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,

\[
\langle E_f \rangle = \alpha_g \langle E_i \rangle + \alpha_s (2k_B T_s),
\]

(1)

where the coefficients \( \alpha_g, \alpha_s \) 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

\[
H = H_g + H_s + V(x, R).
\]

(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, $H_g = p_g^2 / 2m$, with $m$ the atomic mass. $p_g$ 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):

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

(3)

where $k$ indexes the normal modes of frequency $\omega_k$. For a given experimental configuration (Janda et al. 1980, 1983; Hurst et al. 1983), the angle of incidence, $\theta_i$, is fixed. At the beginning of the collision, the interaction potential $V \to 0$ (at $t = t_0$, $R = R^0 \to \infty$), and then $H_g$ and $H_z$ 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

$$H_g = \sum_k \omega_k J_k / 2\pi = \sum_k \omega_k (n_k + 1/2)\hbar$$

(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 $\phi_k$. 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 $\phi_1$ and $\phi_2$.

Within a classical scenario, the gas-solid collision is simulated by an ensemble of trajectories. For every trajectory, the initial kinetic energy is fixed, $E = (\mathcal{J}_1^2 + (\mathcal{J}_2^2)/2m$. The initial orientation is fixed at $\theta_i$, $\phi_1^0$, $\phi_2^0$ are fixed so that $R^0$ is some large value and $V(x, R) \to 0$. 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)

$$(n_k + 1/2) = \left[ \exp(\hbar \omega_k / k_B T) - 1 \right]^{-1} \approx k_B T / (\hbar \omega_k),$$

(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 $\theta_f$, 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)

$$dH_g / dt = -\{H, H_g\} = -\{V, H_g\} = L_x(t) H_g,$$

(6)

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

$$H_g(t = \infty) - H_g(t_0) = E_f - E_i = G(\{V\}; \mathbf{J}_0, \mathbf{w}^0; \mathcal{J}_0^0, \phi_0^0),$$

(7)

where

$$G(\{V\}; \mathbf{J}_0, \mathbf{w}^0; \mathcal{J}_0^0, \phi_0^0) = \left[ \int_{t_0}^\infty dt' \int_{t_0}^\infty dt'' L_v(t') H_g + \int_{t_0}^\infty dt' \int_{t_0}^\infty dt'' L_v(t') L_v(t'') H_g \right] + \ldots$$

$$J = J_0, \mathbf{w} = \mathbf{w}^0; \mathcal{J} = \mathcal{J}_0^0, \phi = \phi_0^0$$

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

$$E_f - E_i = G(\{V\}; 0, w^0; 0, \phi^0) + \sum_{i=1}^{2} \frac{\partial G}{\partial J_i} J_i^0 + \sum_{k=1}^{\infty} \frac{\partial G}{\partial J_k} J_k^0 + \ldots$$

(9)

$$= G(\{V\}; 0, w^0; 0, \phi^0) + 2 \frac{\partial G}{\partial E_i} E_i + (2k_B T_e) \sum_{k} \frac{1}{\hbar \omega_k} \frac{\partial G}{\partial J_k} + \ldots$$

with

$$\alpha_0 = G(\{V\}; 0, w^0; 0, \phi^0),$$

(11a)

$$\alpha_g = 2(\partial G/\partial E_i),$$

(11b)

$$\alpha_s = \sum_{k} (\partial G/\partial J_k)/\omega_k.$$  

(11c)

This analysis yields explicit expressions for the coefficients $\alpha[\ldots 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 $T_e \to 0$, $E_i \to 0$, it can be seen that $\alpha_0 = 0$. Taking these limits separately yields $\alpha_g < 0, \alpha_s > 0$. 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 $T_e$, 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 $T_e$. 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, $H_s$ 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,

$$\langle E_f \rangle = \alpha_g \langle E_i \rangle + \alpha_s (2k_B T_e) + \beta_1 N + \beta_2 N^2 + \ldots,$$

(12)

or at fixed $E_i$ and $T_e$,

$$\langle E_f \rangle = \beta_0 + \beta_1 N + \beta_2 N^2 + \ldots,$$

(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 interpreta-
tion of empirical coefficients, such as appear in (1), (12) or (13), in terms of inelastic
state-to-state quantities.

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