Experimental estimate of energy accommodation coefficient at high temperatures

I. S. Altman,[1,2] D. Lee,[1] J. Song,[1] and M. Choi,[1,*]
[1]National CRI Center for Nano Particle Control, Institute of Advanced Machinery and Design,
School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, Korea
[2]Physics Department, Odessa National University, Dvoryanskaya 2, 65026, Odessa, Ukraine
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The energy accommodation coefficient (EAC), which is used to characterize gas-surface interactions, was experimentally estimated at high temperatures. A method utilizing laser irradiation to heat up nanoparticles that are generated in a flame was proposed. From the obtained dependence of particle temperature upon laser power, the EAC was derived to be approximately equal to 0.005, which agrees nicely with our recent rigorous theoretical result. It indicates that the efficiency of heat transfer between gas and particles is sufficiently small in high temperature system at large Knudsen numbers.

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I. INTRODUCTION

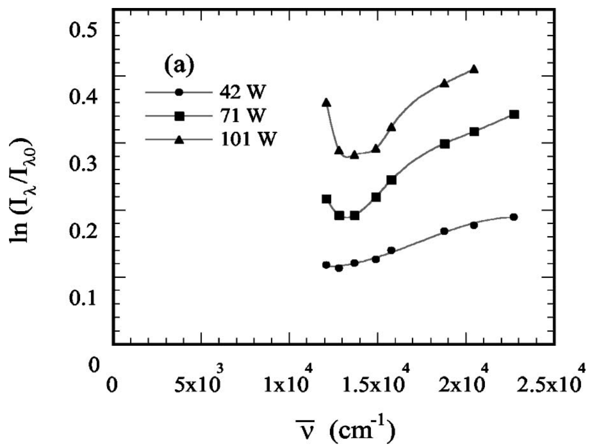
Different accommodation coefficients have been traditionally used to describe the interaction between a gas and a condensed body [1]. These coefficients have been extensively studied both theoretically and experimentally [1–9]. In addition to being of scientific significance, the values of accommodation coefficients are very important for different practical applications. In particular, the flame synthesis of nanoparticles requires an understanding of the macroscopic average heat transfer between gas and nanoparticles in the flame. The efficiency of this heat transfer that occurs in free-molecular regime of collisions is defined by the energy accommodation coefficient (EAC), which should be known to describe the particle temperature history. This leads to a need to know the EAC at high temperatures. In order to verify the EAC used, its theoretical and experimental values should be compared. Such a comparison has been successfully made at low temperatures. However, there is some uncertainty at high temperatures, because of a lack of experimental information.

It should be mentioned that two different approaches, in principle may be used to model gas-surface interactions, classical and quantum-mechanical models. The soft-cube model, for instance, was used as a classical model for EAC calculation [2]. In this model, a surface particle is attached by a single spring to a fixed lattice. Here we avoid discussing the detail of such models, but note that it is usually very difficult to satisfy the principle of detailed balancing in the framework of the classical model. Furthermore, one of the main postulates of the classical consideration, related to the continuity of energy transferred at the gas-surface collision, violates the discrete character of oscillator energy states [10]. In terms of the quantum-mechanical modeling of EAC, the condensed body is considered as an ensemble of phonons. Unlike the classical consideration, the quantum-mechanical model itself satisfies the detailed balancing. However, the problem with the unitarity appears at the probability calculation that may lead to the loss of generality of the quantum-mechanical result.

Recently, it was proposed to apply quantum mechanics in order to get the upper estimate of the EAC value at high temperatures instead of seeking its exact calculation that is the unsolvable problem, in principle [11]. The result based on detailed balancing alone shows that the EAC is bounded above by an expression that asymptotically tends to zero [11]. Then, for instance, independently on the gas-surface molecule mass ratio, the EAC value is less than 0.01 at a typical temperature of approximately 2000 K in the flame aerosol systems. Such an estimate would be useful for different applications, such as the laser-induced incandescence technique [12] for *in situ* sizing of aerosols. The smallness of EAC is very important for the description of nanoparticle formation in a flame, and leads to some critical behavior in the particle growth [13]. It should be pointed out that the general result of classical models, like the soft-cube model, is that EAC tends asymptotically to the limited value at an infinite temperature. This value is determined by the ratio of the masses of the gas molecule and the surface particle. The EAC may be small in the case of a small mass ratio and close to unity in the case of gas and condensed molecules of similar masses. Thus the value of EAC was found experimentally to be approximately 0.015 for He-W and 0.9 for Xe-W system at low temperatures [14]. Measurements at intermediate temperatures indicate that the EAC value may decrease with the increase of the condensed body temperature [9]. To our knowledge, the measurement of EAC at high gas and condensed body temperatures has not been done yet. A measurement of EAC at high temperatures is needed to determine the appropriate choice for EAC modeling. The importance of the knowledge of the EAC value at high temperatures for various applications should also be taken into account.

