Gas-Condensed Phase Interactions: Flame-Surface Heat Exchange

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A burning solid-phase energetic material characteristically develops a thin liquid layer between the solid material itself and the flame. Whether the combustion occurs entirely in the gas phase or whether condensed-phase reactions contribute significantly, the net burning rate necessarily depends on the temperature of this liquid layer.[1] Our particular focus is on the heating of the surface as a result of energy transfer from hot gas-phase combustion products. With these results in hand, it will be possible to predict the steady-state surface temperature by balancing the energy input, from gas-surface energy transfer and the exothermicity of any condensed-phase reactions, with the energy loss stemming from evaporation of the liquid. (This particular component of the overall project will be carried out by Dr. Rice at ARL.) The ultimate product of this work will be a first-principles molecular-level description of the burning rate of the energetic material in a form suitable for melding with the steady-state continuum combustion model of Miller and Anderson,[1] one that will be comparable with the detailed molecular description of the gas-phase combustion reactions already included in the model.

The simulation of gas-surface energy transfer has a long history, but nearly all of the work has focused on the impinging of gases on solid surfaces, either clean or covered in part with an adsorbate. This area of research dates back at least as far as the work of J. K. Roberts,[2] whose interest lay in the determination of thermal accommodation coefficients. (Coincidentally, one of our late Missouri colleagues, L. Thomas, devoted four decades to the measurement of energy exchange between gases and hot polycrystalline filaments.[3]) Shortly following the appearance of more detailed, energy-resolved gas-solid scattering experiments, the first simple theoretical models appeared, models which met with modest success in describing the simplest elastic and inelastic collisions. (The various “cube models” that appeared in the 1960’s are notable products of this work).[4] More complicated models soon followed. For example, over a decade ago we examined Ar atom scattering from a W(110) surface as a function of Ar adsorbate surface coverage, surface temperature, and angle of incidence.[5] An example of the results that emerged from that work is shown below.

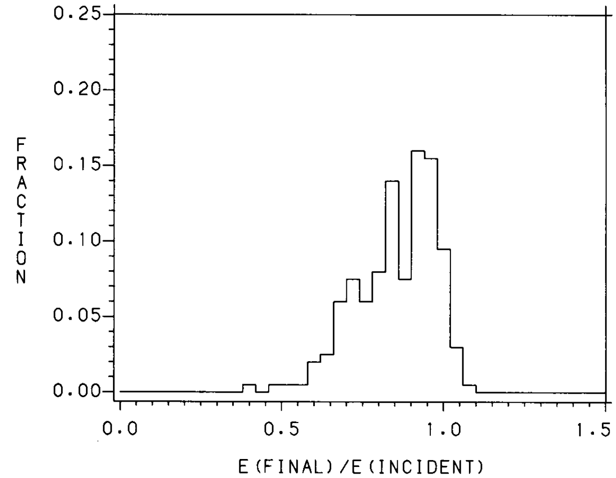

Fig. 1. Energy distribution of Ar atoms directly scattered from a clean W(110) surface. The values of the incident energy, angle, and initial surface temperature are, respectively, 0.25 eV, 30°, and 77 K.

Studies of gas-liquid energy transfer are far fewer in number, however, with the work of Nathanson and co-workers[6-10] constituting nearly all of the recent investigations. They have examined several systems (e.g., HCl, HBr, and HNO_3 scattering from D_2O/D_2SO_4; Xe scattering from squalane; Ar scattering from a Bi:Ga alloy and from In; Ar scattering from perfluorinated polyethers) by collecting TOF spectra at various scattering angles. They also have performed, in collaboration with Gerber[10,11] and Skinner,[8] simulations of energy transfer in a few of these systems. However, in those systems simulated (Ar/In, and Xe/squalane), they have not undertaken extensive incident angle averaging, nor have they chosen to make a systematic study of surface temperature effects.

The actual simulation methodology that we will use is reasonably standard.[12] (We have in hand several of our own codes, as well as Hase and co-workers' *VENUS* code,[13] that shall provide a starting point for the required code development.) The model of the condensed phases will consist of a few layers of material held rigid in its solid-state geometry, on top of which liquid layers will be equilibrated via a thermostatted molecular dynamics (MD) calculation. (MD simulations are based on the integration of Hamilton's equations of motion,

$$\dot{\mathbf{q}} = \frac{\partial H}{\partial \mathbf{p}}, \quad \dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} = -\frac{\partial V}{\partial \mathbf{q}}$$

where $(\mathbf{q},\mathbf{p})$ are the coordinate and conjugate momentum vectors, and H is the classical Hamiltonian function, which is just the sum of the kinetic and potential (V) energies. Thermal equilibration in these calculations may be obtained either by momentum scaling or by coupling the system to an auxiliary degree of freedom. In addition, appropriate periodic boundary conditions will be imposed to eliminate edge effects in two dimensions.[12]) Except for the temperature regime, which is that appropriate to the liquid system, and the number of "mobile" layers included, these simulations are comparable with those that we performed in previous work.[5] Combustion product species, moving with a distribution of kinetic energies consistent with the exoergicity of the gas-phase reactions, will then be collided with the simulated surface at incident angles chosen at random from a uniform distribution. We will then analyze the energy of the scattered species to quantify the energy transfer to the surface. The input to these calculations will be potential energy parameterizations, which will be provided by the Brenner and Thompson groups. (In a real system it is possible, of course, for the impinging species to react with the surface species. Thus accurate *reactive* potential functions will be required.)

