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TRANSPORT AND INTERFACIAL PHENOMENA IN MULTI-PHASE COMBUSTION SYSTEMS

AFOSR Grant No. 97-1-0266
Principal Investigator: Daniel E. Rosner

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PIADC INFORMATION
TRANSPORT AND INTERFACIAL PHENOMENA IN MULTIPHASE COMBUSTION SYSTEMS

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Approved for public release; distribution is unlimited

Results of a 3-year research program, leading to 17 archival papers, are summarized here, covering the four basic areas: A) Laser-Induced Incandescence (LII) for soot measurements at atmospheric pressure and high pressures; B) Thermophoresis-based particle diagnostic techniques; C) Simulation methods for aerosol populations described by two (or more) "state variables"; and D) Particle deposition from soot populations. As examples, we found that the small Knudsen number (high pressure) limit, Laser-Induced Incandescence (LII) can be used to infer aggregate size distributions, pdf(N). This requires improved estimates of the optical and heat transfer properties of fractal aggregates, also obtained under the present program (Filippov and Rosner, 1998, 1999, Filippov et al. 1999). Our thermophoresis/soot deposition research has led to a novel and quite convenient method (called TPD) to track local soot volume fractions in laminar flames, most recently including flames deliberately 'doped' with possible soot pre-ursors. A versatile Monte-Carlo-based (MC-) simulation of the population balance equation PBE has also been developed (Tandon and Rosner, 1999, Rosner and Yu, 1999) and successfully demonstrated for the important 2-state variable case in which each non-spherical particle in the population is characterized by its volume v and surface area, a. Even in this bi-variate case, "self-preserving" (constant shape pdf) asymptotic solutions have been found (Tandon and Rosner, 1999; in both the continuum and free-molecular limits (Rosner and Yu, 1999), and their physically important 'mixed moments' calculated.

Laser-induced incandescence, soot morphology, aggregated particles, particle mass transport, thermophoresis, Brownian diffusion, particle sampling, nano-particle formation/restructuring in flames, deposition rate theory

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1. INTRODUCTION

The performance of aircraft gas turbine engines under sooting conditions and/or ramjets burning slurry fuels (leading to oxide aerosols and deposits), depends upon the formation and transport of small particles of complex morphology, often in highly non-isothermal combustion gas boundary layers (BLs). Aggregate formation / transport are also important in chemical reactors used to synthesize/process aerospace materials, including turbine blade coatings, optical waveguides, ceramic precursor powders,...). Accordingly, this research was directed toward providing chemical propulsion system engineers with rational new predictive techniques to deal with particle formation-transport-deposition phenomena, accounting for significant non-spherical particle morphology effects. An interactive experimental/theoretical approach was used to gain an understanding of performance-limiting mass/energy transfer-phenomena at or near interfaces. This included the development/exploitation of laboratory burners and new diagnostic/characterization techniques (Sections 2.1,2.2). Resulting experimental data, together with the predictions of asymptotic theories were then used to propose and verify rational engineering correlations for future design/optimization.

2. SUMMARY OF PRINCIPAL RESEARCH ACCOMPLISHMENTS‡

Most of the results obtained under Grant AFOSR 97-1-0266 can be divided into the subsections below:

2.1 Laser-Induced Incandescence (LII) for Soot Measurements: New 'Modalities'

While instantaneous, local soot volume fractions and spherule sizes are sufficient for some purposes (especially in predicting the structure of atmospheric pressure flames), a knowledge of the aggregate size distribution (ASD or pdf(N), where N is the number of spherules in a 'fractal-like' aggregate) is essential to predict the radiative properties and, say, health effects of sooting combustors. Rapid response LII access to such information would also permit the development of local aggregate number density pdfs and relevant 'scatter' diagrams in turbulent sooting flows, thereby facilitating the development of more realistic soot models for such environments. Under the present grant we carried out an analysis (Filippov et al. 1999a); which demonstrated, for the first time, that in the small Knudsen number (eg. high pressure) limit, LII can be used to infer aggregate size distributions. We exploited an improved theoretical knowledge of the optical and heat transfer properties of fractal aggregates (Filippov and Rosner, 1998,1999, Filippov et al. 1999b). We showed that the 'accessible' domain (on the plane of aggregate population spread vs. geometric mean number of spherules per aggregate, N_e) includes most soot cases of practical interest.

2.2. Development of 'Thermo-Phoresis-Based' Particle Diagnostic Techniques

In this program we developed/demonstrated two thermophoresis-based methods for measuring absolute local soot volume fractions, f_p, in both co-flow and counterflow laminar diffusion flames. The first, called Thermocouple Particle Densitometry (TPD)(McEnally et.al.(1997)), exploits the laws governing thermocouple response to thermophoretic soot deposition, as first suggested by the PI in 1985. This 'TPD' research has led to a novel and quite convenient method to track local soot volume fractions in laminar flames, most recently including flames deliberately 'doped' with possible soot pre-cursors (McEnally and Pfefferle,1998). Remarkably, the method responds to transparent soot (condensed PAHs, important in soot inception) to which ordinary laser light extinction (LLE) is "blind" (McEnally et al., 1998, Koylu et al. 1998). A combination of TPD and more classical methods of analysis is expected to shed new light on the role these ubiquitous "transparent" particles, found very early in hydrocarbon vapor/air diffusion flames, play in the overall soot formation process.

‡ For research collaborators consult Sections 3, 5
The second, related technique, which we call Thermophoretic Sampling Particle Diagnostic (TSPD) (Koylu, et al. (1997)) is an extension of TEM-based thermophoretic sampling to also obtain absolute, local soot volume fractions, again making use of the laws governing thermophoretic soot deposition (eg., Rosner et al. (1991,1992)).

