Technical Notes

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Direct Simulation of Chemical Reactions

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Introduction

THE Direct Simulation Monte Carlo method (DSMC) of Bird[1] has been developed over a number of years and is now regarded as a powerful tool for the investigation of flows with Knudsen number greater than about 0.005. One of the most important applications of this computational technique is in the analysis of re-entry flow phenomena[2] in which a significant degree of chemical nonequilibrium exists. Procedures for modeling chemical reactions within the DSMC framework have been developed by Bird.[3,4] It is the purpose of this Note to report on instabilities in these formulations and to introduce a new simplified method in which such difficulties are removed.

Procedure of Bird

The rate of change in number density of a species A is usually described by

$$\frac{-\,\mathrm{d}n_A}{\mathrm{d}t} = k_f(T)n_A n_B - k_r(T)n_C n_D \tag{1}$$

where n_A, n_B are the reactants, n_C, n_D are the products, and k_f and k_r are the forward and reverse rate coefficients for the reaction. These coefficients are normally expressed as a function of temperature in the form:

$$k_f(T) = \Lambda T^b \exp(-E_a/kT) \tag{2}$$

where E_a is the activation energy of the reaction and k is Boltzmann's constant. Λ and b are constants that are best found from the best fit of experimental data.

From classical collision theory, the forward reaction may be written[1]

$$k_f\, n_A n_B = n_A \nu_{AB} \int_{\frac{E_a}{kT}}^{\infty} f\left(\frac{E_c}{kT}\right) P_r\left(\frac{E_c}{kT}\right) \mathrm{d}\left(\frac{E_c}{kT}\right) \tag{3}$$

where ν_{AB} is the collision rate for species A and B, f is the distribution function for the collision energy E_c, and P_r is the fraction of collisions having sufficient energy to react that do react. This quantity is usually referred to as the steric factor, and is also a function of the collision energy.

A useful collision model employed in the DSMC method is the Variable Hard Sphere (VHS) developed by Bird.[4] In this model, the mechanics of the collision follows that for a hard sphere, while the total collision cross section is given as a function of the relative collision velocity. For such a gas, it may be shown that

$$f\left(\frac{E_c}{kT}\right) = \frac{1}{\Gamma(\epsilon + 2 - w)} \left(\frac{E_c}{kT}\right)^{\epsilon + 1 - w} \exp\left(\frac{-E_c}{kT}\right) \tag{4}$$

where $\epsilon = \overline{\epsilon_A + \epsilon_B}$ is the average number of internal degrees of freedom which contribute energy to the breaking of chemical bonds during collision. This quantity is termed here as the internal mode contribution (IMC) and is an unknown property of the molecules.

Referring to Eq. (3), it is noted that the collision rate may be expressed as

$$\nu_{AB} = n_B \overline{\sigma_T c_r}$$

where σ_T is the total collision cross section and c_r is the relative velocity of collision. For a VHS gas, it may be shown[5] that

$$\overline{\sigma_T c_r} = \frac{2\sigma_{\mathrm{ref}}}{\sqrt{\pi}} [(2 - w)T_{\mathrm{ref}}]^w \left(\frac{2k}{m_r}\right)^{1/2} T^{1/2 - w} \tag{5}$$

where σ_{ref} defines a reference cross section at a temperature T_{ref}.

By substitution of Eqs. (2), (4), and (5) into Eq. (3), the following expression is obtained:

$$k_f = \Lambda T^b \exp(-E_a/kT)$$

$$= \frac{2\sigma_{\mathrm{ref}}}{\sqrt{\pi}} [2 - w]^w \frac{\Gamma(2 - w)}{\Gamma(\epsilon + 2 - w)} \left(\frac{2k}{\mathrm{m}_r}\right)^{1/2} T^{1/2 - w}$$

$$\int_{\frac{E_a}{kT}}^{\infty} P_r\left(\frac{E_c}{kT}\right) \left(\frac{E_c}{kT}\right)^{\epsilon + 1 - w} \exp\left(\frac{-E_c}{kT}\right) \mathrm{d}\left(\frac{E_c}{kT}\right) \tag{6}$$

