AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **74**, 4741 (1981); doi: 10.1063/1.441625 View online: http://dx.doi.org/10.1063/1.441625 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v74/i8 Published by the American Institute of Physics.

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## Energy transfer in atom-surface scattering: Sum rules and velocity distributions

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Velocity distributions for Ar atoms scattered from a polycrystalline tungsten surface<sup>1(a)</sup> and for Xe scattered from  $Pt(111)^{1(b)}$  have recently been measured for a wide range of incident supersonic beam energies and surface temperatures. It was concluded that direct, single encounter, inelastic scattering is the most important process and is characterized for Ar/W by a simple linear relationship

$$\langle \mathbf{K}, \mathbf{E}, \rangle_{\text{out}} = 0.83 \langle \mathbf{K}, \mathbf{E}, \rangle_{\text{in}} + 0.40 \ k_B \ T_s \ . \tag{1}$$

Here  $T_s$  is the surface temperature and the mean kinetic energy of gas molecules from a surface or an effusive source at the temperature T is  $2k_B T$ , where  $k_B$  is the Boltzmann constant. In this note we will be concerned with this direct process, and not the indirect processes.<sup>1(b)</sup>

Linear relationships between final and initial mean values of kinematic observables play a central role in the information theoretical approach to collision processes<sup>2</sup> and are called sum rules. In this note we shall derive a sum rule of the form (1) starting from a macroscopic approach to energy transfer in multistate systems.<sup>3</sup> Since Janda *et al.*<sup>1</sup> have also measured the velocity distributions, their results serve to demonstrate the special relevance of sum rules in the information theoretic approach, namely, when a sum rule of the form (1) obtains, an incident thermal velocity distribution will lead to a scattered velocity distribution which is also thermal, but with a different value of the temperature.

The derivation of the sum rule is based on the assumption that the solid can be considered to be a collection of harmonic modes (phonons, electron-hole pairs, etc.) which interact with the colliding atoms and whose excitation level is changed by that interaction. Given a thermal distribution of incident atoms, the macroscopic *assumption* is that the average energy of each mode relaxes toward equilibrium with a single relaxation time  $\tau$ . It then follows<sup>3</sup> that for *each* mode

$$\sum_{v'} (E_v \cdot - E_v) k(v - v') = \kappa(\langle E_v \rangle - E_v) , \qquad (2)$$

where  $E_v$  is the energy of level v of the mode and  $\langle E_v \rangle$ is the average energy of the mode if it were in thermal equilibrium with the (thermal) beam of incident atoms. k(v - v') is the rate constant of v - v' transfer due to collisions and  $\kappa = (n\tau)^{-1}$ , where n is the density of the incident beam. For simplicity we will take all modes to have the same frequency, although this is not essential. We now average Eq. (2) over the initial distribution in  $E_v$  (i.e., according to the temperature  $T_s$  of the solid) and sum over all modes. The left-hand side of Eq. (2) is then the average energy gain of the solid and thus the average energy loss of the colliding atoms  $\langle K. E. \rangle_{in}$  $-\langle K. E. \rangle_{out}$  per collision. The right-hand side is  $[\langle \langle E_v \rangle \rangle_T - \langle \langle E_v \rangle \rangle_{T_s}]$ . The subscripts T and  $T_s$  refer to the different thermal distributions used in the two averages. T is the temperature of the incident beam [used to define  $\langle E_v \rangle$  in Eq. (2)]. We replace  $\langle \langle E_v \rangle \rangle_{T_s}$  by its high temperature value  $k_B T_s$ , <sup>6</sup> and replace  $\langle \langle E_v \rangle \rangle_T$  $= k_B T$  by the mean kinetic energy of the beam with which the solid is in equilibrium, i.e.,  $\langle K. E. \rangle_{in}/2$ . With these replacements, Eq. (2) can be written as

$$\langle \mathrm{K.E.} \rangle_{\mathrm{out}} = \left(1 - \frac{\kappa}{2\omega}\right) \langle \mathrm{K.E.} \rangle_{\mathrm{in}} + \left(\frac{\kappa}{\omega}\right) k_B T_s .$$
 (3)

