

Cluster Size Distribution for Free Molecular Agglomeration

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1. INTRODUCTION

Dobbins and Megaridis (1) have observed soot agglomerates in a diffusion flame via thermophoretic sampling. The agglomerates are made up of spherules with a typical diameter of about 30 nm. A characteristic of the agglomerate is the relatively low density of the structure with much open space as indicated in Fig. 1. This study is concerned with modeling the agglomeration growth process.

Within the flame, the mean free path of the gas is on the order of 300 nm. Under these conditions, the particle continues in a straight path for a distance long compared to the particle size. Such behavior is termed free molecular. Mountain *et al.* (2) and Sullivan *et al.* (3) developed a computational technique for simulating particle agglomeration under these conditions, though in these studies the investigators were limited to a total of 500 primary particles in their simulations. The results were very limited in regard to the size distribution function. In this study, we have extended the simulations to 8000 primary particles in order to determine the size distribution function for agglomerates in the free molecular limit.

In addition to the computer simulation results, an expression for the coagulation kernel is developed based on the apparent fractal structure of the agglomerate and the free molecular particle dynamics condition. The size distribution function appropriate to the coagulation kernel is derived in the limit of long time based on the dynamic scaling analysis of van Dongen and Ernst (4). We also directly compute the size distribution function based on a numerical solution of the coagulation equation.

Previous studies of free molecular particle coagulation have been based on spherical particles. Lai *et al.* (5) have shown that free molecular coagulation with coalescence leads to a so called self-preserving size distribution. Dobbins and Mulholland (6) considered simultaneous particle formation and free molecular growth, but again with the assumption of spherical particle shape. They find that for conditions similar to those existing in a flame, the simultaneous particle formation can lead to a much broader size distribution than the self-preserving distribution obtained by Lai *et al.* As indicated above, the soot in the flame exists as an agglomerate. It is of obvious interest to determine the size distribution, structure, and growth kinetics for agglomerates.

Meakin *et al.* (7) have studied the effect of the cluster diffusivity on the resulting cluster-size distribution. In their study, the diffusion coefficient of a cluster of size k is assumed to be proportional to k^γ . Meakin *et al.* find a critical value of γ , $\gamma_c \approx 1/2$, at which the shape of the cluster-size distribution crosses over from a monotonically decreasing function to a bell-shaped curve. A Monte Carlo simulation is used with the diffusional motion of the clusters represented by random walks on a three-dimensional cubic lattice. In all cases considered, the primary particle size corresponds to one lattice site and the diffusion step is one lattice site. This differs from the free molecular condition that the particle move several particle

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diameters before changing its trajectory. It is this latter case of free molecular motion that is the focus of this paper.

2. Description of Computer Simulation

The initial condition consists of 8000 spheres of mass m_0 and unit diameter σ randomly located in a cube of size L . The initial velocities are obtained using a random number generator which produces normally distributed numbers with unit variance so that the particles are in thermal equilibrium with the background gas through which they diffuse.

The dynamics of a particle are governed by the Langevin equation

$$d(mv_x)/dt = -m\beta v_x + f_x \quad [1]$$

where v_x is the x th cartesian component of the velocity of the center of mass of the agglomerate of mass m and f_x is a stochastic force satisfying $\langle f_x^2 \rangle = 2\beta mk_B T$. As can be seen from Eq. [1], β^{-1} represents the relaxation time of the agglomerate. The numerical solution of Eq. [1] to obtain the velocity and coordinates for each particle after a time interval h is described in Mountain et al. (2).

After each time interval h , the system is examined to see if any agglomeration events have occurred. It is assumed that whenever two particles "touch", they stick and the resulting agglomerate diffuses as a rigid assembly. Also, the agglomerates are thermally accommodated after each collision, since thermal accommodation with the host gas may not occur before a second collision at the high particle concentration.

The product $m\beta$ in Eq. [1] is termed the friction coefficient, K . We approximate the friction coefficient of k spheres as k times the friction coefficient of a single sphere. In making this approximation we neglect the shielding effect of the other spheres, but for a tenuous, low density agglomerate this is a reasonable first approximation. Both the mass m and the friction coefficient K are proportional to the number of particles in the agglomerate k ; therefore, β is independent of the size of the agglomerate in this independent particle approximation. Dividing both sides of Eq. [1] by m , it is seen that the quantity β is the controlling parameter for the particle dynamics.