In the procedure formulated by Bird, a steric factor was chosen such that the expression in Eq. (6) has the same temperature exponent b as the rate coefficient. For the VHS gas, Bird[4] proposed a steric factor of the form:

$$P_r\left(\frac{E_c}{kT}\right) = \frac{\alpha\Lambda\sqrt{\pi}}{2\sigma_{\mathrm{ref}}} \frac{\Gamma(\epsilon + 2 - w)}{\Gamma(2 - w)E(\epsilon + 3/2 + b)} \left(\frac{m_r}{2k}\right)^{1/2 - w}$$

$$\left[\frac{m_r}{2(2 - w)kT_{\mathrm{ref}}}\right]^w \left(1 - \frac{E_a}{E_c}\right)^{\epsilon + 1 - w} \left(\frac{E_c - E_a}{k}\right)^{b - 1/2 + w} \tag{7}$$

where α has a value of one for like and two for unlike collision partners.

When this expression is integrated in Eq. (6), the right-hand side reduces to the required analytical result.

Calculations

For any given reaction, a variety of rate constants Λ and b appear in the literature, thus throwing doubt on any particular

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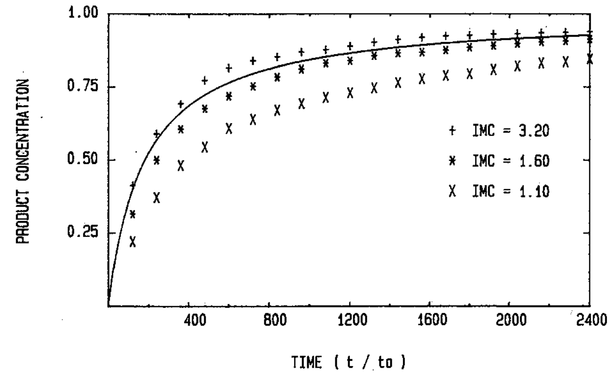

Fig. 1 **Reaction paths for several values of IMC using Bird's steric factor.**

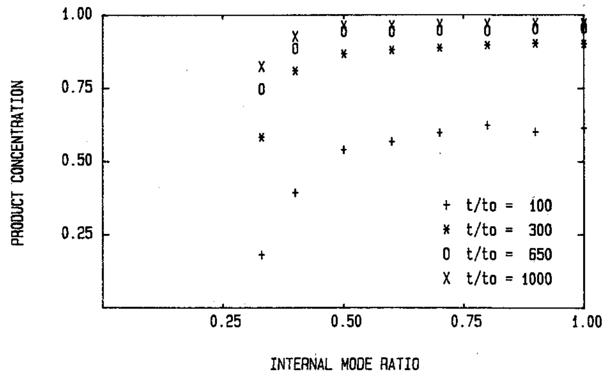

Fig. 2 **Concentration of NO at various time stations for several values of IMR using Bird's steric factor, where t_o is the mean time between collisions.**

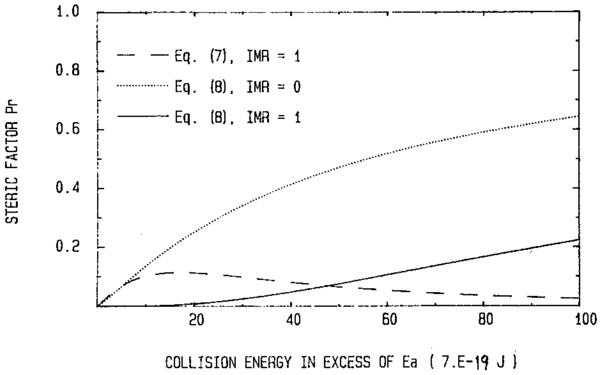

Fig. 3 **Steric factors as a function of collision energy in excess of the activation energy E_a.**

