# Energy accommodation of gas molecules with free-standing films of vertically aligned single-walled carbon nanotubes

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**Abstract.** The scattering process of gas molecules on vertically aligned single-walled carbon nanotubes (VA-SWNTs) was investigated by the molecular beam technique. To investigate interactions between VA-SWNT films themselves and helium gas molecules without the presence of substrates, free-standing films were used. The scattered molecules are divided into three components; reflected molecules, diffusively transmitted molecules, and directly transmitted molecules without interaction with SWNTs. Even with the thin film, most molecules have interacted with the films, which suggests that most molecules have interacted at the randomly oriented layer at the topmost of the films. Because of low accommodation coefficients of helium gas, VA-SWNTs films are thought to be useful as a surface modification to enhance energy accommodation.

**Keywords:** Gas-surface interaction, Molecular beam, Carbon nanotubes
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## INTRODUCTION

Single-walled carbon nanotubes (SWNTs) [1] are one of carbon materials which have rounded shapes with six-membered carbon. SWNTs have recently drawn increasing attention from scientific and technological points of view because of their outstanding physical properties [2] such as high thermal conductivity, electric conductivity and optical anisotropy. When they are created by the chemical vapor deposition (CVD) with appropriate conditions, the uniform films grow consisting of vertically aligned SWNTs (VA-SWNTs) [3].

Because of their unique morphology, high aspect ratio and high thermal conductivity, the films of VA-SWNTs have drawn increasing attention for various kinds of mechanical applications, such as nanoscale gas sensors [4] and gas storage devices [5]. Among various kinds of applications, we focused on their potential applications as surface modifications to control gas-surface interactions, because their nanoscale fin-like structure would increase collisions between gas molecules and solid surfaces. According to our previous study [6], energy accommodation of gas molecules to the solid surface with VA-SWNTs was significantly increased compared to the bare surfaces. It is still unclear, however, about the detailed scattering behavior of gas molecules in the films, such as penetration depth of gas molecules to the frequency, collision times, or scattering distribution for various film thicknesses. The detailed understanding of the scattering process would also reveal geometrical structures and the growth process of VA-SWNT films, where feedstock gas molecules have to diffuse through the growing films to reach catalyst nanoparticles on the substrates.

In this paper, we present the scattering experiments of gas molecules on VA-SWNT films using the molecular beam technique to reveal interactions between the films and gas molecules. The experiments were conducted with helium molecules, which tend to exhibit low energy accommodation coefficients because of its large mass mismatch to surface atoms. Because of this behavior, helium is a good proving species to observe the energy transfer enhancement by surface modifications with VA-SWNTs. To investigate the interactions between the films themselves and gas molecules without the presence of substrates, we used free-standing films of VA-SWNTs [8]. The time-of-flight distributions and the angular distributions of reflected or transmitted molecules were measured to analyze the scattering mechanism. We also measured intensity of transmitted molecules for different film

thicknesses. We found that energy accommodation was significantly enhanced even without substrates, and most molecules interacted at the randomly oriented top layer of the films

## EXPERIMENT

The samples used were the films of VA-SWNTs grown on quartz glass substrates by the alcohol CVD method [3]. After the samples were made, they were transferred to the stainless-steel plates which have a hole of a diameter of 2 mm to make free-standing films (Fig.1(a)). SWNTs in the films are intertwined to form bundles, which typically consist of less than ten SWNTs per bundle, and have an average diameter of 2 nm [9-11]. Figure 1(b) shows the secondary electron microscopy (SEM) images of the samples. They show that the thicknesses of the samples were approximately 20 μm, 4 μm and 0.1 μm. The sample consists of two layers [12]; the randomly oriented layer at the top in which SWNTs grow randomly, and the aligned layer below in which SWNTs are aligned vertically [13]. The thickness of any randomly oriented top layer is known to remain roughly constant regardless of the overall film thickness. These samples are estimated to have the porosity of 97% [14] although the detailed structure is still unclear. The temperatures of samples were kept at room temperature during the measurements.