The free molecular condition corresponds to the particle relaxation time, β^{-1} , being long compared to the time, $\tau = (m_0 \sigma^2 / k_B T)^{1/2}$, to free stream a particle diameter; that is,

$$\beta \tau \ll 1. \quad [2]$$

The following result is derived for $\beta \tau$ in the free molecular limit in Mountain et al. (2):

$$\beta \tau = 4P(2m_0 m_g)^{1/2} / (\rho_g k_B T), \quad [3]$$

where m_0 is the mass of an individual sphere, ρ_g refers to the density, and m_g is the mass of the gas molecules. The surface accommodation is assumed to have a value of unity. The simulations are carried out for $\beta \tau = 0.2$, which corresponds to a 16 nm particle diameter for a 1500 K flame temperature, and for $\beta \tau = 0.05$, which corresponds to a 6 nm diameter. The density of the individual particle is taken to be 2.0 g/cm³ and ambient pressure is assumed.

Another important parameter concerning the simulation is the number density, ρ , defined as the number of particle per volume, where volume is in units of σ^3 . Simulations were performed for the following values of ρ : 0.05, 0.0167, and 0.005. Even the lowest of these densities is several orders of magnitude larger than the value of about 10^{-6} observed in flames. The density dependence of the results

provides insight regarding the applicability of the simulations to an actual flame. A value of ρ of 0.005 is the lowest density for which the simulation can be carried out for 8000 particles with 5 runs to obtain adequate statistics using a Cyber 205 computer⁴.

3. RESULTS

While the primary focus of this study is the results regarding the size distribution function, it is also of interest to analyze the structure of the agglomerates and the cluster growth rate. The structural information will be used in the next section for deriving an effective collision kernel for the agglomerates. Given the collision kernel, the size distribution can be determined as shown in the next section. The cluster growth rate is of interest in its own right but is also needed for obtaining the scaled size distribution function.

3.1 Structure

The structure of the agglomerates is quite open as indicated in Fig. 1 for a planar projection of the structure. It is also seen that there is a similarity between the actual structure of soot produced by an acetylene diffusion flame and the results of the computer simulation. As has been demonstrated in a number of studies of agglomerate growth including Meakin (8,9) and Mountain *et al.* (2), the degree of openness can be conveniently characterized in terms of a fractal dimensionality, D_f , which in the case of an agglomerate is conveniently defined by the equation

$$k \propto R_g^{D_f} \quad [4]$$

where R_g is the radius of gyration of the cluster. In Fig. 2, $\log R_g$ is plotted versus $\log k$ for the case $\beta\tau=0.05$ and $\rho=0.005$. A linear least square fit of the data over the range 10-500 in k with a uniform weighting on a log scale leads to $D_f=1.91\pm 0.06$. The choice of the lower bound is determined by onset of power law behavior and the upperbound by condition that agglomerate not extend from one edge of the cell to the other. As indicated in Table I, the mean values of D_f are in the range 1.89 - 2.07. This is to be compared with a value of $D_f=1.87\pm 0.04$ obtained by Meakin (10) for cluster in the size range 10-500 with $\rho=0.005$. The model used by Meakin consists of random linear trajectories by both particles and clusters. The model was originally introduced by Sutherland and Goodarz-Nia (11). This model would correspond to the limiting case $\beta\tau=0$ for the free molecular simulation.

3.2 Cluster Growth

The average cluster size, \bar{k} , is defined by

$$\bar{k} = N_0 / N(t) \quad [5]$$

where N_0 is the number of primary particles and $N(t)$ is the total number of clusters at time t . In Fig. 3, \bar{k} is plotted versus number of time steps, t_N , on a log-log plot for all of the simulations. The mean cluster size increases asymptotically as

$$\bar{k} \propto t^z \quad (t \rightarrow \infty) \quad [6]$$

The exponent z is obtained from a linear least square fit of the log-log plot for the

⁴Certain commercial equipment is identified in this paper to specify adequately the calculation method. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

range in t over which $20 < \bar{k} < 100$. As indicated in Table I, there seems to be a decrease in z with decrease in density.

