

Accommodation Coefficients for Hydrogen Molecules on Graphite Surface

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Abstract. The scattering of hydrogen molecules from graphite surface was studied through molecular dynamics simulation. The trajectories of the hydrogen molecules and surface atoms were calculated. The distributions of velocity and energy after reflection were obtained depending on direction and quantity of the initial velocity. The energy and tangential momentum accommodation coefficients were calculated for cases where incident velocity distribution can be approximated by maxwellian function and mean velocity is negligible. Obtained coefficients are in satisfactory agreement with experimental data.

Keywords: molecular dynamics, tangential momentum and energy accommodation coefficients, hydrogen, graphite surface.

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Initially the gas atom scattering was investigated as applied to rarefied gas aerodynamics for aviation and space technology. Recently the attention to this field is also concerned with development of micro and nanotechnologies: gas-surface interaction is significant for studying flow in micro and nanostructures [1].

In this work the scattering of hydrogen molecules from graphite surface was studied. The reflection trajectories were computed through molecular dynamics simulation. Graphite surface was simulated by carbon atom layers (see fig.1). The Newton's equations for hydrogen molecule and carbon atoms were integrated with constant time step $\Delta t = 0.5 \cdot 10^{-15}$ s (leap-frog method) with periodic border conditions. The interaction between carbon atoms was expressed by two-particle potential $U_{CC}(r) = K(r - b)^2$ with parameters from [2] $K = 326$ J/m², $b = 1.4$ Å. The Lennard-Jones potential with parameters $\epsilon = 2.4$ meV, $\sigma = 3.37$ Å was used to describe interaction between atom pairs from different graphite layers [3, 4]. The interaction between carbon atom and hydrogen molecule was expressed by Lennard-Jones potential with $\epsilon = 2.76$ meV, $\sigma = 3.17$ Å [4].

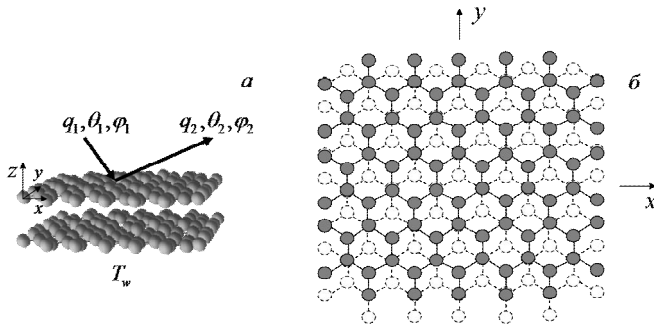


FIGURE 1. Computation scheme and graphite surface structure

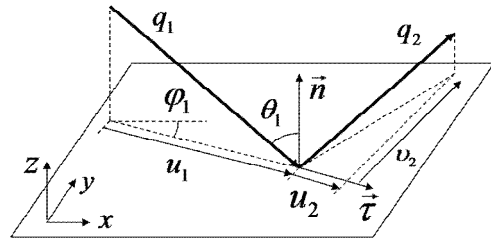


FIGURE 2. Velocities before and after reflection

Before the reflection trajectories computation the graphite structure was prepared by molecular dynamics simulation with temperature control. It is necessary for relaxation atom velocities, which were initially distributed

according with maxwellian function, and to equalize surface temperature. Obtained structure was used as initial for scattering computations.

Initially the hydrogen molecule was placed in $x = x_1, y = y_1, z = h$ with velocity \bar{q}_1 ($0 < q_1 \leq 10^4$ m/s, $0 \leq \theta_1 < \pi/2, 0 \leq \varphi_1 < 2\pi$; see fig.2). The coordinates x_1, y_1 were uniformly distributed, $h = 15A$. The simulation was up to molecule escaped from surface ($z > h$) or time limit $t_{\max} = 10^6 \cdot \Delta t$ was exceeded. This t_{\max} was sufficient for interaction and escape from surface in majority of cases. Even at low temperatures only negligible number of trajectories (less than 0.05%) were terminated by time out.