It is very difficult to measure the EAC at high temperatures using usual techniques [1]. In this paper we propose an approach that allows us to estimate the value of EAC at high temperatures. The idea of this approach lies in the study of heating up silica nanoparticles by a laser irradiation directly within a flame that generates these particles. The main difficulty is the principle impossibility of measuring the actual particle temperature. However, only a knowledge of particle

*Corresponding author. Email address: mchoi@plaza.snu.ac.kr



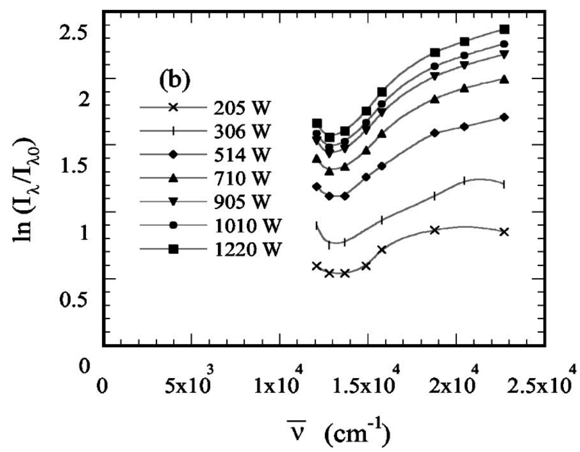


FIG. 1. Ratio of flame radiation intensities with and without laser irradiation for different laser powers.

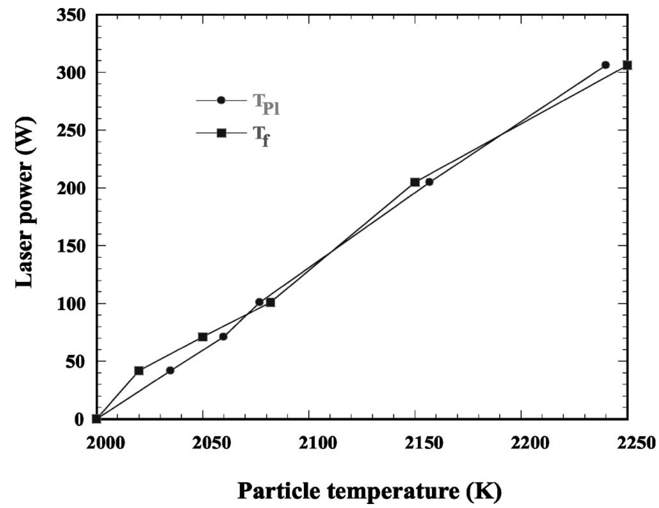


FIG. 2. Dependence of particle temperature on laser power: T_{P_l}, the present study; T_f Ref. [18].

temperature changes within the laser beam is sufficient for the EAC estimate. Motivated by this, we developed a technique to extract these temperature changes from the variations of flame luminosity during laser irradiation. The obtained dependence of the particle temperature upon the laser power allows us to estimate the EAC value. To the best of our knowledge, it was found to be very small at high temperatures for the first time in the system of gas and condensed molecules of similar masses.

II. METHOD AND RESULTS

According to the usual approach to EAC determination, the temperature difference between a condensed body and gas should be measured at a known heat flux. In the case of a particle within a flame, these values cannot be directly measured. However, the determination of the changes of the particle temperature at the known variations of heat flux allows us to extract EAC. In the case of a nanoparticle existing in a flame, the variation of heat flux between the particle and the gas may be realized by heating up the particle by a CO_2 laser beam, for example [15]. The main problem is then to obtain the change of particle temperature. It should be noted that absolute measurement of particle temperature within a flame is impossible in principle, because of a lack of *a priori* information about particle emissivity [16,17] In order to determine the change of particle temperature, we used the result of the measurement of the luminosity of the flame when irradiated by a CO_2 laser [17]. The luminosity was measured from the flame region where only spherical particles exist [15].

The CO_2 laser irradiation leads to particle heating and a change of flame luminosity. The measured ratio of the flame radiation intensities I_λ at the wavelength λ with and without laser irradiation is given by

$$\ln\left(\frac{I_\lambda}{I_{\lambda_0}}\right)=\ln\left(\frac{f_V}{f_{V_0}}\right)+\frac{hc}{k_B}\bar{\nu}\left(\frac{1}{T_{P_0}}-\frac{1}{T_P}\right)+\ln\left[\frac{q(\lambda,T_P)}{q(\lambda,T_{P_0})}\right], \tag{1}$$