Figure 2 illustrates the configurations of the experiment. The experiment was conducted in an ultrahigh vacuum chamber equipped with a supersonic molecular beam source at room temperature [7]. The sample holders were mounted on a sample manipulator, which can rotate to change the beam incident angle $\theta_i$. We used helium gas as the incident gas, the translational energy of which was about 0.06 eV. Before entering the chamber, the beam was modulated by a random chopper, whose slit pattern was determined by the M-sequence random number [15]. The time-of-flight (TOF) distribution for the pulsed beam was recovered by calculating the cross-correlation of measured signal and the modulation sequence. The chopper disk has two cycles of the M-sequence with $N$=255 and was rotated with a period of 5100 μs, so that the temporal resolution was maintained at 10 μs. After the molecular beam entered into the films, it was scattered or transmitted from the free-standing films. The time-of-flight (TOF) distributions of these scattered molecules were detected using a quadrupole mass spectrometer (QMS), which could move along the chamber wall to detect molecules for each scattering angles.

The TOF distribution $S(t)$ for pulsed beam is expressed as the convolution integral

$$S(t) = \int_{-\infty}^{\infty} R(t-\tau)[\gamma P_{dir}(\tau) + (1-\gamma)P_{ads}(\tau)]d\tau\,, \tag{1}$$

where $R(t)$ is the TOF distribution of incident beam from the chopper to the surface of a sample, $P_{dir}(t)$ and $P_{ads}(t)$ the TOF distributions of molecules scattering from the surface to the QMS. We assume that TOF of scattered molecules can be expressed as superposition of the direct inelastic scattering component $P_{dir}(t)$, and the trapping-desorption component $P_{ads}(t)$, with a weighting factor $\gamma$ $(0 \le \gamma \le 1)$ [16]. The former component is poorly accommodated to the surface temperature and has a low translational energy and a large drift velocity, while the latter is completely accommodated to the film. Specifically, they are assumed to follow Maxwell-Boltzmann distribution and expressed as

$$P_{dir}(t) = \begin{cases} \dfrac{c_1}{t^4}\exp\left\{-\dfrac{1}{{\alpha_1}^2}\left(\dfrac{L}{t}-U\right)\right\} & (t>0) \\ 0 & (t\le 0), \end{cases} \tag{2}$$

$$P_{ads}(t) = \begin{cases} \dfrac{c_2}{t^4}\exp\left\{-\dfrac{1}{{\alpha_2}^2}\left(\dfrac{L}{t}\right)\right\} & (t>0) \\ 0 & (t\le 0), \end{cases} \tag{3}$$

$$\alpha_i = \sqrt{2k_B T_i / m} \quad (i = 1, 2), \tag{4}$$

where $L$ is the distance between the surface and the QMS, $U$ is the drift velocity, $\alpha_1$ and $\alpha_2$ are the most probable speeds expressed in equation (4), $c_1$ and $c_2$ are the normalization constants, and $k_B$ the Boltzmann constant, $T_1$ is the translational temperature of the direct inelastic component, while $T_2$ is the translational temperature of the trapping-

desorption component, which is equal to the surface temperature of the film. We determined the parameters $\alpha_1$, $\alpha_2$, $U$, $T_1$ and $\gamma$ by a least square fit. The mean translational energies of each component are given by

$$E_1 = \frac{1}{2} m\alpha^2 \times \frac{\sqrt{\pi} S(15/4 + 5S^2 + S^4)\{1 + \mathrm{erf}(S)\} + (1/2 + S^2)(4 + S^2)\exp(-S^2)}{\sqrt{\pi} S(3/2 + S^2)\{1 + \mathrm{erf}(S)\} + (1 + S^2)\exp(-S^2)}, \tag{5}$$

$$E_2 = m\alpha_2^{\,2}, \tag{6}$$

where $m$ is the mass of a gas molecule, and $S$ the speed ratio defined by $U/\alpha_1$. We can thus evaluate the mean translational energy of scattered molecules with