2.3 Simulation Methods for Aerosol Populations Described by 2 (or More) "State Variables"

Based on the expectation that 'sectional' (finite-difference) methods will become problematic for the ultimate prediction of multi-variate pdfs for sooting, turbulent combustors, we have developed/illustrated a more versatile Monte-Carlo-based (MC-) simulation of the population balance equation PBE (Tandon and Rosner, 1999, Rosner and Yu, 1999) and successfully demonstrated the efficacy of this approach for the an important 2-state variable case in which each non-spherical particle in the population is characterized by its volume and surface area. Even in this bivariate case we have found "self-preserving" (constant shape pdf) asymptotic solutions (Tandon and Rosner, 1999(continuum regime); and, for the free-molecule regime, Rosner and Yu, 1999). While these "self-preserving" solutions may not apply locally to the dynamical situation of many real flames, including the TMA-seeded atmospheric pressure counter-flow diffusion flames on which we have considerable experimental data (Xing et al., 1997,1999), they are of considerable theoretical interest, and can be used to predict many observable properties of 'coagulation-aged' aerosol populations, including mass deposition rates (Rosner et al. 1998,2000)). As a corollary of this research, we have developed methods to predict the decisive mean spherule size (which fixes the specific surface area of such aerosols)(see, Xing and Rosner, 1999); and even the spherule size distribution (Rosner and Yu 2000).

2.4 Prediction of Particle Deposition from Soot Populations

The fact that smokes or mists of aerospace and environmental interest are comprised of particles both large and small compared to the prevailing gas mean-free-path inevitably complicates accurate predictions of, say, total mass deposition rates to confining walls by the mechanism of convective-Brownian diffusion (Sc>>1), or thermophoresis, across laminar or turbulent boundary layers. However, since all individual particle transport properties are sensitive to the prevailing Knudsen number based on particle diameter, this must be accurately taken into account. In the present program we extended previous results from this laboratory to show how deposition rates from a flowing stream of coagulation-aged polydispersed spherical particles in the Knudsen transition regime can be predicted by systematically correcting results more easily calculated for the (hypothetical) reference case of mono-dispersed spheres, either in the continuum or free-molecule limit. For this purpose we carried out "once-and-for-all" quadratures over the Cunningham-Millikan "slip-flow" function, and the Talbot thermophoretic function (Rosner and Khalil, 2000) with appropriate quasi-self-preserving particle size distribution (PSD-) functions, using recent information on the effective spreads ($\sigma_{eq}$) of these near-log-normal PSDs associated with Brownian coagulation in the transition regime. Whether the deposition mechanism is Brownian diffusion (Rosner, 1998) or thermophoresis (Rosner and Khalil, 2000), this led to rational "universal" correlations, in terms of the prevailing Knudsen number based on mean particle size in the population, which will drastically simplify and accelerate such particle deposition rate calculations in the future.
3. ADMINISTRATIVE INFORMATION: PRINCIPAL PERSONNEL, PRESENTATIONS, APPLICATIONS, "TECHNOLOGY TRANSFER"

The following sub-sections summarize some pertinent facets of the abovementioned Yale HTCRE Lab/AFOSR (nominally 3 year-) research program of management interest:

3.1 Principal Research Personnel

The present results (summarized in Sections 2 and 5 and the 17 papers prepared under this program) are mainly due to the contributions of the individuals listed in Table 3.1-1, which also indicates the overall role of each researcher. It is noteworthy that, in addition to the results themselves, this program has simultaneously contributed to the research training of PhD students: M. Zurita, and Y. Xing. The latter, recently completed a post-doctoral position at Johns Hopkins Univ., and was runner-up for the 1999 ACS/Colloid Div. V. LaMer Award (based on outstanding dissertation research). He is now in an excellent position to make future contributions to technologies oriented toward high-tech aerospace materials synthesis/processing.

Table 3.1-1 Summary of Principal Research Participants on AFOSR Grant: 97-1-0266: TRANSPORT PHENOMENA AND INTERFACIAL PHENOMENA IN MULTIPHASE COMBUSTION SYSTEMS

<table>
<thead>
<tr>
<th>Name</th>
<th>Statusa</th>
<th>Date(s)</th>
<th>Principal Research Activityb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filippov, A.V.</td>
<td>PDRA-RS/S</td>
<td>9/97-11/99</td>
<td>LII theory for pdf(d_i) and pdf(N)</td>
</tr>
<tr>
<td>Xing, Y.</td>
<td>GRA-PDRA</td>
<td>4/97-6/98</td>
<td>Particle prod./char. in CDFs</td>
</tr>
<tr>
<td>Yu, S.</td>
<td>PDRA</td>
<td>10/98-7/99</td>
<td>MC Simulation of soot coagulation</td>
</tr>
<tr>
<td>Zurita, M</td>
<td>GRA</td>
<td>1/99-11/99</td>
<td>LII theory; Aggregate properties</td>
</tr>
</tbody>
</table>

a PDRA=Post-doctoral Research Asst
b GRA= Graduate Research Assistant (V=Visiting)
PI = Principal Investigator
RS/S=Research Scientist/Scholar

3.2 Cooperation with US Industry

While the research summarized here was principally supported by AFOSR under Grant 97-1-0266, the Yale HTCRE Laboratory has also been the beneficiary of occasional smaller grants from U.S. industrial corporations, including groups within ALCOA, GE, DuPont, Union Carbide (now Advanced Ceramics Corp.) and Shell, as well as the feedback and advice of scientists/engineers from these/other corporations. We appreciate this level of collaboration, and expect that it will accelerate inevitable applications of our results in areas relevant to their technological objectives (see, also, Section 3.4, below).

Periodically, our results are picked up and used by aerospace-oriented industrial contractors, or corporations engaged in ancillary chemical industry. However, no bona-fide "Technical Transition" was identified by the PI during this particular interval.
3.3 External Presentations, Research Training, and Pedagogical Impact

Apart from the 17 publications cited above and itemized in Sections 5, we have presented some 20 technical talks on the subject matter of this Grant. With few exceptions these have been at national meetings of the Combustion Inst., AIChe, and AAAR, or as University seminars (as documented in our earlier Annual Reports on this grant).