About $10^6 - 10^7$ trajectories were computed for each wall temperature $T_w = 87K, 283K, 1120K$ for different $q_1 = |\bar{q}_1|, \theta_1, \varphi_1, x_1, y_1$ (fig.2). Mean velocities \hat{u}_2 and \hat{v}_2 were computed by coordinate (x_1, y_1) averaging of corresponding velocities u_2 и v_2 (fig.2). It was obtained that dependence \hat{u}_2 и \hat{v}_2 on φ_1 is not essential and \hat{v}_2 is negligible (fig.3). Such result was obtained for all q_1, θ_1 and considered wall temperatures T_w . Therefore the scattering on studied surface is isotropic and velocity \hat{u}_2 is function of T_w, q_1, θ_1 : $\hat{u}_2 = \hat{u}_2(T_w, q_1, \theta_1)$. For molecule kinetic energy $e_2 = mq_2^2/2$ the similar result was obtained: $\hat{e}_2 = \hat{e}_2(T_w, q_1, \theta_1)$.

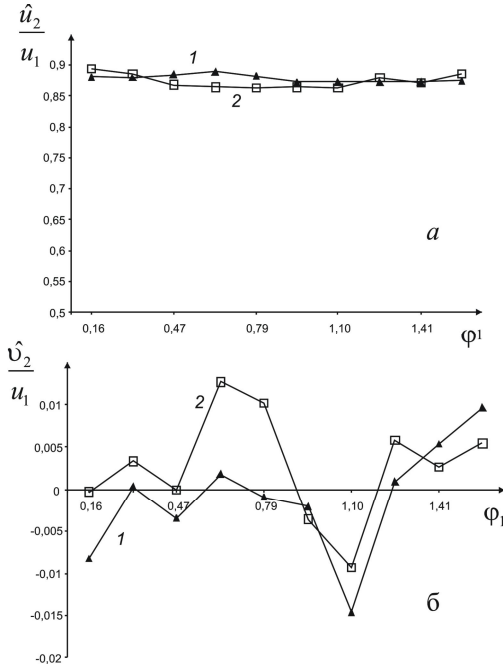


FIGURE 3. Mean velocities \hat{u}_2 and \hat{v}_2 dependence on φ_1 ($T_w = 283K, q_1 = 1800$ m/s, $\theta_1 = \pi/4$): 1- one carbon layer, 2- two carbon layers

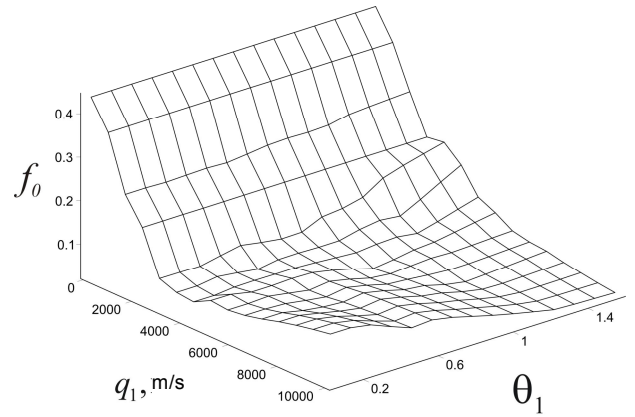


FIGURE 4. Tangential momentum accommodation coefficient f_0 for monovelocity beams ($T_w = 283K$)

The computation showed that in case of hydrogen on graphite surface at temperate velocities only one carbon atom layer was enough for simulation. An increasing of the layers number did not affect on scattering results (see fig.3). It can be explained by low interlayer interaction in comparison with covalent bonds. Note that in case of heavy gas particles and high incident energies it is necessary to simulate several carbon atom layers [3].

Tangential momentum accommodation coefficient f_0 for monovelocity beams depending on T_w, q_1, θ_1 is

$$f_0(T_w, q_1, \theta_1) = \frac{u_1(q_1, \theta_1) - \hat{u}_2(T_w, q_1, \theta_1)}{u_1(q_1, \theta_1)}$$

where $u_1(q_1, \theta_1) = q_1 \sin \theta_1$ – tangential velocity before reflection. Coefficient f_0 for $T_w = 283K$ is presented on fig.4.

In papers [5, 6] hydrogen-graphite interaction was experimentally investigated as applied to heat transfer between symmetric surfaces in free molecular regime. In this case velocity distribution function can be approximated by maxwellian function. In spherical coordinates

$$F(\vec{q}_1, T, \vec{U}) = \beta^3 \pi^{-3/2} q_1^2 \sin \theta_1 \exp\left(-\beta^2(\vec{q}_1 - \vec{U})^2\right), \quad \beta = \sqrt{\frac{m}{2kT}}$$

where T – gas temperature, \vec{U} – mean velocity.