$$E_f = \gamma E_1 + (1-\gamma)E_2. \tag{7}$$

Since the scattering directions of molecules are on the plane spanned by the normal vector of the surface and the velocity vector of the incident molecules, where our measurements were limited to the in-plane, we assumed that the mean translational energy and intensity of gas molecules depends only on the angle between the scattering direction and surface normal. Thus we can estimate the energy and intensity of molecules on the plane. The energy accommodation coefficients $\alpha$ are defined by

$$\alpha = (\overline{E}_f - \overline{E}_i)/(2k_B T_s - \overline{E}_i), \tag{8}$$

where $\overline{E}_i$ is the mean translational energy of the incident beam, $T_s$ the surface temperature. Note that $2k_b T_s$ is the mean translational energy of desorbing gas molecules from the equilibrium state on the surface. According to Table 1, $\alpha$ is usually about 0.3 ~ 0.4 to the bare surfaces even though the surfaces are contaminated. Helium, a light molecule, tends to show low energy accommodation coefficients because of its large mass mismatch to the surface atoms. As reported previously, energy accommodation coefficient show a high value on quartz substrates with VA-SWNT film, proving effectiveness of the film as a surface modification material to enhance energy accommodation between solid surfaces and gas molecules.

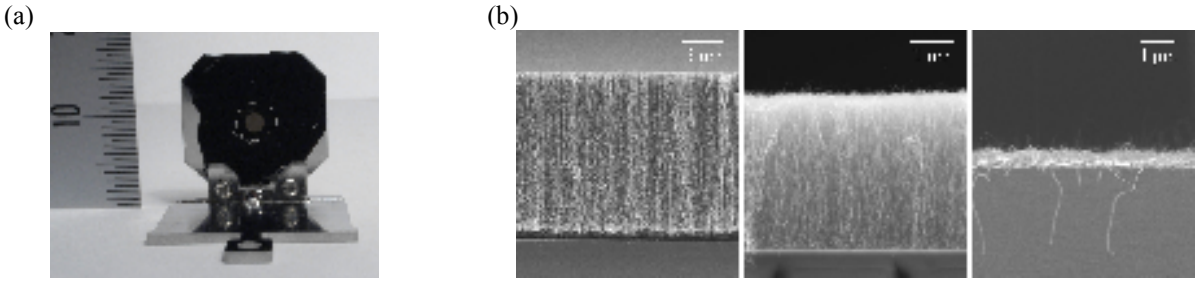



**FIGURE 1.** (a) The sample holder for free-standing samples, (b) the SEM images of VA-SWNT films grown on quartz substrates: the side view images of the films with thicknesses of 20 μm (left), 4 μm (center), and 0.1 μm (right).

