

Sum rules in inelastic gas-surface scattering

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Abstract. An explanation for sum-rules observed in gas-surface scattering is offered via a classical scaling theory for inelastic collisions.

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1. Introduction

A series of elegant experiments have been carried out recently by Janda and co-workers (Janda *et al* 1980, 1983; Hurst *et al* 1983) on the scattering of supersonic monoenergetic beams from clean metal surfaces. One result from these studies is that the average final kinetic energy of the scattered particle, $\langle E_f \rangle$, depends on the average initial kinetic energy, $\langle E_i \rangle$, and the surface temperature, T_s , via a simple linear relationship,

$$\langle E_f \rangle = \alpha_g \langle E_i \rangle + \alpha_s (2k_B T_s), \quad (1)$$

where the coefficients α_g, α_s depend only on the scattering angle, and k_B is the Boltzmann constant. A number of theoretical models (Baker and Auerbach 1979; Grimmelman *et al* 1980; Levine and Silbey 1981) have offered an explanation of the above result, which has since been seen to hold in a model semiclassical study of gas-surface scattering as well (Agarwal and Raff 1982).

The purpose here is to point out that an equation such as (1), termed a sum-rule (Levine and Silbey 1981), derives from a recently formulated classical scaling theory (DePristo 1981; Ramaswamy 1984a) for inelastic processes. The scaling approach, described below, offers a novel viewpoint of the inelastic scattering process, and permits a different interpretation of the experimental results (see also Richard and DePristo 1983).

2. Scaling theory

For convenience we consider a coplanar scattering geometry, for which the total Hamiltonian is given as

$$H = H_g + H_s + V(\mathbf{x}, \mathbf{R}). \quad (2)$$

The origin of the coordinate system (see, for example, Goodman 1975; Bernasek and Somorjai 1975) is located on the surface of the solid; the subscripts s and g denote solid and gas respectively, and V is the interaction potential. For an atomic gas particle, H_g is

Dedicated to Prof. Sadhan Basu on the occasion of his 65th birth anniversary.

merely the kinetic energy, $H_g = p_R^2/2m$, with m the atomic mass. p_R is the momentum conjugate to the coordinate R , which describes the position of the gas particle relative to the origin. (We will confine our attention to this simple case). The surface Hamiltonian can be expressed in terms of normal-mode coordinates (Kittel 1971; Goldstein 1980):

$$H = \sum_k (\dot{x}_k^2 + \omega_k^2 x_k^2)/2, \quad (3)$$

where k indexes the normal modes of frequency ω_k . For a given experimental configuration (Janda *et al* 1980, 1983; Hurst *et al* 1983), the angle of incidence, θ_i , is fixed. At the beginning of the collision, the interaction potential $V \rightarrow 0$ (at $t = t_0$, $R = R^0 \rightarrow \infty$), and then H_g and H_s are individually constants of the motion. We transform to an action-angle representation (Goldstein 1980) at $t = t_0$: the actions are the constants of motion. Thus

$$H_s \rightarrow \sum_k \omega_k J_k / 2\pi = \sum_k \omega_k (n_k + 1/2) \hbar \quad (4)$$

where J_k are the surface action variables (or alternatively, the n_k are the phonon occupancies). The angle variables conjugate to these actions are ω_k . Similarly, the 'parallel' and 'perpendicular' components of the momentum of the gas particle are action variables as well, $\mathcal{J}_1 = p_\perp$, and $\mathcal{J}_2 = p_\parallel$, with conjugate angle variables ϕ_1 and ϕ_2 .

Within a classical scenario, the gas-solid collision is simulated by an ensemble of trajectories. For every trajectory, the initial kinetic energy is fixed, $E = [(\mathcal{J}_1^0)^2 + (\mathcal{J}_2^0)^2]/2m$. The initial orientation is fixed at θ_i . ϕ_1^0, ϕ_2^0 are fixed so that R^0 is some large value and $V(\mathbf{x}, \mathbf{R}) \rightarrow 0$. The value of all variables at $t = t_0$ is indicated by superscript 0. The phonon occupancies (Kittel 1971) are related to the surface temperature (in the high temperature approximation) through (Kittel 1971)

$$(n_k + 1/2) = [\exp(\hbar\omega_k/k_B T_s) - 1]^{-1} \approx k_B T_s / (\hbar\omega_k), \quad (5)$$

which fixes the initial surface actions J_k^0 . What differ from trajectory to trajectory are the surface angle variables, \mathbf{w}^0 . This leads to a distribution in the scattering angle θ_f , and the final kinetic energy E_f .