The pedagogical impact of the PI's AFOSR research will be considerably augmented when Dover Publications (Mineola, NY) markets an updated paperback reprint of his 1986 textbook-treatise during the summer of 2000. This 'reprint' will actually contain a 50 page Supplement which cites many recent papers, including those supported by this Grant.

3.4 Applications of Yale-HTCRE Lab Research Results; Technology Transfer

As an indication of the worldwide scientific impact* of this 3-year OSR-supported program, some 150 citations have appeared under the PI's name: Rosner, D.E. in Science Citation Index. It has been gratifying to see direct applications of this generic AFOSR-supported particle and vapor mass transfer research in more applications-oriented investigations reported in recent years, as documented in our earlier Annual Reports. During this reporting period there were apparently no new bona-fide 'transitions' to report, although our recent OSR research on particle deposition and impact-induced erosion is being used in the land-based combustion turbine industry, including that concerned with energy recovery at chemical plants (Private Communications related to the PI’s consulting activities). Applications in other fundamentally-oriented research programs are easier to discover and track. For example, the PI has become aware that ‘TPD’, a thermophoretically-based technique for determining local soot volume fractions and temperatures in laminar flames (see Section 2.2), is currently being used at UCLA, VPI and UTRC. This technique, a 'byproduct' of our OSR-sponsored particle deposition research (Section 2.4), is quite attractive because it is simple, completely independent of particle optical properties, and applicable to very low soot volume fractions.

4. CONCLUSIONS

This 3-year AFOSR program was motivated by the fact that the ability to reliably predict the local concentration, sizes, transport properties and stability of aggregated flame-generated particles (carbonaceous soot, B$_2$O$_3$, Al$_2$O$_3$, ...), often in the size range of only tens of nanometers, in high pressure, high temperature environments, is important for many technologies relevant to the U.S.A.F., especially jet engine combustor design. As one important overall result, we have shown that soot aggregates from a wide variety of organic and inorganic combustion systems exhibit mechanistically significant morphological and transport property similarities (Rosner et.al.,1997, Koylu et.al.,1995,1997, Xing et.al., 1997,1999). Indeed, our results for the transport properties of soot aggregates can now be used in more accurate models of soot dynamics in laminar and turbulent flames. Moreover, we have also provided properties needed to correctly interpret the results of recently introduced laser diagnostics as applied in research on soot formation/suppression at high pressures (e.g., laser-induced incandescence (LII)). These experimental techniques, together with closely coupled theoretical calculations of particle birth/dynamics in counterflow diffusion flames and mixing/boundary layers, have led to a significantly improved understanding of combustion-generated ultra-fine particles, including their sampling, coagulation, restructuring and deposition dynamics.
5. REFERENCES

5.1 BACKGROUND PUBLICATIONS


Roth, P. and Fillippov, A.V.(1996), "In Situ Ultra-fine Particle Sizing by a Combination of Pulsed Laser Heat-up and Particle Thermal Emission",*J. Aerosol Sci.*, **27** 95-104


5.2 PUBLICATIONS WHICH APPEARED BASED ON GRANT AFOSR 97-1-0266


Filippov, A.V., Rosner, D.E (1998), "Particle-to-Gas Energy Transfer During Laser-Induced Incandescence", *J. Aerosol Sci.(Elsevier)* 29 , Suppl. 1, S583-S584,


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Xing, Y., Synthesis and Morphological Evolution of Inorganic Nano-particles in Gas Phase Flames, PhD Dissertation, Yale University Graduate School, Chemical Engineering Dept., December 1997

5.3 PUBLICATIONS SUBMITTED/IN PRESS BASED ON GRANT AFOSR 97-1-0266


LIST OF ABBREVIATIONS

ALS Angular Light Scattering  BL Boundary layer
CDF Counterflow diffusion flame  TEM Transmission Electron Microscopy
CVD Chemical vapor deposition  CRF Combustion Research Facility
Df Fractal dimension  GRA Graduate research Asst.
G/S Gas/solid interface  JTPV "Jump" Thermophoretic Velocimetry
LDV Laser Doppler Velocimetry  LII Laser-induced incandescence
LLS Laser light scattering  LTCE local thermochem. equilibrium
PBE Population Balance Eq.  pdf Probability density function
PI Principal Investigator  PSD Particle size distribution
MRS Materials Research Society  TMA Trimethyl aluminum
VS Visiting Scholar  TPD Thermocouple Particle Densitometry
TSPD Thermophoretic sampling particle diagnostic
TPV Thermophoretic velocimetry

*Full-length reprints previously unavailable are reproduced in Section 6 (along with Forms 298)

6. APPENDICES (Complete Previously Unreported Papers on GRANT AFOSR 97-1-0266; including Form 298 for each)

PIADC Survey INFO (cf. Sections 5.2, 6):

PI DATA

Name: Daniel E. Rosner
Institution: Yale University
Contract/Grant No.: AFOSR 97-1-0266

NUMBER OF GRANT CO-INVESTIGATORS

Fac. 1  Post-docs. 2  Grad Students 2  Other 1
PUBLICATIONS RELATED TO AFOREMENTIONED GRANT

Name of Journal: J. Nanoparticle Research, (Special Issue on Vapor Phase Synthesis of Nano-particles)
Title of (Invited) Article: "Prediction of Spherule Size in Gas Phase Nano-Particle Synthesis
Authors: Xing, Y. and Rosner, D. E.
Publisher: Kluwer
Volume: 1 Pages: 277-29 Month Published: July(?), Year: (1999)

Name of Journal: J. Aerosol Sci
Title of Article: "Particle Morphology and Knudsen Transition Effects on Thermophoretically Dominated Mass Deposition Rates From 'Coagulation-Aged' Populations"
Authors: Rosner, D. E. and Khalil, Y.F.
Publisher: Elsevier
Volume: 31 Pages: 273-292 Month Published: March Year: (2000)

HONORS/AWARDS RECEIVED: Senior Scientist Research Award of the AAAR

Professor Daniel E. Rosner of the Yale Department of Chemical Engineering, has just been named as the 1999 D. Sinclair Award Winner of the American Association of Aerosol Research (AAAR). Presented October 13, 1999 in Tacoma WA at the 18th Annual Mtg. of AAAR, a society devoted to the science and technology of gas-borne particulate matter, this award recognizes sustained excellence in aerosol research and technology by an established scientist. Professor Rosner, who joined the Yale ChE Faculty in 1969 after 10 years of industrial research experience, is the author of over 230 research publications, many dealing with the synthesis, coagulation, restructuring kinetics, transport properties, and detection/characterization of gas-borne particles, often with dimensions as small as 10 nanometers. Such particles are important in air pollution control engineering and semi-conductor processing, as well as the industrial scale production of high-value ultra-fine powders, pigments, and optical wave guide fibers.