Here  $\omega$  is the collision rate. Equation (3) is of the same form as and numerically consistent with the experimental result (1), yielding  $(\kappa/\omega) = 0.4$ , which is clearly the probability of energy transfer per collision.<sup>7</sup> Note also that  $\kappa/\omega = Z/Z_{\nu} = Z\tau$ , where Z is the number of collisions per unit time, while  $Z_{\nu} = 1/\tau$  is the number of energy-transfer collisions per unit time.

From a collision-theoretic, microscopic, point of view, the sum rule (2) can be derived for simple Hamiltonians of atom-oscillator collisions,<sup>2</sup> the Landau-Teller model,<sup>3</sup> and recently for a hard cube model.<sup>9</sup> While analytical derivations are necessarily restricted to very simple models (e.g., harmonic oscillators), the sum rule is typically found valid<sup>4</sup> even for collisions where anharmonicity and/or multiquantum transitions are important.

From a dynamical point of view, a sum rule is the signature of a time-dependent constant of the motion.<sup>5</sup> For the present problem, the linear relationship (1) implies that there is a time-dependent constant of the motion I(t), which can be well approximated as I(t)= a(t) K. E. + b(t) 1, where a(t) and b(t) are time dependent coefficients, K.E. is the kinetic energy of the beam, and 1 is the identity operator. It then follows that *if* the initial velocity distribution in the beam can be specified as a distribution of maximum entropy subject to the constraints of (i) normalization and (ii) given  $(K. E.)_{in}$ , then the final velocity distribution will be one of maximum entropy subject to (i) normalization and (ii) given  $(K.E.)_{out}$ . It is worth emphasizing that this result not only specifies the functional form of the final velocity distribution but it also predicts the value of the Lagrange parameter (using the given value of  $(K.E.)_{out}$ ). In particular, for the problem at hand it follows that for an incident thermal velocity distribution, the functional form of the velocity distribution of the scattered atoms will remain thermal. Only the mean kinetic energy (or, equivalently, the temperature) will have a different value. Given the incident flux velocity distribution<sup>10</sup> [Eq. (1) of Ref. 1(a)], it was possible to fit the scattered flux velocity distribution to the same functional form, for both specular and normal directions, with the width of the outgoing velocity distribution equal to  $0.4k_BT_s/m_{\rm Ar}$  in the case of Ar/W.

The information theoretic results are thus in total agreement with the experimental measurements<sup>1</sup> of the direct inelastic scattering of rare gas atoms from metal surfaces.

- <sup>b)</sup>Work supported by the NSF (grant # DMR 78-24185) and the U. S./Israel Binational Science Foundation.
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- <sup>6</sup>The form valid for all T is  $\hbar\omega \left[\exp(\hbar\omega/k_B T_s) 1\right]^{-1}$ .
- <sup>7</sup>This form of Eq. (3) is similar to that for the energy accommodation coefficient [see Eq. (10) of Ref. 1(a)] and identifies that quantity with  $\kappa/2\omega \approx 0.2$ . Measurement of the EAC<sup>8</sup> for Ar on W yield EAC  $\approx 0.19$  for  $T_{gas} \gtrsim 350$  K, in good agreement with the experiments of Janda *et al.*
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- <sup>9</sup>E. Grimmelmann, J. Tully, and M. Cardillo, J. Chem. Phys. 72, 1039 (1980).
- <sup>10</sup>The forefactor  $v^3$  in Eq. (1) of Ref. 1 is the proper prior functional dependence for a flux velocity distribution. It is also the origin of the equality  $\langle K.E. \rangle_{in} = 2k_BT$  used in the derivation of Eq. (3).