It was shown above that scattering is isotropic. Mean velocity \vec{U} was assigned parallel with x-axis. Tangential momentum accommodation coefficient f and energy accommodation coefficient α were

$$f = \frac{P_1 - P_2}{P_1}, \quad \alpha = \frac{E_1 - E_2}{E_1 - E_w}$$

where P_1, E_1 – tangential momentum and energy of incident molecules, P_2, E_2 – tangential momentum and energy of reflected molecules, $E_w = 2kT_w$ – molecule energy if they were reflected with maxwellian distribution function with wall temperature T_w . In spherical coordinates

$$\begin{aligned} P_1 &= \frac{1}{N_1} n \int_0^\infty \int_0^{2\pi} \int_0^\pi (mq_1 \sin \theta_1 \cos \varphi_1) q_1 \cos \theta_1 F(\vec{q}_1, T, \vec{U}) dq_1 d\theta_1 d\varphi_1 \\ E_1 &= \frac{1}{N_1} n \int_0^\infty \int_0^{2\pi} \int_0^\pi \left(\frac{mq_1^2}{2}\right) q_1 \cos \theta_1 F(\vec{q}_1, T, \vec{U}) dq_1 d\theta_1 d\varphi_1 \\ P_2 &= \frac{1}{N_1} n \int_0^\infty \int_0^{2\pi} \int_0^\pi (m \cdot \hat{u}_2(T_w, q_1, \theta_1) \cdot \cos \varphi_1) q_1 \cos \theta_1 F(\vec{q}_1, T, \vec{U}) dq_1 d\theta_1 d\varphi_1 \\ E_2 &= \frac{1}{N_1} n \int_0^\infty \int_0^{2\pi} \int_0^\pi \hat{e}_2(T_w, q_1, \theta_1) \cdot q_1 \cos \theta_1 F(\vec{q}_1, T, \vec{U}) dq_1 d\theta_1 d\varphi_1 \end{aligned}$$

where n – numerical density, m – molecule mass, $N_1 = n/(2\sqrt{\pi}\beta)$ – incident flow.

Accommodation coefficients f and α are depended on mean velocity U . In studied case the flow mean velocity is negligible in comparison with mean thermal velocities [6]. The accommodation coefficients for slow flows can be obtained at $\beta U \rightarrow 0$:

$$\begin{aligned} F &= F_0 + \beta U \cdot 2\beta q_1 \sin \theta_1 \cos \varphi_1 \cdot F_0 + O(\beta^2 U^2), \quad F_0 = F(\vec{q}_1, T, 0) \\ P_1 &= mU, \quad E_1 = 2kT + O(\beta^2 U^2) \\ P_2 &= mU 4\sqrt{\pi} \beta^3 \int_0^\infty \int_0^{2\pi} \int_0^\pi \hat{u}_2 q_1^2 \cos \theta_1 \sin \theta_1 \cos^2 \varphi_1 F_0(\vec{q}_1, T) dq_1 d\theta_1 d\varphi_1 + O(\beta^2 U^2) \\ E_2 &= 2\sqrt{\pi} \beta \int_0^\infty \int_0^{2\pi} \int_0^\pi \hat{e}_2 q_1 \cos \theta_1 F_0(\vec{q}_1, T) dq_1 d\theta_1 d\varphi_1 + O(\beta^2 U^2) \\ f &\rightarrow f_*(T, T_w) = 1 - 4\sqrt{\pi} \beta^3 \int_0^\infty \int_0^{2\pi} \int_0^\pi \hat{u}_2 q_1^2 \cos \theta_1 \sin \theta_1 \cos^2 \varphi_1 F_0(\vec{q}_1, T) dq_1 d\theta_1 d\varphi_1 \\ \alpha &\rightarrow \alpha_*(T, T_w) = \frac{2kT - 2\sqrt{\pi} \beta \int_0^\infty \int_0^{2\pi} \int_0^\pi \hat{e}_2 q_1 \cos \theta_1 F_0(\vec{q}_1, T) dq_1 d\theta_1 d\varphi_1}{2kT - 2kT_w} \end{aligned}$$

Obtained coefficients $f_*(T, T_w)$ for $T_w=87, 283, 1120\text{K}$ are presented on fig.5 (curves 1–3 accordingly). Coefficient $f_*(T, T_w)$ decreases with gas temperature T rising. At high T coefficient $f_* < 0.2$ for each wall temperatures. At low gas temperature the dependence on wall temperature is considerable.