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9
Prediction of spherule size in gas phase nanoparticle synthesis

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Surprisingly, there is still no rational yet practical method to reliably predict absolute ‘primary’ nanospherule sizes and, hence, specific surface areas, in gas phase flame nanoparticle synthesis. The present paper summarizes our approach to this important problem, using a plausible and tractable coagulation-coalescence (two-rate process) model, but with an important modification to the rate of nanoparticle coalescence. The Smoluchowski equation is used to describe the particle Brownian coagulation rate process (free-molecule regime), together with the assumption that the particle population follows a self-preserving size distribution. The decisive coalescence process, driven by the minimization of surface energy of the coalescing nanoparticles, is presumed to occur via the mechanism of surface diffusion. However, a curvature-dependent energy barrier for surface-diffusion is proposed, taking into account the extended ‘surface-melting’ behavior of nanoparticles. This is shown here to have the effect of accelerating the coalescence rate of touching nanoparticles, leading to absolute sizes (at the predicted onset of aggregate formation) in encouraging agreement with available experiments. It was found that the coalescence rate, especially with a curvature-augmented surface diffusivity, is far more sensitive to particle size than is the Brownian coagulation rate. As a result, when cast in terms of characteristic process times, a distinct crossover generally exists, allowing the determination of observed ‘primary’ spherule sizes within larger aggregates. This approach is successfully applied here to several published synthesis examples of vapor-derived nanosized alumina and titanias. Its broader implications for nanoparticle synthesis in non-isothermal reactors, including our own counterflow diffusion flame reactor, are also briefly summarized.
Prediction of spherule size in gas phase nanoparticle synthesis

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Department of Chemical Engineering, High Temperature Chemical Reaction Engineering Laboratory, Yale University, New Haven, CT 06520-8206, USA. **Present address: Department of Chemical Engineering, Johns Hopkins University, Baltimore, MD 21218 (E-mail: yungchuan.xing@yale.edu); ***Author for correspondence (E-mail: daniel.rosner@yale.edu)

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Key words: nanoparticles, specific surface area, surface melting, coalescence, surface diffusion, flame particle synthesis

Abstract

Surprisingly, there is still no rational yet practical method to reliably predict absolute 'primary' nanospherule sizes and, hence, specific surface areas, in gas phase flame nanoparticle synthesis. The present paper summarizes our approach to this important problem, using a plausible and tractable coagulation-coalescence (two-rate process) model, but with an important modification to the rate of nanoparticle coalescence. The Smoluchowski equation is used to describe the particle Brownian coagulation rate process (free-molecule regime), together with the assumption that the particle population follows a self-preserving size distribution. The decisive coalescence process, driven by the minimization of surface energy of the coalescing nanoparticles, is presumed to occur via the mechanism of surface diffusion. However, a curvature-dependent energy barrier for surface-diffusion is proposed, taking into account the extended 'surface-melting' behavior of nanoparticles. This is shown here to have the effect of accelerating the coalescence rate of touching nanoparticles, leading to absolute sizes (at the predicted onset of aggregate formation) in encouraging agreement with available experiments. It was found that the coalescence rate, especially with a curvature-augmented surface diffusivity, is far more sensitive to particle size than is the Brownian coagulation rate. As a result, when cast in terms of characteristic process times, a distinct crossover generally exists, allowing the determination of observed 'primary' spherule sizes within larger aggregates. This approach is successfully applied here to several published synthesis examples of vapor-derived nanosized alumina and titania. Its broader implications for nanoparticle synthesis in non-isothermal reactors, including our own counterflow diffusion flame reactor, are also briefly summarized.

1. Introduction

Aerosol processes for producing ultrafine inorganic particles have a long history, especially the use of gas phase flames to synthesize pigments (e.g. TiO2), which can be traced back roughly half of a century. Flame processes are still widespread in industry to economically generate fine powders, including non-pigmentary applications in which the premium is placed on specific surface area rather than visible light scattering power. Unfortunately, the fundamentals of particle formation in such environments are not well understood, especially particle growth kinetics in the early 'nanoparticle' formation stages. This is partly due to the fact that processes at these early stages are extremely fast (Pratsinis, 1998), mostly taking place

*Invited paper
on a sub-millisecond time scale. Additionally, physicochemical properties of particles on the nanometer scale are not well documented.