## A mean free path kinetic theory of void diffusion in a porous medium with surface diffusion. Asymptotic expansion in the Knudsen number

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One of the simplest models for gaseous diffusion is the so-called mean free path kinetic theory<sup>1,2</sup> for the self diffusion of "tagged" molecules in a pure gas at uniform pressure. The mean free path model allows us to formulate a kinetic theory of void gas diffusion in the transition region between bulk and Knudsen diffusion and simultaneously include local surface diffusion along the pore walls. The free path probabilities  $K_1(\mathbf{r}, \mathbf{r}') d^2 \mathbf{r}$ that a molecule leaving the pore wall at r' will experience its next collision within the element of wall surface  $d^2\mathbf{r}$  at  $\mathbf{r}$ ,  $K_2(\mathbf{r}, \mathbf{r}')d^2\mathbf{r}$  that a free path that begins with a molecular collision in an void volume located at  $\mathbf{r}'$  will end with a wall collision within the element of wall surface  $d^2\mathbf{r}$  at  $\mathbf{r}$ , and  $K_3(\mathbf{r},\mathbf{r}')d^3\mathbf{r}$  that a free path that begins with a molecular collision in the void at r' will end with a molecular collision within the element of void volume  $d^3\mathbf{r}$  at  $\mathbf{r}$  can be calculated from elementary kinetic theory<sup>1,2</sup> in terms of the mean free path lfor molecule-molecule collisions with diffusive cosine scattering at the pore walls

$$K_{i}(\mathbf{r},\mathbf{r}') = \left[-\frac{4\eta(\mathbf{r}')\cdot\rho}{\rho}\right]^{(3-i)(2-i)/2} \left[\frac{l\eta(\mathbf{r})\cdot\rho}{\rho}\right]^{2^{i}(3-i)/4} \times (4l\pi\rho^{2})^{-1}\exp(-\rho/l) , \quad i=1, 2, 3, \qquad (1)$$

where  $\rho = (\mathbf{r'} - \mathbf{r})$ , and the unit normal  $\eta(\mathbf{r})$  at  $\mathbf{r}$  points into the void volume. Note that any of the three free path probabilities are zero if the straight line molecular path between  $\mathbf{r}$  and  $\mathbf{r'}$  is blocked by intervening solid material.

Suppose across a thick slab of statistically homogeneous material running between the parallel planes x = 0 and x = L we maintain a difference  $\Delta c = c_0 - c_L$  in the molecular number density. A variational principle for the effective diffusivity  $D_e$  (molecular flux per unit  $|\Delta c|/L$ ) was formulated in Ref. 3. To include surface diffusion, we need only add on an additional term in the surface diffusion coefficient  $D_s$ , the two dimensional gradient along the surface  $\nabla_s$ , and the Henry's law isothermal adsorption constant  $K_H$ :

$$(\Delta c/L)^{2} VD_{e} \leq (\overline{v}/8K_{H}^{2}) \int \int K_{1}(\mathbf{r},\mathbf{r}') [f_{s}(\mathbf{r}) - f_{s}(\mathbf{r}')]^{2} d^{2}\mathbf{r} d^{2}\mathbf{r}' + \beta \int \int K_{2}(\mathbf{r},\mathbf{r}') [f_{s}(\mathbf{r})/(\beta K_{H}) - f(\mathbf{r}')]^{2} d^{2}\mathbf{r} d^{3}\mathbf{r}' + (\beta/2) \int \int K_{3}(\mathbf{r},\mathbf{r}') [f(\mathbf{r}) - f(\mathbf{r}')]^{2} d^{3}\mathbf{r} d^{3}\mathbf{r}' + (D_{s}/K_{H}) \int [\nabla_{s}f_{s}(\mathbf{r})]^{2} d^{2}\mathbf{r} d^{3}\mathbf{r}$$

$$(2)$$

J. Chem. Phys. 74(8), 15 Apr. 1981

0021-9606/81/084742-02\$01.00

<sup>&</sup>lt;sup>a)</sup>Work supported by the Air Force Office of Scientific Research and the U. S. Israel Binational Science Foundation (BSF), Jerusalem, Israel.