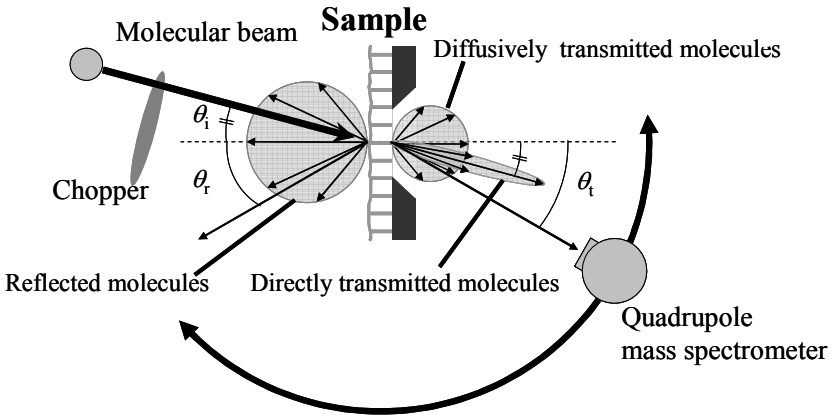



**FIGURE 2.** The schematic illustration of the experiments with the free-standing film.

**TABLE 1.** The energy accommodation coefficients of He gas molecules on various surfaces

| Surface | Temperature[K] | α |
|---|---|---|
| Quartz substrate with Co-Mo catalyst nanoparticles | Room temperature | 0.34 |
| Nickel (gas covered) [17] | 273 | 0.360 |
| Nickel (gas covered) [18] | Room temperature | 0.385 |
| Tungsten (gas covered) [19] | 331 | 0.0186 |
| Tungsten (gas covered) [18] | Room temperature | 0.470 |
| Platinum (gas covered) [17] | 273 | 0.17 |
| Platinum (gas covered) [18] | Room temperature | 0.368 |
| VA-SWNT film on quartz substrate (4 μm in thickness) [6] | Room temperature | 0.97 |
| VA-SWNT film on quartz substrate (0.1 μm in thickness) [6] | Room temperature | 0.82 |

## RESULTS AND DISCUSSION

Figures 3 and 4 show the normalized TOF distributions and the angular distributions of helium molecules scattered on the free-standing films with thicknesses of 0.1μm, 4μm and 20μm. As shown in Fig. 2, $\theta_i$ is the beam incident angle, $\theta_r$ and $\theta_t$ are the scattering angles for reflected and transmitted molecules, respectively.

The scattered molecules are divided into three components; molecules reflected from the substrates, directly transmitted molecules without interaction with the films, and diffusively transmitted molecules having interacted with the SWNTs. The degree of interaction between gas molecules and the films was evaluated from their TOF distributions.

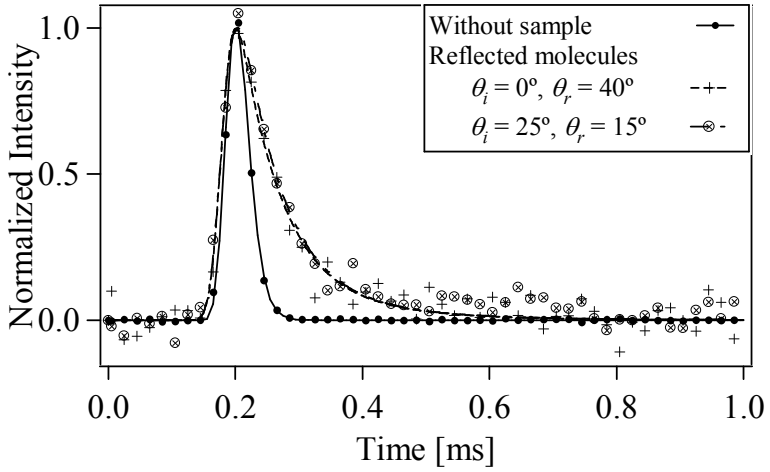
Figure 3 shows the normalized TOF distributions of each component. The data of 'without sample' means the TOF distribution of the incident beam with the sample retracted from the beam path. The TOF distributions of reflected molecules (Fig. 3(a)) are almost the same regardless of the incident angle and reflected angle, suggesting that the amount of the energy transfer during the scattering is independent of these angles. The accommodation coefficients were about 0.8, showing quite effective energy accommodation in spite of large mismatch between helium molecules and surface atoms. Figure 4 shows the angular distribution of reflected molecules for incident angles of $0^\circ$ and $25^\circ$. The angular distributions roughly follow the cosine distribution. The diffusive (i.e. cosine) distribution originates from the complicated structure of the top portion of the film layer, which makes the scattering direction independent of the incident angle. Since molecular dynamics simulations [19] predict inefficient energy transfer during a single scattering event of helium on SWNT surface ($\alpha \sim 0.25$), we believe that incident molecules collide with SWNTs surfaces several times before leaving the film.

The normalized TOF distributions of directly transmitted molecules ($\theta_t = 0^\circ$) agree with that of the incident beam with the sample retracted from the beam path (Fig. 3(b)). This means that these molecules do not interact with the films at all and preserve their incident velocities. As the transmitting angle $\theta_t$ off the beam axis increases, the TOF distribution becomes broader and approaches that corresponding to perfect accommodation.