An alternative method for determining the exponent z is suggested by the analysis of van Dongen and Ernst (4). They obtain the following relationship between \bar{k} and t_N :

$$\bar{k} \propto (t_N + t_N^0)^z \quad [7]$$

The value of t_N^0 is obtained as the value for which $\log(\bar{k})$ versus $\log(t_N + t_N^0)$ has no curvature. The value of the exponent z obtained in this way is also given in Table I.

In Fig. 4, all of the data is reduced to a single curve by plotting \bar{k} vs. τ_1 , where

$$\tau_1 = (t/\tau)\rho \quad [8]$$

3.3 Cluster Size Distribution

The cluster-size distribution, N_k , is plotted in Fig. 5 at several times. As a test for the existence of a self-preserving cluster distribution, we also plot the size distribution in terms of the similarity variables, ψ and η , introduced by Friedlander (12),

$$N_k = \bar{k}^2 N_0 \psi(\eta) \quad [9]$$

$$\eta = k/\bar{k} \quad [10]$$

It is seen from Fig. 6 that the similarity variables do reduce all of the cluster-size distributions to a single curve. The possibility of deriving this universal size distribution is treated in the next section.

Perhaps the size distribution function affording the best comparison with experiment is the number distribution in terms of the radius of gyration, R_g .

$$dN/dR_g = AD_r R_g^{-1} N_k \quad [11]$$

Such a size distribution is plotted in Fig. 7. While it may not be practical to evaluate R_g for every cluster by electron microscopy, one might rapidly determine an effective size of the agglomerate based on its length and width.

4. Coagulation Equation

The most widely used tool for studying irreversible clustering phenomena in many fields of science is Smoluchowski's coagulation equation:

$$\dot{n}_k = k \sum K(i, j) n_i n_j - n_k \sum K(k, j) n_j \quad [12]$$

where n_k is the number concentration of clusters of size k and $K(i, j)$, the coagulation kernel, represents the rate coefficient for a specific clustering mechanism between clusters of sizes i and j . Below an estimate is made for the coagulation kernel for the case of free molecular growth and then Eq. [12] is solved analytically in the asymptotic limit as well as numerically. Finally the results are compared with the results of the computer simulation.

4.1 Coagulation Kernel

For the case of small droplets that coalesce upon contact, the free molecular coagulation kernel is given by

$$K(i, j) = a(i^{1/3} + j^{1/3})^2 (1/i + 1/j)^{1/2} \quad [13]$$

$$a = (3v_0/4\pi)^{1/6} (6k_B T/\rho_g)^{1/3} . \quad [14]$$

The first factor in Eq.[13] corresponds to the size dependence of the collision cross section and the second term to the dependence of the average relative velocity on the reduced cluster mass. The quantity $K(i,j)$ given above is essentially identical to the kinetic theory prediction of the volume swept out per second by colliding molecules.

The collision cross section of two low density agglomerates (fractal objects with Hausdorff dimension $D_f=1.9$) in free flow (ballistic trajectories) is much larger than for compact spheres, mainly because of their large radii of gyration,

$$R_g \propto k^{1/D_f} .$$

However, there is a subtlety in the argument. Since $D_f < 2$, the planar projection of a cluster or cross-sectional area (see Fig. 1) is still a fractal object with Hausdorff dimension $D_f=1.9$. Therefore, the effective scattering area for two free moving fractal clusters with $D_f < 2$ and sizes i and j respectively is:

$$\begin{aligned} \text{cross-section} &\propto (R_g(i) + R_g(j))^{D_f} \\ " \quad " &\propto (i^{1/D_f} + j^{1/D_f})^{D_f} \end{aligned} \quad [15]$$

If however the fractal dimension of the clusters would be $2 \leq D_f \leq 3$, then their projections would be compact objects and their collision cross-section would be:

$$\begin{aligned} \text{cross-section} &\propto (R_g(i) + R_g(j))^2 \\ " \quad " &\propto (i^{1/D_f} + j^{1/D_f})^2 \end{aligned} \quad [16]$$

Note that the cross-section in both cases [15] and [16] is bounded by $\text{const.} \cdot x \cdot j$ for $j \gg i$. This is a physically obvious requirement. Equation [16] for $D_f < 2$ would violate this condition (See Mountain *et al.*(2)).

