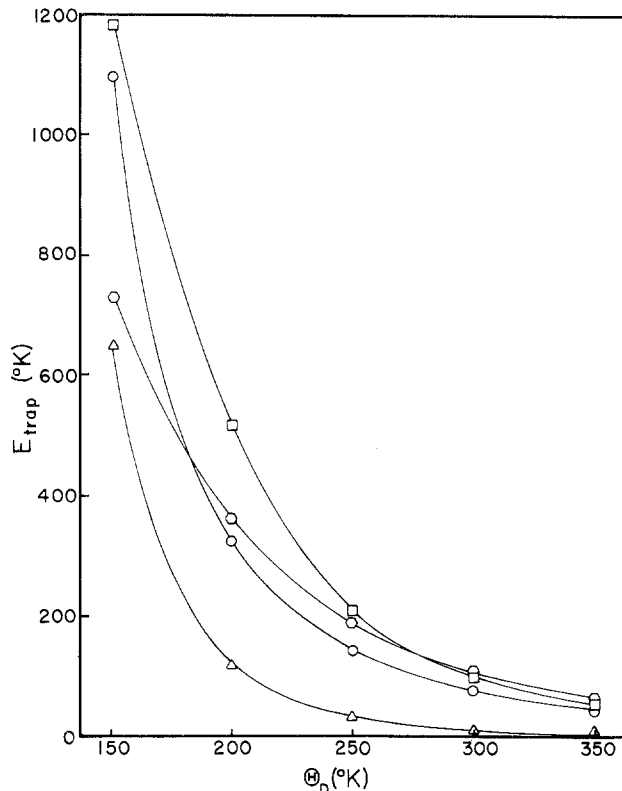
the solid (Figure 3c) yields a two-particle collisional problem. The Brownian approximation is, however, unsatisfactory. Since it implies that the bath responds instantaneously to the primary zone, processes short on the time scale τ_D will clearly be treated improperly. Longer time-scale processes are also incorrectly described by this overly naive modeling (see below); memory effects cannot be ignored.

The GLE (eq 1), as mentioned, may be solved by standard numerical techniques familiar from conventional classical trajectory studies if the present convergent heat-bath modeling scheme is adopted. The random force $R_\beta(t)$, however, provides a new computational feature, that of numerically generating the noise which represents the action of the heat bath. While the statistical sampling of an entire function, i.e., $R_\beta(t)$, rather than a few numbers may appear formidable, the problem in practice is not difficult. Procedures have been developed based on the Fourier construction of the noise[8] and on the direct generation of the time integrals over the noise required for numerical propagation of the equations of motion.[18] Other methods[19] have been developed based on the observation that for particular choices of the friction kernel the noise can be treated as the "projection" of a simpler (Markoff) process. Thus an important practical advantage of the Langevin theory is that the numerical methods necessary for its implementation closely resemble those that have already been well developed within the context of ordinary classical trajectory studies.

Sample Results

A selection of recent results found via the GLE approach are presented in this section. These early calculations are based on the simplest qualitatively correct solid models, assume only one primary zone solid atom, and employ model gas/solid potentials. Thus the theoretical results agree only qualitatively with experiments. Moreover, only simple scattering and adsorption–desorption processes have been studied. Much more realistic calculations as well as studies of dissociation, diffusion, and reaction, however, are planned or under way. The major roadblock to truly realistic calculations is, as in gas-phase problems, the lack of accurate information about gas/solid potential functions. Some encouraging progress, however, has recently been reported[20] for rare gas/metal potentials.

The model results obtained so far, however, have already led to increased insight into gas/solid dynamics. In Figure 5, we demonstrate the great importance of the heat-bath effect on adsorption (and hence, by detailed balance, desorption) phenomena. Figure 5 gives[21] the maximum gas beam energy at which an argon atom will trap (trapping threshold) on four model metal surfaces at $T_s = 0$ K as a function of surface Debye temperature, $\Theta_D = \hbar\omega_D/k_B$. [We choose $T_s = 0$ K for illustration purposes since no Monte Carlo sampling occurs for this case; thus, results are not obscured by statistical error. Qualitatively similar results are obtained for finite temperature solids.] Notice that the trapping threshold for an uncoupled single oscillator (Einstein) solid model (Figure 3b) is less than half that for a generalized

(18) J. D. Doll and D. R. Dion, *J. Chem. Phys.*, **65**, 3762 (1976).
(19) M. Shugard, J. C. Tully, and A. Nitzan, *J. Chem. Phys.*, **66**, 2354 (1977).
(20) J. E. van Himbergen and R. Silbey, preprint.
(21) B. J. Garrison and S. A. Adelman, submitted to *Surface Science*.

Figure 5. Trapping threshold for Ar/Ag scattering vs. surface Debye temperature, Θ_D. A Morse potential, $W(r,R) = D_e[e^{-2\alpha[R-r]} - 2e^{-\alpha[R-r]}]$, with parameters $D_e = 417.8$ K, $\alpha = 1.69$ Å^{-1}, is employed. (O) Single Brownian oscillator approximant to Debye heat bath (Figure 2); (△) Einstein model [$\theta(t) = R_\beta(t) = 0$ in eq 1]; (□) Debye friction model, $\beta_D = (\pi/6)\omega_D$; (□) Single Brownian oscillator fit friction model, $\beta_f = 0.268\omega_D$.