In earlier laboratory studies of flame-synthesized powders, Ulrich and co-workers (Ulrich, 1971; Ulrich & Subramanian, 1977) attempted to predict silica spherical size in laminar and turbulent flames. In their seminal work, they suggested that Brownian coagulation and coalescence were the rate processes determining observed particle size and morphology, with growth from the vapor phase (CVD or vapor deposition) playing a secondary role. In their work, particle formation was simply interpreted as resulting from coagulation, followed by rapid coalescence as a result of surface-energy driven viscous flow. Semi-quantitative comparison with experiments revealed some discrepancies, attributed to inaccuracies of available experimental measurements. In a more recent study, Koch & Friedlander (1990a) have suggested a more convenient, asymptotically valid form for aggregate sintering rate in terms of surface areas. In their work a characteristic coalescence time was introduced, expressed in multiples of the 'monomer particle' sintering time. The latter was based on the sintering of spherical particles via viscous flow or solid-state diffusion. Other studies (Lehtinen et al., 1996a,b; Koch & Friedlander, 1990b; Tandon & Rosner, 1996; Flego & Ladon, 1995; Krueger et al., 1993; Hebble & Saffrin, 1989) were principally concerned with the primary particle growth by sintering within aggregates, in which two or more constituent spheres (adjacent 'primary' particles) stick together. Typically, in all of these studies, it has been assumed, either explicitly or implicitly, that macroscopic material properties can be applied to nanoparticles. While this can be valid for large particles (often 100 nm and depending on material), for much smaller particles (ca. 10 nm) this assumption can evidently result in large errors in the predicted coalescence rate (Wa et al., 1993; Xing et al., 1996). Since aerosol particles are basically developed from their precursors, much smaller 'parent' particles, and must go through a nanoparticle stage, it is very important to understand the coalescence of isolated nanoparticles, before addressing aggregate restructuring. It is now well known that when matter is sufficiently finely divided, especially down to the nanometer scale, many of its physical and chemical properties differ significantly from the corresponding bulk values (see, e.g., Lehtinen et al., 1992). Therefore, property changes associated with particle sizes in the nanometer range must be taken into account.

More generally, particle formation from the vapor phase consists of four basic steps, not necessarily purely sequential: vapor phase chemical reaction, nucleation of the supersaturated vapor product to form embryonic particles, primary particle growth by vapor condensation and/or heterogeneous chemical reaction, and particle growth as a result of particle-particle collisions, usually associated with their Brownian motion. The rates of these processes can be conveniently ordered in terms of their corresponding characteristic times (Rosner, 1996), and, when compared in this way, there is often only one or two that is rate-controlling step (Xing et al., 1996). Thus, for many metal oxides produced in flames (e.g., Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub>) it is found that their critical nucleus radii, formally calculated from the Gibbs-Kelvin equation, are of the order of their molecular radii. This follows from the smallness of the oxide equilibrium vapor pressure at the temperature at which the oxide vapor is chemically produced. For example, the equilibrium vapor pressure of alumina at 1000 K is approximately 10<sup>-10</sup> Pa, but the vapor pressure for alumina particle formation in laboratory reactors usually exceeds 10 Pa. Such high local supersaturation, according to classical nucleation theory, easily makes every product molecule, here Al<sub>2</sub>O<sub>3</sub>(g), a 'stable nucleus'. In such cases, as a useful soil reaction engineering (SRE) simplification, particle 'nucleation' may be considered virtually instantaneous, and explicitly neglected (Ulrich, 1971). Therefore, if the vapor presor does not chemically persist, particle growth in such environments can be regarded as the result of (post-reaction) physical coagulation and coalescence processes. Conditions for the validity of this idealized two-stage process model are easily satisfied if the precursors vapor reaction (often hydrolysis) is sufficiently fast, which is true for many metal oxide precursors in current use, especially organosilicate molecules (Xing et al., 1996).

Adopting this two-process picture, and following Ulrich (1971), and Koch & Friedlander (1990a), in Section 2, we apply the Smoluchowski coagulation rate equation in a non-isothermal environment representative of a wide variety of aerosol synthesis processes. To more accurately describe the observed coalescence rate of nanoparticles, we introduce a microscopic but quasi-continuum model based on the 'surface melting concept' (Section 2.3). This concept leads us to a curvature-dependent and significantly enhanced surface self-diffusion coefficient for the coalescence of nanoparticles. Moreover, at the prevailing temperatures we show that the coalescence rate associated with this modified surface diffusivity is much more sensitive to particle size than in the Brownian coagulation rate. Therefore, a distinct 'crossover' generally exists between the two relevant characteristic times as a function of particle size, allowing a determination of the ('primary') spherical size, and this 'crossover size' will often remain 'frozen in'. Specifically, in Section 3, predictions using this approach will be shown to be in encouraging agreement with available experimental results on alumina and titania nanoparticles synthesized from several different gas phase flames (Xing et al., 1996; Zhu & Pratsinis, 1996; Rulison et al., 1996), and 'non-flame' aerosol reactors (Okayama et al., 1989).

2. Theory

2.1. Particle environments of interests

Two canonical classes of environment situation considered here are flames (or other aerosol reactors) which produce a 'cooling' or 'heating' temporal environment as seen by the particle population. Particle evolution in a 'cooling' flame, i.e. one in which the temperature is decreasing with particle residence time, may be divided into three stages, as shown schematically in Figure 1a: (1) coagulation-controlled regime, (2) coalescence-controlled regime, and (3) a (short) transient stage where the coagulation and coalescence times are comparable. In a 'heating' flame environment in which the temperature is increasing with particle residence time (see Figure 1b), particle growth may have one or all of the stages in the 'cooling' case, depending on heating rate and local temperature. If the residence time is long enough, the final product can conceivably be spherical particles because the temperature will ultimately exceed the melting temperature of the material, and all aggregates will collapse. For other aerosol reactors, a temperature history can be similarly expressed. Nevertheless, in all cases, there is an initial stage in which the particles are formed, as illustrated in Figure 1. This stage is characterized by coagulation with instantaneous coalescence, i.e. coagulation-controlled. Because we are interested in rate processes determining nanoparticle sizes, the formula below is focused on this stage.