The agglomerate speed is not affected by the particle structure based on the equipartition of energy so that the coagulation kernel for the agglomerate in the free molecular limit is given by

$$K(i,j) = a_1 (i^{1/D_f} + j^{1/D_f})^{D_f} (1/i + 1/j)^{1/2} . \quad [17]$$

Van Dongen and Ernst (4) have obtained asymptotic solutions to the coagulation equation, Eq.[14], for coagulation kernels classified on the basis of three exponents defined below:

$$K(ai, aj) = a^\lambda K(i, j) = a^\lambda K(j, i) , \quad [18]$$

$$K(i, j) \approx i^\mu j^\nu \quad (j \gg i; \lambda = \mu + \nu) . \quad [19]$$

For $K(i,j)$ given by Eq.[17], $\lambda = 1/2$, $\mu = -1/2$, and $\nu = 1$. For $\lambda \leq 1$, van Dongen and Ernst (4) show that the exponent z is given by

$$z = 1/(1 - \lambda) . \quad [20]$$

So for $\lambda = 1/2$, $z = 2$. The general form of the reduced size distribution for large η is given by van Dongen and Ernst (13).

$$\psi(\eta) = A \eta^{-z} \exp(-\alpha \eta) , \quad \eta \rightarrow \infty . \quad [21]$$

For coagulation kernels with $\nu < 1$, the θ exponent is simply given by $\theta = \lambda$. However, for kernels with $\nu = 1$, such as given in Eq.[17], the θ exponent is more complicated. It has been calculated by van Dongen and Ernst (13), and we conclude from their Eqs.[12] through [15] that the exponent θ is determined from the following transcendental equation:

$$J(\theta) = 0, \quad [22]$$

where $J(\theta)$ is defined by

$$J(\theta) = \int_0^1 dx (K(x, 1-x) [x(1-x)]^{-\theta} - x^{\mu-\theta}) - \int_0^{\infty} dx x^{\mu-\theta}. \quad [23]$$

Since the first integrand diverges at $x=0$, an asymptotic expansion is made for the integrand to obtain the small x contribution to the integral. For the remainder of the range in x , the integration is obtained numerically. For the case $D_c = 1.90$, we obtain $\theta = 0.72$.

For large values of D_c the asymptotic solution of Eq.[23] is (14)

$$\theta = 1/2 + 2^{1-D_c} / \pi \quad (D_c \gg 1)$$

This relation gives at $D_c = 1.9$ the fair estimate $\theta = 0.67$ and at $D_c = 1$ is even close to the exact value $\theta = 1$.

The size distribution plots given in Fig. 6 suggest a power law region followed by an exponential region. However, one finds a wide range in the value of θ , 0.4 to 0.8, depending on the range in η over which the line is drawn. A better method is to first obtain k from the large η asymptotic slope of $\ln \psi$ vs η and, then obtain θ from the slope of $k\eta + \ln \psi$ vs $\ln \eta$. This approach applied to the case $\beta_T = 0.05$ and $\rho = 0.005$ yields $\alpha = 0.67$ and $\theta = 0.53$ compared to the predicted value of θ of 0.72. There is still some ambiguity in the value of θ , because of the interplay between the value of α and θ . That is, a lower value of α and a larger value of θ will also lead to a good fit to the simulation results.

In the limit of small cluster size and long time, van Dongen and Ernst (4) predict that

$$\psi(\eta) \propto \eta^{-2} \exp(-1/\eta^k) \quad \text{for } \eta \rightarrow 0. \quad [24]$$

Unlike this predicted exponential behavior, it appears that $\psi(\eta)$ decreases only slightly for small η . Presumably this discrepancy results from the simulations not being carried out to long enough time.

Another approach to comparing the results of the simulations with coagulation theory is to numerically solve for N_k vs k from Eq.[13] based on the kernel given by Eq.[17]. One thousand twenty four coupled rate equations given by Eq.[13] were solved by the Runge Kutta method with fourth order predictor corrector. This is analogous to the technique used by Hidy et al. (15,16) for solving the coagulation equation. Starting from a monodisperse size distribution as in the simulations, it was found that the loss of mass due to particles reaching $k=1024$ represented a 4% effect when the total number concentration had dropped by a factor of 100. It is seen from Fig. 6 that the reduced size distribution obtained from the numerical solution of the coagulation equation is both self-preserving and agrees very well with the results of the computer simulation. The value of the exponent z characterizing the cluster growth rate is found to be in good agreement with the computer simulation results (1.84 for the coagulation equation vs 1.72 for the simulation).