Since the measurement is carried out at a specific scattering angle, this corresponds to sampling only a specific set of initial surface-angles, \mathbf{w}^0 . We are interested in determining the variation in the final kinetic energy with changing initial conditions. The equation of motion for the kinetic energy of the gas, H_g , is (Ramaswamy 1984a)

$$dH_g/dt = -\{H, H_g\} = -\{V, H_g\} = L_v(t)H_g; \quad (6)$$

$\{, \}$ is the Poisson bracket. Equation (6) can be solved implicitly to yield

$$H_g(t = \infty) - H_g(t_0) = E_f - E_i = G(\{V\}; \mathbf{J}^0, \mathbf{w}^0; \mathcal{J}^0, \phi^0), \quad (7)$$

where

$$G(\{V\}; \mathbf{J}^0, \mathbf{w}^0; \mathcal{J}^0, \phi^0) = \left[\int_{t_0}^{\infty} dt' L_v(t') H_g + \int_{t_0}^{\infty} dt' \int_{t_0}^{t'} dt'' L_v(t') L_v(t'') H_g + \dots \right] \mathbf{J} = \mathbf{J}^0, \mathbf{w} = \mathbf{w}^0; \mathcal{J} = \mathcal{J}^0, \phi = \phi^0 \quad (8)$$

Note that the RHS of (8) is evaluated at the *initial* values of all variables. For a particular scattering angle, θ_f , the RHS can be expanded in a Taylor series in the initial action variables to yield

$$E_f - E_i = G(\{V\}; \mathbf{0}, \mathbf{w}^0; \mathbf{0}, \phi^0) + \sum_{l=1}^2 \frac{\partial G}{\partial \mathcal{I}_l^0} \mathcal{I}_l^0 + \sum_{k=1} \frac{\partial G}{\partial J_k^0} J_k^0 + \dots \quad (9)$$

$$= G(\{V\}; \mathbf{0}, \mathbf{w}^0; \mathbf{0}, \phi^0) + 2 \frac{\partial G}{\partial E_i} E_i + (2k_B T_s) \sum_k \frac{1}{\hbar \omega_k} \frac{\partial G}{\partial J_k^0} + \dots$$

$$= \bar{\alpha}_0 + \bar{\alpha}_g E_i + \bar{\alpha}_s 2k_B T_s, \quad (10)$$

with

$$\bar{\alpha}_0 = G(\{V\}; \mathbf{0}, \mathbf{w}^0; \mathbf{0}, \phi^0), \quad (11a)$$

$$\bar{\alpha}_g = 2(\partial G / \partial E_i), \quad (11b)$$

$$\bar{\alpha}_s = \sum_k (\partial G / \partial J_k^0) / \omega_k. \quad (11c)$$

This analysis yields explicit expressions for the coefficients $\bar{\alpha}$ [through (8) and (11)], and it is clear that these are independent of the surface temperature or the incident kinetic energy, but depend on the scattering angle. Further, taking the limit $T_s \rightarrow 0$, $E_i \rightarrow 0$, it can be seen that $\bar{\alpha}_0 = 0$. Taking these limits separately yields $\bar{\alpha}_g < 0$, $\bar{\alpha}_s > 0$. These observations are in accord with experimental results (Janda *et al* 1983; Hurst *et al* 1983). Since the scaling form holds (DePristo 1981; Ramaswamy 1984a) for each initial kinetic energy at fixed T_s , the proper relationship for average energies, (1), is regained.

It must be noted that (10) is in principle (DePristo 1981; Ramaswamy 1984a) an infinite expansion in the initial constants of the motion—here E_i and T_s . It is an *empirical* observation (Agrawal and Raff 1982; Janda *et al* 1980, 1983; Hurst *et al* 1983) that for gas-metal inelastic scattering the higher order terms are negligible. One can therefore expect departures from this simple behaviour when the conditions for the validity of the linear scaling approximation are not satisfied.

3. Discussion

The applicability of the scaling in the present context suggests some interesting extensions. For a molecular gas incident on a surface, H_g will include an internal molecular Hamiltonian in (2). Then the Taylor series expansion in (9) will involve the actions (or quantum numbers) corresponding to the internal degrees of freedom as well. The scaling law that obtains then is similar to (10), with additional terms in the *initial* quantum numbers of the gas molecule,

$$\langle E_f \rangle = \alpha_g \langle E_i \rangle + \alpha_s (2k_B T_s) + \beta_1 N + \beta_2 N^2 + \dots, \quad (12)$$

or at fixed E_i and T_s ,

$$\langle E_f \rangle = \beta_0 + \beta_1 N + \beta_2 N^2 + \dots, \quad (13)$$

which is the usual form of the scaling law in atom-molecule collisions (Ramaswamy and Bhargava 1984). (We have considered a single internal degree of freedom for the gas

molecule, and the quantum number is denoted by N). It would be of interest to determine whether such behaviour is indeed followed in an initial state-selected experiment. In another context, we have shown (Ramaswamy 1984b; Ramaswamy and Bhargava 1984; Bhargava and Ramaswamy 1985) that the scaling coefficients can be given precise quantum-mechanical meaning, since they are related to quantum transition probabilities. A full scaling analysis would thus make possible the interpretation of empirical coefficients, such as appear in (1), (12) or (13), in terms of inelastic state-to-state quantities.

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