2.2. Brownian coagulation of particle populations

In an isothermal isobaric environment, coagulation of particles (see, e.g., Friedlander, 1977) leads to a decrease in particle number density, while maintaining the condensed phase volume fraction constant. If instantaneous coalescence of the colliding particles is assumed, and particle growth via heterogeneous oxidation of surviving vapor precursor is neglected, the particle production rate can be expressed in terms of the continuous form of the Smoluchowski equation (Friedlander, 1977):

\[
\frac{dn}{dt} = \int_0^\infty \beta(v', v) n(v') n(v) \frac{dv'}{v} - \int_0^\infty \frac{dn}{dv(v) n(v)} dv,
\]

where \( n(v) \) is the number density of particles in the size range \( v \pm (1/2) dv \). The collision frequency function appearing in Eq. (1), in the free molecule regime, may be written (Friedlander, 1977):

\[
\beta(v, v') = \frac{3}{4\pi} \left( \frac{\rho_a T}{\rho} \right)^{1/2} \left( \frac{1}{1 + v/v'} \right)^{1/2} \left( 1 - \frac{1}{1 + v/v'} \right)^2
\]

where \( k_b \) is the Boltzmann constant, \( T \) the temperature, and \( \rho_a \) the density of the condensed phase. Since the primary spheres observed in an aerosol process are generally small (less than 50 nm) when compared to the gas mean free path at the synthesis temperature, we only consider this so-called free molecule regime (Eq. 2). The decay in the total number density of particles is obtained by summing Eq. 1 over all particle sizes:

\[
\frac{dn}{dt} = \int_0^\infty \beta(v, v) n(v) \frac{dv}{v},
\]

Furthermore, in all cases, there is an initial stage in which the primary spheres are formed, as illustrated in Figure 1. This stage is characterized by coagulation with instantaneous coalescence, i.e., coagulation-controlled. Because we are interested in rate processes determining nanoparticle sizes, the formula below is focused on this stage.

\[
\eta = v/\dot{c}, \quad \psi(\eta) = n\eta^3/N, \quad \dot{u} = \dot{\psi}/N,
\]

(4)
of particles per unit mass of gas,
\[ N = \frac{\phi}{N_p} \]  
and the particle volume per unit mass of gas,
\[ \phi_v = \frac{\phi}{\rho_p} \]  
where \( \rho_p \) is the gas phase local density. Substituting these relations into Eq. 5 and defining the average particle diameter via
\[ \bar{d}_p = \left( \frac{6}{\pi} \right)^{1/3} \left( \frac{5\phi_v}{\pi N_p} \right)^{1/3}, \]
we obtain the evolution equation:
\[ \frac{d\bar{d}_p}{dt} = \left( \frac{\alpha_{so} \phi_v}{2\tau} \right) \cdot \frac{12k_bT_0}{\rho_p} \cdot \left( \frac{1 + \frac{\lambda}{\tau} t}{T_0} \right)^{-1/2} \left( \bar{d}_p \right)^{-1/2} \]
\[ - \left( \frac{k_b}{18\rho_p \tau} \right) \cdot \left( 1 + \frac{\lambda}{\tau} t \right) \cdot \left( \bar{d}_p \right)^3, \]
where use has been made of Eq. (7), \( dN_p = (18\rho_{so}/\eta_{so})d\bar{d}_p \) and \( \rho_{so}/\rho_{so} = T_0/T \) (the ideal gas equation of state). As before, the subscript 0 refers to the initial state. Note that Eq. (10) contains on the right hand side a term that results from the non-isothermal conditions, i.e. temperature-induced expansion of the local gas phase.

A relaxation time for particle-particle collisions, hereafter called the coagulation time, \( \tau_c \), can be defined to characterize the coagulation rate process. This characteristic time in (Xing et al., 1996; Friedlander, 1977)
\[ \tau_c = \frac{2}{BN} \]  
where from Eq. (2) the value of rate constant \( \beta \) is
\[ \beta = 4 \left( \frac{3}{4\pi} \right)^{1/2} \left( \frac{12k_bT_0}{\rho_p} \right)^{1/2} \left( \frac{T}{T_0} \right)^{1/2} (\bar{d}_p)^{1/2} \]
and
\[ N = \left( \frac{\phi_v}{v} \right) \left( \frac{T}{T_0} \right) \rho_{so} \]

2.3. Surface melting of small particles

Before we address the coalescence rate and associated characteristic time, it is necessary to develop a microscopic approach to the surface state of small particles. Surface melting of solid has been studied for clusters (Berry, 1997), small particles (Kofman et al., 1994) and flat surfaces (Platz et al., 1990). Both simulation and experiment have shown that disordering of surface atoms/molecules occurs far ahead of the bulk solid phase at elevated temperatures due to the broken bonds associated with surface atoms (Ichinose et al., 1992; Bicout et al., 1993). Experimental observation also revealed that small particles undergo surface melting process (Chen et al., 1988), which may lead to near-instantaneous coalescence at low temperatures (Huang et al., 1991).

The thickness of the disordered surface layer, or quasi-liquid layer, can be shown to depend on both particle size and absolute temperature; and the surface melting temperature can be obtained at a fixed thickness of melted-surface layer. In the following we approach this problem through a simple thermodynamic formulation.

The melting temperature, \( T_{m} \), of a particle of radius \( r \), can be expressed (Couchman & Jensen, 1977),
\[ T_{m} = 1 - \frac{3}{L_r} \left[ \rho \frac{\Delta H_m}{\rho \Delta f} \right]^{1/3}. \]  
where \( T_{m} \) is the melting temperature of the corresponding bulk solid \( (r \to \infty) \); \( L_r \) is the latent heat of fusion per unit volume of solid; \( \rho \) and \( \rho_e \) are surface energies of the solid/gas and liquid/gas interfaces; and \( \rho \) and \( \rho_e \) are the densities of the participating solid and liquid phases. Now consider a particle undergoing the surface melting process, as illustrated in Figure 2. As the temperature is increased, a disordered (melted) surface layer is formed on the particle. Then, the Helmholtz free energy difference per unit area between a surface-melted particle and a particle in the solid state of the same mass can be written (Xing, 1997; Xing & Rosner, 1997):
\[ \Delta f = \left( \frac{LT_{m}T}{3T_m} \right) \cdot (\delta - 3\delta + \delta^3) \cdot (1 - 6) \]
\[ \cdot (\rho - \rho_e - \rho_e(1 - 3\delta)^2). \]  
where \( \delta = \xi r / \xi \) is a dimensionless length with \( \xi \) being the surface liquid layer thickness; \( T = (T_{m} - T)/T_{m} \)
Figure 3. Schematic diagram of the surface melting processes. A particle is considered solid at 0 K and liquid at its melting temperature, \( T_{ms} \). For intermediate temperatures, the particle is considered in a 'surface melted' state.