Langevin oscillator. The heat bath in the GLE calculation is treated in the single Brownian oscillator model (Figure 3a), but convergence studies[8] show this leads to minor error. Moreover, local friction models (Figure 3c) for the solid [$\beta(t) = 2\beta\delta(t)$] are inadequate. The percent many-body contribution to the trapping threshold increases with Θ_D. This is because the speed of sound in the solid and hence the degree of lattice involvement during the collision increase with Θ_D.

More generally, the degree of lattice involvement increases with the ratio of the collision time t_c to τ_D. This ratio is proportional to $\omega_D t_c$. For $\omega_D t_c \ll 1$, heat-bath effects are negligible and an Einstein model (Figure 3b) is adequate. For $\omega_D t_c \gg 1$, the simple friction model (Figure 3c) *may* be adequate. We thus expect that the magnitude of the heat-bath effect will depend importantly only on $\omega_D t_c$. This is, in fact, true,[21] as shown in Figure 6. We see that the ratio $\Delta E_M|\Delta E$ of many-body energy transfer to Einstein (M = E) and friction models (M = D and f) depends mainly on $\omega_D t_c$; that is, the ratios are largely independent of m, Θ_D, exponential potential range parameter α_r, T_s, and incident gas-beam energy E_i except through the effect of these parameters on $\omega_D t_c$. The absolute energy transfers are, of course, very sensitive to separate variation of all these parameters. For $\omega_D t_c > 1.0$, the Einstein model predicts energy transfers that are <60% of the many-body results. Even for $\omega_D t_c \gg 1$, the friction models fail. Thus the single Brownian oscillator heat-bath model provides the simplest adequate solid model.
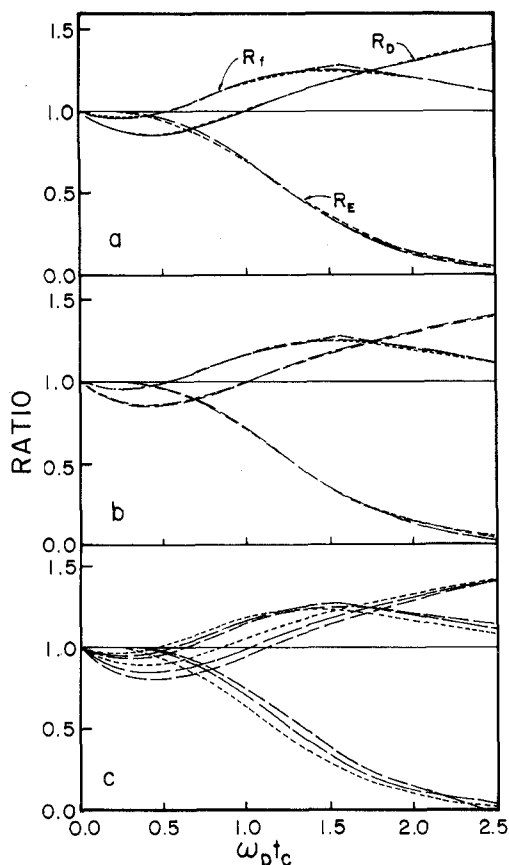
Figure 6. Ratios $R_M = \Delta E_M / \Delta E$ as a function of $\omega_D t_c$; M = E = Einstein model, M = f = friction model using β_f (Figure 5), M = D = friction model using β_D (Figure 5). Surface atom mass is appropriate to Ag in all cases, and an exponential potential $W(r,R) = e^{-\alpha_r[R-r]}$ is employed; $t_c \equiv \alpha_r^{-1}(M/2E_i)^{1/2}$ where E_i = incident beam energy. Variations of E_i, gas atom G, Θ_D, and α_r are studied. (a) (G, Θ_D, d$_r$) Ne, 151°, 1.0 Å^{-1} (—); Ne, 151°, 1.8 Å^{-1} (— —); Ne, 151°, 3.0 Å^{-1} (- - -). (b) (G, Θ_D, α_r) Ne, 151°, 1.8 Å^{-1} (—); Ne, 350°, 1.8 Å^{-1} (— —); Ne, 550°, 1.8 Å^{-1} (- - -). (c) (G, Θ_D, α_r) He, 151°, 1.8 Å^{-1} (—); Ne, 151°, 1.8 Å^{-1} (— —); Ar, 151°, 1.8 Å^{-1} (- - -).