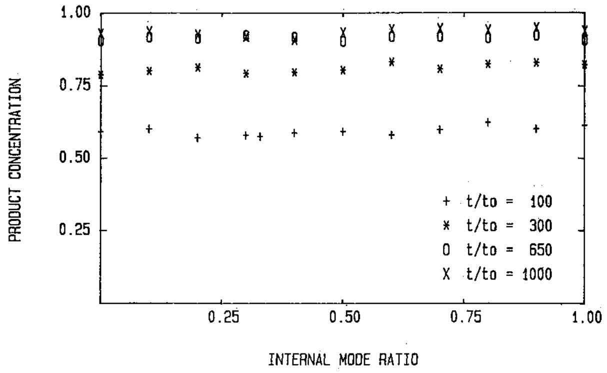

Fig. 4 **Concentration of NO at various time stations for several values of IMR using the new steric factor.**

combination ΛT^b. It is more appropriate to rely on the values of k_f and k_r determined experimentally than to adhere to some best-fit procedure. In addition, the question of the amount of energy contributed by the internal modes (IMC) must be addressed. Ideally, the value of ϵ chosen should not affect the rate of chemical change in the simulation data.

Several reaction schemes typical of those encountered in re-entry flow have been examined using the steric factor given in Eq. (7). Discussion is made here of a particular example in which the application of Bird's steric factor caused difficulties.

For the reaction $N_2 + O_2 \rightleftharpoons 2NO$, the following rate data are referred to by Vincenti and Kruger.[6] $\Lambda = 4.6 \times 10^{18}$ m^3 mole^{-1}s^{-1}, $b = -2.5$, $E_a/k = 64{,}600$ K. This reaction scheme has been investigated at a temperature at which the average of the rotational and vibrational degrees of freedom of nitrogen and oxygen is equal to 3.2. This is therefore the maximum value of IMC for this reaction. The effect of IMC on the reaction path was investigated and typical results are shown in Fig. 1. It is clear that the choice of IMC directly alters the degree of chemical activity calculated. As it is not possible to predetermine an appropriate value for the IMC, this aspect of Bird's expression can become undesirable.

The cause of the difficulties lies in the $(E_c - E_a)^{\epsilon + 1/2 + b}$ term in Eq. (7). If $(\epsilon + 1/2 + b)$ is negative, then as $(E_c - E_a)$ tends to zero, the reaction cross section becomes infinitely large. The IMC is therefore constrained by $\epsilon \geq -1/2 - b$. If the internal mode ratio (IMR) is defined as the IMC value ϵ chosen over its maximum value, then for the reaction considered above it follows that IMR ≥ 0.625. This aspect of the steric factor is observed in Fig. 2 where the instability is still observable from IMR = 1/3.2 to 0.5.

Simplified Formulation of the Steric Factor

The difficulties encountered above could be avoided by simply selecting a sufficiently large value for IMR. Indeed, it is common for IMR to be chosen as unity for all chemical reactions considered in DSMC calculations. However, the rate data associated with certain reactions set values of b so low that even IMR = 1 leads to numerical instability (see Ref. 7). In addition, it is physically unrealistic to assume that all of the available internal energy may be expended in the breaking of chemical bonds. As an alternative, a steric factor is proposed in which the value of the rate constant is reproduced by the integral in Eq. (6), and the arbitrary temperature dependence is ignored. Again the steric factor is presented in a VHS format, and is given by

$$P_r\left(\frac{E_c}{kT}\right)=\frac{\alpha k_f}{\exp(-E_a/kT)}\,\frac{\sqrt{\pi}}{\sigma_{\mathrm{ref}}\Gamma(2-w)}\left(\frac{m_r}{2kT}\right)^{1/2-w}\left[\frac{m_r}{2(2-w)kT_{\mathrm{ref}}}\right]^{w}\left(1-\frac{E_a}{E_c}\right)^{\epsilon+1-w} \tag{8}$$

It is readily seen in this expression that the value of IMR is no longer in any way restricted. The steric factors given in Eqs. (7) and (8) are plotted in Fig. 3 for the reaction scheme previously described. Bird's expression is plotted for IMR = 1, while the new model has been calculated for both IMR = 0 and 1.