In the initial year of this work, we shall concentrate on code development and calibration in simple systems. Our first target system will be Ar scattering from liquid In, for which Nathanson and co-workers already have reported limited simulations.[8,11] (Both Lennard-Jones and embedded atom In potentials have been considered previously. The simpler Lennard-Jones potential parameterization will be quite sufficient for the code calibration that is the principal goal of this initial study.) While this system is obviously without interest with regard to the combustion of energetic materials, it nonetheless affords an opportunity for investigating in a systematic fashion how gas-liquid energy transfer depends on surface temperature. (By the principle of corresponding states, the actual identity of the species is not important. What *is* important is that we will be looking at a Lennard-Jones model system in a temperature regime characteristic of a bulk liquid.)

Even a variation of this simple system, though, affords an opportunity to address a practical problem that arises in modeling real energetic material combustion. Real systems involve heterogeneous surfaces, with the RDX "foam" being a particularly complex example.[1] Thus, eventually we will need to be able to deal with energy transfer occurring at the surface of mixtures. An intriguing mixture (in this case an alloy) for which the Nathanson group already has obtained experimental data is the Ar/Bi:Ga system.[7] They have shown that the energy transfer at this liquid alloy surface is strongly temperature dependent, reflecting the temperature dependence of the surface composition. At the lowest temperature studied, the energy transfer is found to be characteristic of pure Bi, although the alloy itself is only 0.02% Bi in Ga. With an increase in temperature, however, the segregation of the Bi to the surface layer is lost, and the energy exchange is characteristic of pure Ga. From a modeling standpoint, a slavish adherence here to the details of Nathanson's Ar/Bi:Ga system is neither critical nor desirable, since that system is not amenable to simulation per se. (One obvious difficulty is that the Bi concentration in the experiments is very low, 0.02%. It is also significant that while liquid metals are often poorly described by pairwise-additive potential functions, it will be of little benefit to us within the scope of this project to refine those functions.)

More important, however, is an extension to a molecular system, one that is relevant to actual combustion. Furthermore, we want to start to make a direct connection with the systems for which kinetics simulations are already available. The combustion of frozen ozone is a particularly attractive system in which to make this first contact between our energy transfer calculations and Miller and Anderson's steady-state combustion model. (We are fully aware that ozone is not our ultimate goal; it is not the practical energetic material that constitutes our ultimate focus. On the other hand, in this simple system—only three combustion equations are involved—it also will be easier to see what modification of the extant model will be required in order to make use of the molecular-level energy exchange results.[14]) While the fundamental approach to the characterization of the energy transfer here will be the same one adopted in our preliminary calibration calculations, we also will need to consider multiple gaseous colliding species and nascent energy distributions. With that in mind, Dr. Miller has volunteered to provide us with the requisite flux data from his model. Throughout we will be collaborating with Profs. Brenner and Thompson to insure that we will have an adequate potential energy parameterization, one that will allow for reactive collision events. Bembenek and Rice[15] recently have shown that oxygen can be modeled successfully, thus we are confident that similarly successful functions can be developed that will permit an accurate description of ozone.

[1] M. S. Miller and W. R. Anderson, Prog. Astronaut. Aeronaut. (Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics) **185**, 501 (2000).

[2] J. K. Roberts, Proc. Roy. Soc., A **129**, 146 (1930).

[3] See, for example, L. B. Thomas, Rarefied Gas Dynamics, Progress in Astronautics and Aeronautics **74**, 83 (1981).

[4] R. M. Logan and R. E. Stickney, J. Chem. Phys. **44**, 196 (1966); R. M. Logan, J. C. Keck, and R. E. Stickney, Rarefied Gas Dynamics **1**, 49 (1967).

[5] D. Zhao and J. E. Adams, Surf. Sci. **171**, 208 (1986).

[6] J. R. Morris, P. Behr, M. D. Antman, B. R. Ringeisen, J. Splan, and G. M. Nathanson, J. Phys. Chem. A **104**, 6738 (2000); M. E. Saecker, S. T. Govoni, D. V. Kowalski, M. E. King, and G. M.

Nathanson, Science **252**, 1421 (1991); M. E. King, G. M. Nathanson, M. Hanning-Lee, and T. K. Minton, Phys. Rev. Lett. **70**, 1026 (1993).

[7] J. A. Morgan and G. M. Nathanson, J. Chem. Phys. **114**, 1958 (2001).

[8] L. Tribe, M. Manning, J. A. Morgan, M. D. Stephens, W. R. Ronk, E. Treptow, G. M. Nathanson, and J. L. Skinner, J. Phys. Chem. B **102**, 206 (1998).

[9] M. E. King, K. M. Fiehrer, G. M. Nathanson, and T. K. Minton, J. Phys. Chem. A **101**, 6556 (1997).

[10] N. Lipkin, R. B. Gerber, N. Moiseyev, and G. M. Nathanson, J. Chem. Phys. **100**, 8408 (1994).

[11] D. Chase, M. Manning, J. A. Morgan, G. M. Nathanson, and R. B. Gerber, J. Chem. Phys. **113**, 9279 (2000).

[12] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1989).

[13] W. L. Hase, R. J. Duchovic, X. Hu, A. Kormornicki, K. F. Lim, D.-H. Lu, G. H. Peslherbe, K. N. Swamy, S. R. Vande Linde, A. Varandas, H. Wang, and R. J. Wolf, *VENUS96*.

[14] M. S. Miller, in *Proceedings of the Materials Research Society Symposium: Decomposition, Combustion and Detonation Chemistry of Energetic Materials*, edited by T. B. Brill, T. P. Russell, W. C. Tao, and R. B. Wardle (Materials Research Soc., Pittsburgh, 1996), p. 169.

[15] S. D. Bembenek and B. M. Rice, J. Chem. Phys. **113**, 2354 (2000).