5. Discussion

The computer simulations of free molecular agglomeration lead to much more rapid growth than is predicted for coalescing droplets in the free molecular limit, which has been the basis for predicting coagulation rates in flames in previous studies (5,6). The agglomeration leads to an exponent z of about 2.0 compared to a value of about 1.2 based on coalescence.

The results of the computer simulations in terms of the fractal structure and the size distribution function seem to vary only slightly with the choice of β (0.2 and 0.05) and ρ (0.05, 0.0167, 0.005). There appears to be a more pronounced affect of the density on the value of the exponent z with the higher density leading to a higher value of z . The value reported by Mountain et al. (2) for a system with 500 primary particles was larger yet with a value of about 2.6 for z . We expect the simulation with the lowest density ($\rho=0.005$) and lowest value of β (0.05) to give the most appropriate value for physical systems. For the limited range in k , Eq.[7] is the most accurate method for determining the exponent z , and this leads to $z=2.05$ for the simulation.

We do not observe as large a density effect in the free molecular limit as has been observed by Mountain et al. (2) in the continuum limit and by Ziff et al. (17) for agglomerates with diffusion coefficient proportional to the cluster size raised to a power.

We find that a coagulation kernel derived based on the fractal structure of the agglomerate leads to an average growth rate and self-preserving size distribution in good agreement with the computer simulations. The computer simulations have not been run for long enough time to afford a comparison with the predicted small η behavior..

Ziff et al. (17) demonstrated that for a size dependent diffusion coefficient the kinetic rate kernel predicted by taking into account the fractal geometry of the agglomerate is in agreement with the computer simulation results. We have shown that in the free molecular limit that using a kinetic rate kernel based on fractal geometry leads to a size distribution in agreement with the computer simulation. One is encouraged to conjecture that the coagulation equation can be applied to agglomerates provided the agglomerate structure information is included in the kinetic rate.

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TABLE I. Exponents D_z and z for Free Molecular Simulations

| βr | ρ | D_z | z^a | z^b | t_N^0 |
|-----------|--------|-----------------|-----------------|-----------------|---------|
| 0.20 | 0.05 | 2.05 ± 0.03 | 1.98 ± 0.05 | | |
| 0.05 | 0.05 | 2.07 ± 0.08 | 2.40 ± 0.16 | 4.06 ± 0.19 | 500 |
| 0.05 | 0.0167 | 1.89 ± 0.08 | 1.92 ± 0.07 | 2.53 ± 0.05 | 900 |
| 0.05 | 0.005 | 1.91 ± 0.06 | 1.72 ± 0.05 | 2.05 ± 0.03 | 2000 |

^a The exponent z is defined by $\bar{k} \propto (t_N)^z$.

^b Here the exponent z is defined by $\bar{k} \propto (t_N + t_N^0)^z$.

Soot (acetylene fuel)

Agglomeration Model



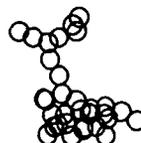
10 Spheres



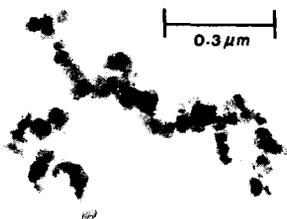
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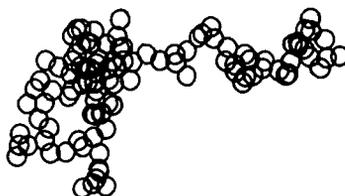
33 Spheres



33 Spheres



107 Spheres



108 Spheres

Fig. 1. Qualitative comparison of soot clusters and clusters obtained by computer simulation of free molecular growth.

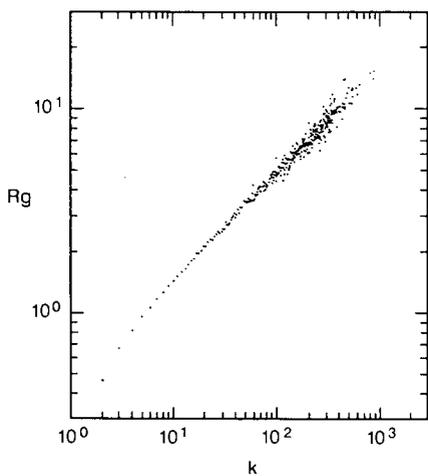


Fig. 2. R_g versus k for $\beta\tau=0.05$ and $\rho=0.005$.