\[
\Theta = \exp \left[ -\frac{\xi}{(1 - \delta)\xi} \right] = \begin{cases} 1, & \text{for a solid surface,} \\ 0, & \text{for a liquid surface,} \end{cases} \tag{15}
\]

is the surface order parameter with \( \xi \) being the liquid correlation length (Van de Veen et al., 1988; Lowen, 1994). This exponential expression accounts only for short-range interactions, as it is suitable for small systems (current case). For long-range interactions (van der Waals forces, not considered here) the order parameter has a power law expression (Lowen, 1994). The equilibrium liquid layer thickness at a given temperature \( T \) can be obtained by minimizing the free energy difference, i.e., by setting \( \delta \frac{\partial F}{\partial \delta} = 0 \) while satisfying the inequality conditions \( \delta \frac{\partial F}{\partial \delta^2} > 0 \) and \( \Delta F \leq 0 \). The surface melting temperature, \( T_{ms} \), of the topmost surface molecules is determined by setting \( \xi \) to that surface layer thickness \( \xi_m \), taken as the lattice length of the corresponding material. In Figure 3 we present the surface melting temperature (topmost layer only) calculated from this formulation. The model material considered here is alumina, whose familiar physical properties are listed in Table 1. For comparison, in Figure 3 we also display the particle melting temperature and the bulk melting temperature contours. As anticipated for small particles, the surface melting temperature deviates appreciably from the particle melting temperature, as well as the bulk melting point. The surface melting temperature is lower as the particle size becomes smaller.

![Diagram of surface melting processes](image)

Table 1. Physical properties of alumina and titanias used in present calculations

<table>
<thead>
<tr>
<th>Properties</th>
<th>Alumina</th>
<th>Titanias</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho (\text{g/cm}^3) )</td>
<td>3.970</td>
<td>4.427</td>
</tr>
<tr>
<td>( T_m (\text{K}) )</td>
<td>2327</td>
<td>2130</td>
</tr>
<tr>
<td>( L (\text{J/g}) )</td>
<td>4.32</td>
<td>3.79</td>
</tr>
<tr>
<td>( \gamma_s (\text{J/m}^2) )</td>
<td>2.3</td>
<td>2.14</td>
</tr>
<tr>
<td>( \gamma_l (\text{J/m}^2) )</td>
<td>0.70</td>
<td>0.34</td>
</tr>
<tr>
<td>( \gamma) (\text{J/m}^2) )</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>( \zeta (\text{A}) )</td>
<td>7.0</td>
<td>8.4</td>
</tr>
<tr>
<td>( \xi_s (\text{A}) )</td>
<td>5.13</td>
<td>4.58</td>
</tr>
<tr>
<td>( \Omega (\text{A}) )</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

\(^*\)Values estimated from the method given in the reference.

2.4. Coalescence models of spherical particles

The driving force for coalescence of touching particles is minimization of the surface energy. Four mechanisms have been proposed for the sintering of powders, i.e., viscous flow, evaporation-condensation, volume diffusion and surface diffusion/boundary diffusion. Only considering condensed phase molecular diffusion, the time for complete coalescence of two spherical particles can be approximated as (Xing et al., 1996; Coblenz et al., 1980)

\[
\frac{r_s}{D \tau_s} = \frac{h_s T_v}{c w_0 D \Omega^2 T_s^2} \tag{16}
\]

where \( w \) is the surface or grain boundary layer width, \( \Omega \) is the molecular volume and \( D \) is the relevant diffusion coefficient, with the units: m/s. The constants are \( a = 3, b = 0 \) and \( c = 120 \) for volume diffusion, \( a = 4, b = 1 \) and \( c = 225 \) for surface diffusion, and \( a = 4, b = 1 \) and \( c = 64 \) for grain boundary diffusion. This expression is formally extrapolated from the initial sintering rate, with later-stage deviations neglected.

2.5. Surface melting and associated surface diffusivity

Although each mechanism can contribute to the ultimate coalescence of particles, many experiments and simulations have demonstrated that surface diffusion is the dominant mechanism for nanoparticles (Bovech & Marks, 1992; Kusonoki et al., 1993; Zacharielle & Carrier, 1994). Since we are dealing with nanoparticles here, only the surface diffusion will be considered below. However, in our discussion, a comparison of the coalescence rates associated with all three mechanisms is given in next section.

The surface self-diffusion coefficient can be generally written (Soomeraj, 1994)

\[
D_s = D_{gs} \exp \left( -\frac{E_s}{RT} \right), \tag{17}
\]

where \( E_s \) is the activation energy for surface diffusion and \( R \) the universal gas constant. Experiments have revealed that the activation energy \( E_s \) and the prefactor \( D_{gs} \) are different at low and high temperatures, generally separated by \( T \approx 0.75 T_m \) for macroscopic surfaces. It also has been shown that the surface diffusion coefficient can be related to the melting point of the material via (Soomeraj, 1994; Seebauer & Allen, 1995):

\[
D_s = D_{gs} \exp \left( -\frac{Q_s T_m}{RT} \right). \tag{18}
\]

where \( Q_s = E_s / T_m \) and has been found to be approximately constant for similar crystalline structure materials (Soomeraj, 1994). Equation (18) was obtained from surface diffusion on macroscopic surfaces. For the nanoparticles considered in the present work the surfaces will melt earlier so that \( T_m \) now is replaced by the surface melting temperature \( T_{ms} \). If we further postulate that \( Q_s \) is explicitly size-independent, then Eq. (18) for small particles becomes

\[
D_s(r) \approx D_{gs} \exp \left( -\frac{Q_s T_{ms}}{RT} \right). \tag{19}
\]
Since \( T_{\text{ref}} \) is related to particle size and material properties, we see that the surface diffusion coefficient is curvature-dependent. Equation (19) is the surface diffusion coefficient that will be used in Eq. (16) (for \( D \)) for calculating the coalescence characteristic time.