Table 2 shows the ratio of each scattering component for different film thicknesses. Even with the film of 0.1 μm in thickness, few molecules are directly transmitted through the film and most molecules are reflected with quite effective energy accommodation. This means that most molecules collide with SWNTs and accommodated to the surface temperature within the randomly oriented layer. With the film of 4 μm in thickness, few molecules are transmitted the film while the ratio of reflected molecules did not change so much. There was no molecules transmitted to the film when the film as thick as 20 μm. From these results, we conclude that most molecules interact with SWNTs in the randomly oriented layer by estimating transmitted molecules with free-standing film.

These discussions demonstrate the effectiveness of the surface modification with VA-SWNT films for enhancing the energy transfer between helium gas molecules and surfaces at around room temperature. Since efficient energy accommodation was achieved even with the film as thin as 0.1 μm for helium, which in most cases hardly accommodate to the surface temperature because of the large mass mismatch described above, the surface modification with VA-SWNTs would work quite effectively for other heavier molecules.

(a)




(b)

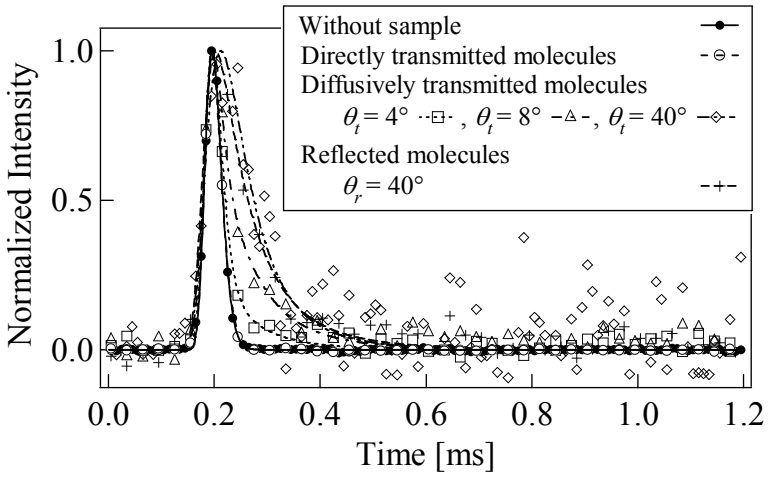



**FIGURE 3**. The TOF distributions of helium molecular beam ( $\overline{E}_i = 0.06$ eV) scattered from a free-standing VA-SWNT film at 300 K with a thickness of 0.1 μm; (a) reflected molecules and (b) directly and diffusively transmitted molecules. The TOF distribution of the incident beam with the sample retracted from the beam path is also plotted for reference.

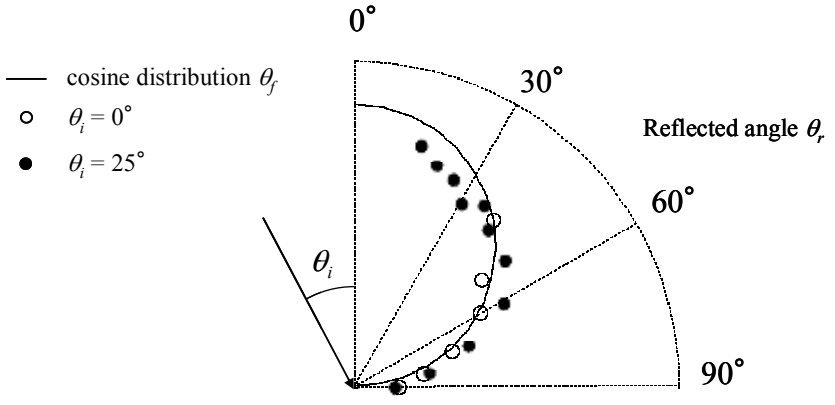



**FIGURE 4.** Angular distributions of reflected molecules when the incident angles are $0^\circ$ and $25^\circ$.

**TABLE 2.** The ratio of each scattering component

| Film thickness [μm] | Reflected molecules | Directly transmitted molecules | Diffusively transmitted molecules |
|---|---|---|---|
| 0.1 | 0.7 | 0.1 | 0.2 |
| 4 | 0.7 | 0.005 | 0.3 |
| 20 | 1 | ~0 | ~0 |