Finally, in Fig. 4, a series of calculations are shown in which the new model has been implemented. It is evident that the difficulties associated with the choice of IMR have indeed been removed.

Concluding Remarks

The steric factor proposed by Bird for the DSMC method is found to be unstable under certain conditions relating to the chemical rate data. Such instabilities have been removed through the introduction of a steric factor in which the value for the rate coefficient at a given temperature appears explicitly.

The new steric factor is found to be an improvement on that of Bird in that the reaction path may be calculated independently of the choice of the internal energy contribution. For a simulation in which the temperature is constant, e.g., in heat bath studies, the new model is just as efficient as Bird's formula. However, for the investigation of flows in which temperature gradients exist, it is necessary to evaluate a local temperature from the molecular data. It is estimated that such procedures incur no more than a 5% computational overhead.

Acknowledgment

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Hydrodynamics of Film Boiling from a Cylinder in Crossflow

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Nomenclature

c = wave speed
n = wave number
p = pressure
q = heat flux
t = time
ΔT_B = degree of liquid subcooling, $T_{\text{sat}} - T_B$
ΔT_w = wall superheat, $T_w - T_{\text{sat}}$
U = velocity
V = freestream velocity approaching a cylinder
W = complex potential
x,y = curvilinear coordinates shown in Fig. 4
z = complex number, $x + y$
γ = amplitude of wave
δ = vapor film thickness
ζ = liquid layer dimension
η = coordinate for vapor film
θ = angle
λ = wavelength
ρ = density
θ = surface tension
ω = frequency

Subscripts
cr = critical
d = most dangerous
i = imaginary
l = liquid
s = separation
sat = saturation
v = vapor
δ = interface

Introduction

FILM boiling during crossflow over cylinders involves several hydrodynamic aspects that make a mathematical prediction of heat transfer difficult. A liquid boundary layer rides over a vapor layer; each layer must be properly represented mathematically and compatibility conditions must be specified at the interface. Also, a wake is formed behind the cylinder. Even though it resembles a cavitation wake in many respects, see Kaul and Witte,[1] its behavior is not very well understood. Furthermore, as the vapor film thins in response to decreasing surface temperature, the vapor film can become unstable causing liquid-solid contact and leading to transition boiling as recently measured by Chang and Witte.[2]

In this paper, we report research into the nature of vapor film crossflow over a cylindrical heater. Photographs of R-11 boiling from a 6.35-mm-diam heater reveal the details of wake formation and behavior near the minimum heat-flux condition. A stability analysis of flow boiling is presented and related to experimental observations. An explanation for the behavior of the vapor wake near the minimum heat flux condition is proposed.

Photographic Observations

Experiments involving film and transition boiling of R-11 from a 6.35-mm-diam heater were performed. The apparatus and details of liquid-solid contract and heat transfer measurements are described in detail by Chang and Witte[2] and Chang[3]; those details will not be repeated here.

Photographs were obtained to better understand forced convection boiling from cylinders. A Nikon 3F camera with a 30-105 zoom lens was used at 1/2000 s with an aperture of 5.6.

Figure 1 shows stable film boiling of R-11 for low velocity, 0.7 m/s, and low subcooling, 3.3°C. Liquid is flowing upward over the heater. The vapor film over the front of the heater is smooth. A separation line can clearly be seen that indicates where a wake is formed on the cylinder. The average separation angle for this case was measured to be 105-deg. This point is just beyond the liquid-solid probe, which can be seen at the 90-deg point. It is clear that the probe did not interfere with the basic boiling process.

Figure 1 shows film boiling just above the minimum point on the boiling curve. The bottom of the heater was covered by a smooth vapor film, while vapor patches were being swept away from the wake by the liquid flow. The effect of drag on the edge of a rough, thick vapor layer in the wake can be seen in this photograph.

Figure 2 shows film boiling at a higher velocity and slightly higher subcooling. The behavior is basically the same except that vapor is torn away from the edge of the vapor wake at more locations than for lower velocities and lower subcoolings.

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