Table I[a]
Thermal Accommodation Coefficients[1a] for Ne/W and Ar/W for $\beta(t) = \beta_0 \tau^{-1} e^{-t/\tau}$

$\hbar\beta_0/k_B$, K	Ne/W		Ar/W
	$\tau = 700$ au[b]	$\tau = 2100$ au	$\tau = 2100$ au
10	0.053	0.050	0.290
20	0.062	0.058	0.367
40	0.071	0.063	0.500
80	0.075	0.069	0.609
150	0.070	0.059	0.508

[a] Gas beam energy, E_i = 400 K, T_s = 100 K, θ_D = 180 K. Morse potentials with parameters D_e = 200 K, α = 1.4 Å^{-1} (Ne/W), and D_e = 950 K, α = 1.8 Å^{-1} (Ar/W), were employed. [b] au = atomic unit.

Many-body influence of neon/tungsten and argon/tungsten thermal accommodation coefficients[18] are given in Table I for a simple model exponential, $\beta(t) = \beta_0\tau^{-1}e^{-t/\tau}$. The accommodation coefficient is found to first increase with β_0 and then decrease. Apparently, very large friction impedes energy transfer.

The main restriction on the theory presented here is the neglect of quantum effects. The magnitude of quantum effects on energy transfer is difficult to pin down since no practical nonperturbative many-body quantum scattering theory yet exists. For He scattering, however, simple distorted Born perturbation

Table II
Generalized Langevin and Distorted Born Accommodation Coefficients ($\times 10^3$) for He/W (Born Results in Parentheses) as a Function of Beam Energy, E_i, and Surface Temperature, T_s[20]

Temp, K	E_i/T_s		
	0 K	300 K	800 K
100	2.78	1.72 ± 0.37	2.14 ± 0.17
	(1.40)	(2.00)	(2.02)
200	4.79	3.83 ± 1.01	4.76 ± 0.28
	(3.62)	(4.54)	(4.59)
300	7.25		7.26 ± 0.33
	(5.98)		(7.17)
400	9.71	8.04 ± 1.22	9.49 ± 0.50
	(8.31)	(9.57)	(9.65)
500	12.2	10.6 ± 1.2	11.4 ± 1.3
	(10.6)	(11.9)	(11.9)
600	14.3	12.9 ± 1.4	12.3 ± 3.3
	(12.7)	(14.1)	(14.2)
700	14.5	14.2 ± 4.9	9.3 ± 10.5
	(14.8)	(16.2)	(16.3)

[a] $W(r,R) = e^{-\alpha_r[r-R]}$ with $\alpha_r = 1.3$ Å^{-1}. The same mode density is employed in GLE and quantum calculations and is derived from a single Brownian oscillator representation of the heat bath.

theory *may* be adequate. He/W accommodation coefficients computed by Shugard, Tully, and Nitzan[19] using both distorted Born and GLE approaches are compared in Table II. The classical theory should fail at low surface temperatures, and the perturbation theory should fail at high beam energies. While the discrepancies between quantum and classical results are consistent with these notions, the striking features of Table II is the remarkable global agreement between quantum and classical results. The small magnitude of the quantum effect for He scattering suggests that for most systems quantum mechanics play a minor role in gas/solid energy exchange. This is important since any full quantum many-body theory will probably be much less convenient than our classical Langevin theory.

Summary and Outlook

The generalized Langevin equation approach to dynamics in many-particle systems has been described, and selected applications of the theory to gas/solid energy-transfer processes have been presented. The idea basic to the theory is that the many-particle system may be partitioned into a primary zone, where the dynamical processes of interest occur, and a heat bath, which comprises the remainder of the system.

Formally exact equations of motion for the primary zone particles may be derived. These resemble the Langevin equation of Brownian motion theory[17] and thus include heat-bath influence through dissipative and random-force terms.

The heat bath may be modeled by fictitious systems which mimic its energy reservoir function. The best fictitious systems appear to be chains of damped, noisy (i.e., Brownian) harmonic oscillators. With this type of heat-bath modeling, the GLE may be solved by standard classical trajectory methods. The simplest model heat bath, a single Brownian oscillator, leads to a *three-particle* trajectory problem for atom/solid scattering.

Particularly exciting is the fact that the new methods are likely to be widely applicable. The idea of partitioning a many-body system into a primary or chemical

zone and a heat bath or physical zone is fruitful for many problems; gas/solid phenomena provides a simple and very important prototype. Vibrational relaxation of a molecule imbedded in a solid matrix, as mentioned in the introduction, is a nonsurface phenomenon which has already been studied[14] utilizing the present ideas.

Among the important problems which could probably be profitably attacked using the Langevin approach are: (i) gas-phase chemical dynamics of polyatomic molecules; (ii) homogeneous nucleation phenomena; (iii) molecular dynamics of liquid evaporation (here, the heat bath could be profitably treated as a hydrodynamic continuum); (iv) dielectric relaxation in solids; (v) particle, exciton, and spin diffusion in solids; (vi) dy-

namics of a monomer imbedded in a polymer chain (here, the Rouse modes of the chain and the solvent would comprise the heat bath). These motions, which may be probed experimentally, contribute importantly to the high-frequency viscoelastic behavior of polymer solutions and melts.

In short, the marriage of chemical and statistical dynamics is likely to add considerably to our understanding of condensed-phase processes at the molecular level.