where $\bar{\nu}\equiv 1/\lambda$ is the wave number, f_V is the particle volume fraction, T_P is the particle temperature in the flame, and q is the ratio of particle emissivity to its radius. Here the subscript 0 denotes the value without laser irradiation. In the case of the linear dependence of $\ln(I_\lambda/I_{\lambda_0})$ on the wave number, the slope of this dependence yields the change of the inverse of the particle temperature. However, regardless of laser power, a similar pattern, showing an inflection point, was found in Ref. [17]. Changes of particle temperature cannot then be directly obtained. The nonlinear behavior of $\ln(I_\lambda/I_{\lambda_0})$ stems from the nonlinear behavior of $\ln[q(\lambda,T_P)/q(\lambda,T_{P_0})]$ as reported in Ref. [17]. The typical logarithm of the ratio of the flame radiation intensities I with and without laser irradiation has been measured in Ref. [17] and is shown in Fig. 1. The wave numbers corresponding to this inflection point are the same for all laser powers used and coincide with the wave number in the inflection point of $\ln[q(\lambda,T_{P_0})]$. This inflection point just allows us to estimate the change of the particle temperature. At the inflection point, the particle temperature change can be expressed as

$$\frac{1}{T_{P_0}}-\frac{1}{T_P}=\frac{k_B}{hc}\left[\frac{d\ln(I_\lambda/I_{\lambda_0})}{d\overline{\nu}}-\frac{q(\lambda,T_{P_0})\frac{\partial^2 q(\lambda,T_P)}{\partial\overline{\nu}^2}-q(\lambda,T_P)\frac{\partial^2 q(\lambda,T_{P_0})}{\partial\overline{\nu}^2}}{q(\lambda,T_{P_0})\frac{\partial q(\lambda,T_P)}{\partial\overline{\nu}}+q(\lambda,T_P)\frac{\partial q(\lambda,T_{P_0})}{\partial\overline{\nu}}}\right]_{infl.p.}. \qquad (2)$$

Since the wave numbers corresponding to the inflection point are the same regardless of the applied laser powers, which means independence on the particle temperature, we can write

$$\frac{\partial^2}{\partial\overline{\nu}^2}[\ln(q(\lambda,T_{P_0}))]_{infl.p.}=0, \qquad (3)$$

$$\frac{\partial^3}{\partial T_P\partial\overline{\nu}^2}[\ln(q(\lambda,T_P))]_{infl.p.}=0. \qquad (4)$$

Using Eqs. (3) and (4) yields

$$\frac{1}{T_{P_0}}-\frac{1}{T_P}=\frac{k_B}{hc}\left[\frac{d\ln(I_\lambda/I_{\lambda_0})}{d\overline{\nu}}-2(T_P-T_{P_0})\frac{\frac{\partial q(\lambda,T_{P_0})}{\partial\overline{\nu}}\frac{\partial^2 q(\lambda,T_{P_0})}{\partial T_{P_0}\partial\overline{\nu}}-\frac{\left\{\frac{\partial q(\lambda,T_{P_0})}{\partial\overline{\nu}}\right\}^2}{q(\lambda,T_{P_0})}\frac{\partial q(\lambda,T_{P_0})}{\partial T_{P_0}}}{q(\lambda,T_{P_0})\frac{\partial q(\lambda,T_P)}{\partial\overline{\nu}}+q(\lambda,T_P)\frac{\partial q(\lambda,T_{P_0})}{\partial\overline{\nu}}}\right]_{infl.p.}. \qquad (5)$$

Since the particle emission coefficient q is due to the tail absorption deep in the forbidden band [17], it is obvious that

$$\frac{\partial q(\lambda,T_{P_0})}{\partial\overline{\nu}}\geqslant 0, \qquad (6)$$

$$\frac{\partial q(\lambda,T_{P_0})}{\partial T_{P_0}}\geqslant 0, \qquad (7)$$

$$\frac{\partial^2 q(\lambda,T_{P_0})}{\partial T_{P_0}\partial\overline{\nu}}\leqslant 0. \qquad (8)$$

Then Eqs. (2)–(8) lead to

$$\frac{1}{T_{P_0}}-\frac{1}{T_P}\geqslant\frac{k_B}{hc}\left[\frac{d\ln(I_\lambda/I_{\lambda_0})}{d\overline{\nu}}\right]_{infl.p.}. \qquad (9)$$

Then the expression

$$\frac{1}{T_{P_0}}-\frac{1}{T_{P_l}}=\frac{k_B}{hc}\left[\frac{d\ln(I_\lambda/I_{\lambda_0})}{d\overline{\nu}}\right]_{infl.p.} \qquad (10)$$

gives a lower estimate T_{P_l} for the particle temperature in the flame irradiated by CO_2 beam. The particle temperature in the flame without CO_2 irradiation, T_{P_0}, is about 2000 K [17]. The lower estimate of the particle temperature calculated in accordance with Eq. (10) is given in Fig. 2. For comparison, the particle temperature T_f obtained by a fitting of $\ln(I_\lambda/I_{\lambda_0})$ dependence [18] is also presented in Fig. 2. This fitting was made on the base of the theory of light absorption in the case of strong Coulomb disorder of heavily doped semiconductors [19]. As can be seen from Fig. 2, the two estimates of particle temperatures that are obtained by different methods give approximately the same values. The similarity of T_{P_l} and T_f is apparently caused by negligible value of the second term on the right-hand side of Eq. (2) calculated at the inflection point. This estimate can then be used to extract the EAC value.