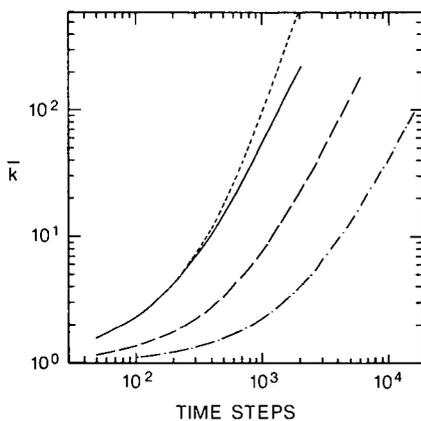


Fig. 3. \bar{k} versus time steps for $\beta\tau=0.2$, $\rho=0.05$ (—); $\beta\tau=0.05$, $\rho=0.05$ (- - -), $\rho=0.0167$ (— —), $\rho=0.005$ (— · —).

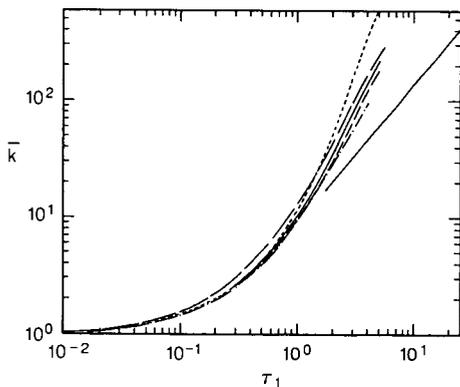


Fig. 4. \bar{k} versus τ_1 , for $\beta\tau=0.2$, $\rho=0.05$ (—); $\beta\tau=0.05$, $\rho=0.05$ (- - -), $\rho=0.0167$ (— —), $\rho=0.005$ (— · —), fractal coagulation (— —), coalescence (—) slope=1.2.

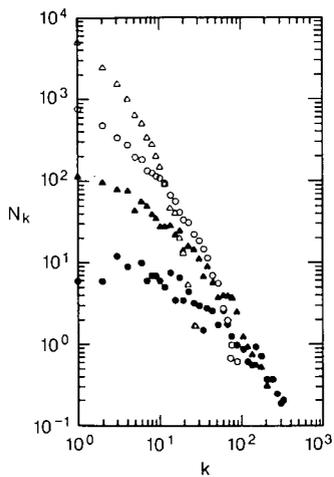


Fig. 5. Size distribution for $\beta r=0.05$, $\rho=0.005$, $t_N=1500(\Delta)$, $t_N=4200(\circ)$, $t_N=8000(\Delta)$, $t_N=16,000(\bullet)$.

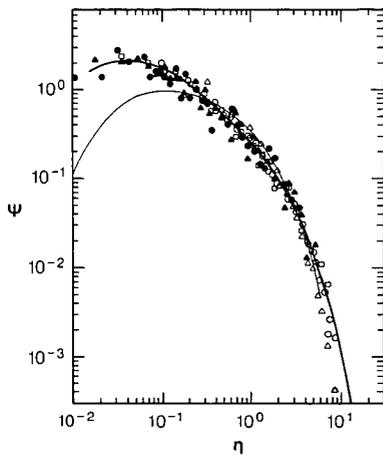


Fig. 6. Self-preserving sized distribution for simulation, fractal coagulation(Δ), coalescence(\square).

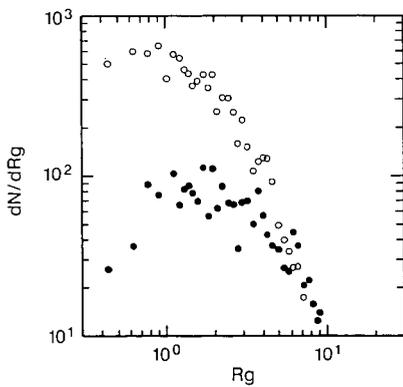


Fig. 7. dN/dR_g versus R_g for $t_N=8000(\circ)$ and $t_N=16,000(\bullet)$.