## CONCLUSION

We have investigated the scattering of helium molecules on free-standing vertically aligned single-walled carbon nanotubes (VA-SWNTs) using the molecular beam technique. The free-standing films made it possible to measure the molecules reaching the bottom of the film and to estimate the penetration depth of gas molecules into the films. Even for the film as thin as 0.1 μm, which consists primarily of the randomly oriented layer, most of incident molecules have interacted with the films, showing quite effective energy accommodation to the surface temperature in spite of large mass mismatch between helium molecules and surface atoms. Our results suggest that VA-SWNT films are promising material for surface modification to promote energy transfer between gas molecules and surfaces.

## REFERENCES


1. S. Iijima and T. Ichihashi, Nature 363, 603-605 (1993).
2. R. Saito et al., Physical Properties of Carbon Nanotubes, London: Imperial College Press, 1998.
3. Y. Murakami et al., Chem. Phys. Lett. 385, 298-303 (2004).
4. P.G. Collins, et al., Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes, Science, **287**, 1801-1804, 2000.
5. C. Liu, et al., Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature, Science, **286**(5542), 1127-1129, 1999.
6. I. Kinefuchi et al., in *Proc. of 26th Int. Symp. on Rarefied Gas Dynamics*, AIP, New York, 2009, pp. 629-634.
7. I. Kinefuchi et al., "Out-of-plane Scattering Distribution of Nitrogen Molecular Beam on Graphite (0001) Surface" in *Rarefied Gas Dynamics: 24th International Symposium on Rarefied Gas Dynamics*, edited by M. Capitelli, AIP Conference Proceedings 762, American Institute of Physics, Melville, NY, 2005, pp. 947-952.
8. Y. Murakami and S. Maruyama. Detachment of vertically aligned single-walled carbon nanotube films from substrates and their re-attachment to arbitrary surfaces. *Chemical Physics Letters*, Vol. 422, No. 4-6, pp. 575–580, 2006.
9. R. Saito, et al., Physical Properties of Carbon Nanotubes, Imperical College Press, London, 1998.
10. R. H. Baughman et al., Carbon Nanotubes—the Route Toward Applications, Science 297, 787, 2002.
11. R. S. Ruoff and D. C. Lorents, Mechanical and Thermal Properties of Carbon Nanotubes, Carbon, 33 (7), 925-930, 1995.
12. Komukai, K.Aoki, H. Furuta, M.Furuta, K.Oura, and T.Hirao, Structual Analysis of High-Density Vertically Aligned Carbon Nanotubes Grown by Thermal Chemical Vapor Deposition with Fe/Al Multilayer Catalyst, *Japanese Journal of Applied Physics*, Vol.45, No. 11, pp.8988-8990, 2006.
13. T. Komukai, et al., Structural Analysis of High-Density Vertically Aligned Carbon Nanotubes Grown by Thermal Chemical Vapor Desorption with Fe/Al Multilayer Catalyst, J. J. Appl. Phys., **45**(11), 8988-8990, 2006.
14. R. Xiang et al., J. Phys. Chem. C 112, 4892-4896 (2008).
15. V. L. Hirschy et al., *The Review of Scientific Instruments*, **42**(3), pp. 381-383(1971).
16. J. E. Hurst et al., Phys. Rev. Lett. 43, 1175-1177 (1979).
17. P. Rolf, Phys. Rev. 65, 185-189 (1944).
18. I. Amdur and L. A. Guildner, J. Am. Chem. Soc. 79, 311-315 (1957).
19. D. V. Roach and L. B. Thomas, "Determination of Thermal Accommodation Coefficients of Gases on Clean Surfaces at Temperatures Above 300 K by the Temperature Jump Method" in Fifth Symposium on Rarefied Gas Dynamics, edited by C. L. Brundin, New York: Academic Press, 1967, Vol. 1, pp. 163-172.
20. K. Bolton and A. Rosen. Computational studies of gas-carbon nanotube collision dynamics. *Physical Chemistry Chemical Physics*, Vol. 4, No. 18, pp. 4481–4488(2002).