The temperature of a particle within a flame irradiated by a laser beam is determined by four physical processes, namely, laser absorption, particle radiation, heat transfer to the surrounding gas, and particle evaporation. For small particles (compared with the mean free path of gas molecule), the following heat balance equation can be written as a function of the particle temperature after consideration of the cases with and without laser irradiation

$$q_0 a\frac{4W}{\pi D^2}\pi a^2=Q_{av}\sigma(T_P^4-T_{P_0}^4)4\pi a^2+\frac{\alpha_E P_g c_t}{8T_g}\frac{\gamma+1}{\gamma-1}(T_P-T_{P_0})4\pi a^2+(G_V-G_{V_0})\Delta H 4\pi a^2, \qquad (11)$$

where W is the applied power of the laser, D is the diameter of the laser beam, q_0 is the particle absorption coefficient at the wavelength of the CO_2 laser (10.6 μm), and σ is the Stefan-Boltzmann constant. Here α_E is the energy accommodation coefficient, P_g is the gas pressure, T_g is the gas temperature, c_t is the average thermal velocity of gas molecules, γ is the ratio of the specific heat of gas at constant pressure to its value at constant volume, G_V is the flux density of vapor leaving the particle, ΔH is the specific heat of evaporation, a is the particle radius, and Q_{av} is the particle absorption efficiency averaged with the Planck function.

It is obvious that

$$q_0 a \frac{4W}{\pi D^2} \pi a^2 \geqslant \frac{\alpha_E P_g c_t}{8T_g} \frac{\gamma+1}{\gamma-1} (T_P - T_{P_0}) 4\pi a^2. \quad (12)$$

Therefore,

$$\alpha_E \leqslant \frac{q_0 a}{\pi D^2} \frac{8T_g}{P_g c_t} \frac{\gamma-1}{\gamma+1} \frac{dW}{dT_P}. \quad (13)$$

We then used the numerical values corresponding to the experiment, which are $q_0 = 1.7\times10^3$ cm^{-1}, $D=3.3$ mm, $a=40$ nm, $T_g=2000$ K, $\gamma=1.4$ (nitrogen), $P_g=1$ atm, $c_t=1230$ m/sec, and the value $(dW/dT_{P_l}) \simeq 1.2$ W/K corresponding to data in Fig. 2. The obtained energy accommodation coefficient is $\alpha_E \leqslant 0.005$. It should be noted that for calculation of q_o we used the optical constant of fused silica at high temperature [20].

III. DISCUSSION AND CONCLUSIONS

In this study we reveal that the upper estimate for the value of the energy accommodation coefficient for the heat transfer between silica nanoparticles and gas is very small. Of course one should be wary about accepting the absolute value of the EAC determined, although the order of magnitude seems to be correct. The possible errors can be attributed to the following. The exact dependence of $W(T_P)$ might be less steep than that of $W(T_{P_l})$, leading to lower values of EAC. In order to avoid a question related to the possible heating of gas by its absorption of laser irradiation, we conducted a special experiment on gas temperature measurement in flame without nanoparticles. The temperature increment was not more than 100 K at a laser power 1000 W. This can lead to an error of the EAC estimate not larger than 15%. Possible gas heating by the energy removal from the silica nanoparticles was disregarded due to the tiny particle volume fraction within flame. It is obvious that the change of the particle temperature is proportional to the particle volume fraction if the gas heating through heat transfer between the irradiated particles and the gas is significant. In order to confirm the negligible gas heating, we experimentally estimated the variation of the particle temperature change in the laser beam at different flame regions, in which the relative particle volume fraction could be determined by scattering measurement [15,21]. The change of particle temperature was found to be not considerably dependent on the particle volume fraction. Therefore, we believe that the obtained upper estimate of the EAC value 0.005 is reasonably accurate. This experimental value is in a good agreement with the theoretically predicted behavior of the EAC at high temperatures [11]. This EAC tendency to become sufficiently low at high temperatures (unlike the value about 1 that has been usually used) is indicative of an inefficiency of heat transfer between the gas and the particle at high temperatures, if gas-particle collisions occur in free-molecular regime. The smallness of the EAC should be taken into account when the heat transfer is considered within the high temperature ultrafine aerosol systems, which are ranged from the combustion nanoparticle synthesis to the interstellar grain formation.

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