Energy accommodation coefficients $\alpha_*(T, T_w)$ for $T_w=87, 283, 1120\text{K}$ are presented on fig.6. Curves 1–3 were computed in this work, curves 4, 5 – in paper [7]. Points 6, 7 correspond to experimental data [5] for $T_w=87, 283\text{K}$ accordingly, 8 – experimental data [6] for $T_w=1120\text{K}$. Obtained α_* (curves 1–3) are in satisfactory agreement with experimental data in the wide range of gas and wall temperatures.

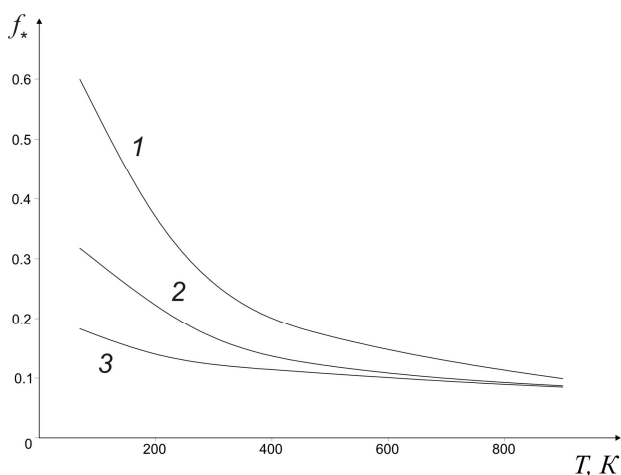


FIGURE 5. Tangential momentum accommodation coefficient f_* : 1, 2, 3 – $T_w=87\text{K}$, 283K , 1120K accordingly

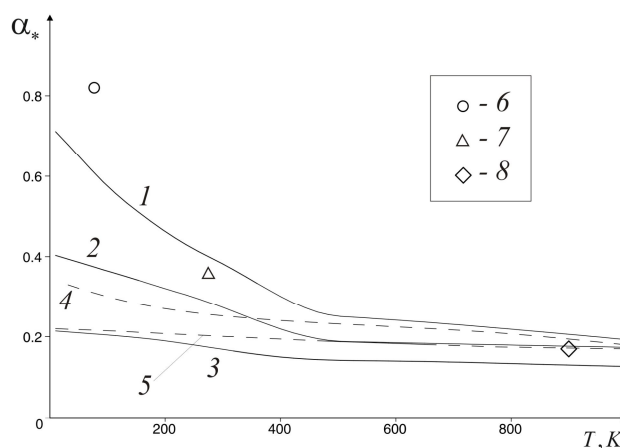


FIGURE 6. Energy accommodation coefficient α_* : 1, 2, 3 – $T_w=87\text{K}$, 283K , 1120K ; 4, 5 – results from [7] for $T_w=100\text{K}$, 1000K ; 6, 7 – experiment [5] for ($T_w=87\text{K}$, $T=77\text{K}$) and ($T_w=283\text{K}$, $T=273\text{K}$); 8 – experiment [6] for $T_w=1120\text{K}$, $T=900\text{K}$

At $T=20\text{--}400\text{K}$ coefficient α_* essentially depends on wall temperature T_w . With an increasing T this dependence becomes weaker and at $T>900\text{K}$ coefficient $\alpha_*=0.12\text{--}0.19$ in the wide range of wall temperatures $T_w=90\text{--}1100\text{K}$.

It was obtained that at low temperatures the time of molecule residence near the surface (physical adsorption) increases. It is in agreement with results [4, 8]. This intensifies the heat and momentum transfer between molecule and atom structure and leads to high quantities of accommodation coefficients.

CONCLUSION

The reflection trajectories of hydrogen molecules from graphite surface were calculated through molecular dynamics simulation. The distributions of velocity and energy after reflection were obtained depending on direction and quantity of the initial velocity. The energy and tangential momentum accommodation coefficients were calculated in the case where incident velocity distribution can be approximated by maxwellian function and mean velocity is negligible. It was obtained that wall temperature T_w essentially influences on accommodation processes at gas temperature $20\text{--}400\text{K}$. With an increasing gas temperature this dependence becomes weaker and at $T>900\text{K}$ coefficient $\alpha_*=0.12\text{--}0.19$ in the wide range of wall temperatures $T_w=90\text{--}1100\text{K}$. This result is in agreement with experimental data and other authors computations.

It was derived that high quantities of accommodation coefficients at low temperatures were caused by increasing the residence time of physically adsorbed molecule.

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