In Figure 4 we plot the corresponding surface self-diffusivity using Eq. (19), together with its macroscopic values (Eq. (18)). We see that the enhancement of the surface diffusion coefficient is significant for small particles. Given a temperature, the ratio can be several decades. Such large diffusion coefficients make it possible for small particles to coalesce ‘surprisingly’ rapidly (see next section for a quantitative comparison).

3. Results and discussion

3.1. Coagulation of spherical nanoparticles

Coagulation with a self-preserving size distribution has been extensively used to describe particle evolution in flames (Ulbrich & Subramanian, 1977; Wu et al., 1993; Matsoukas & Friedlander, 1991). Given Eq. (10) for particle coagulation, it is not difficult to find the isothermal solution by simply setting \( \lambda = 0 \), leading to the well-known result \( \delta_\nu \sim \nu^{2/5} \). Equation (10) is a generalized form allowing changes in gas temperature and can be solved for any value of the heating time \((\lambda / T_{\text{ref}})^{-1}\). In flames of short residence time and small cooling or heating rate, the second term in Eq. (10) is much smaller than the first term when particles are small. Therefore, the second term on the right side of Eq. (10) can be neglected for nanoparticle formation. Integration of Eq. (10) leads to,

\[
\delta_\nu = \left( \frac{5}{2} \frac{D_\nu 2 \nu_0 T_{\text{ref}}}{\nu_0 T_{\text{ref}}} \right)^{1/2} \left( \frac{1}{\nu_0 T_{\text{ref}}} - 1 \right) + (\delta_\nu \nu_0^{1/5})^{2/5},
\]

or explicitly in time:

\[
\delta_\nu = \left( \frac{5}{2} \frac{D_\nu 2 \nu_0 T_{\text{ref}}}{\nu_0 T_{\text{ref}}} \right)^{1/2} \left( \frac{1}{\nu_0 T_{\text{ref}}} - 1 \right) + (\delta_\nu \nu_0^{1/5})^{2/5},
\]

For purposes of discussion, alumina was used in our calculations because of its well-known physical properties (see Table 1) and the availability of aerosol evolution measurements (Xing et al., 1999). In Figure 5 we plot the results for the coagulation of nanoparticles starting from molecular monomers. As is seen, particle growth is directly related to the precursor loading and initial temperature. Additionally, residence time has a more pronounced effect on particle size in high temperature-gradient flames than in an isothermal environment. However, for the short residence times considered here the calculated results show only a small deviation, as illustrated in Figure 5. The small deviation is due to the slow cooling/heating rates and short residence time, since under these conditions we can approximate the time term as \((1 + \lambda / T_{\text{ref}})^{-1} \approx \lambda / (2T_{\text{ref}})\). But as the particles grow larger the deviation becomes larger, and the higher order terms can no longer be neglected. The effects of the particle loading can also be seen in Figure 5, which shows that higher loading leads to larger particles at the same residence time.

3.2. Coalescence of spherical nanoparticles

We begin our discussion of the coalescence of nanoparticles with an overview of why sintering models using macroscopic properties necessarily fail for nanoparticle formation from the gas phase. We first compare the coalescence time for two touching particles via three of the sintering mechanisms, i.e. volume diffusion, grain boundary diffusion and surface diffusion (see last section). Using alumina and titania as model materials (see Table 1 and Table 2 for their physical properties), we calculate the coalescence times for spherical particles of radius of 5 and 10 nm at temperature, for example, 800 K. The results are assembled in Table 3. We see that the coalescence times obtained from the macroscopic model can be as long as months or even years for these nanoparticles, whereas in real situations, the residence time and the coagulation time are much shorter (ca. ms). Therefore, if particle coalescence were governed by these macroscopic properties, nanoparticles would never coalesce in the available residence time. This contradicts the experimental results, in which spheres of several tens of nanometers have been synthesized.

Using the surface curvature-dependent diffusivity, Eq. (19), we obtain the results plotted in Figure 6. Within the size range under consideration, we find that the coalescence times are many orders of magnitude smaller than those obtained from using bulk properties. Such dramatic changes make it possible to sinter particles of up to tens of nanometers in a much shorter time (ca. 1 ms). The sharp decrease of coalescence time results from the decrease in particle size.

### Table 2. Diffusion coefficients* and activation energies for surface diffusion (s), grain boundary diffusion (b) and volume diffusion (v) of alumina and titania

<table>
<thead>
<tr>
<th>Properties</th>
<th>Alumina</th>
<th>Titania</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_s ) (m²/s)</td>
<td>( 1.0 \times 10^{-10} )</td>
<td>( 1.6 \times 10^{-10} )</td>
</tr>
<tr>
<td>( D_v ) (m²/s)</td>
<td>( 0.86 )</td>
<td>( 3.13 )</td>
</tr>
<tr>
<td>( E_s ) (kJ/mol)</td>
<td>258</td>
<td>313</td>
</tr>
<tr>
<td>( E_v ) (kJ/mol)</td>
<td>284</td>
<td>313</td>
</tr>
</tbody>
</table>

*The diffusion layer width is assumed to be 1 nm (Cobenz et al., 1989).
Table 5. Order of magnitude comparison of time scales using microscopic properties for different sintering mechanisms. Volume diffusion, grain boundary diffusion and surface diffusion (T = 800 K)

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle</th>
<th>Volume</th>
<th>Grain boundary</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>radius (nm)</td>
<td>t_v (ms)</td>
<td>t_gb (ms)</td>
<td>t_s (ms)</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>5</td>
<td>10^3</td>
<td>10^6</td>
<td>10^9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>10^4</td>
<td>10^7</td>
</tr>
<tr>
<td>TiO_2</td>
<td>5</td>
<td>10^4</td>
<td>10^7</td>
<td>10^10</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>10^5</td>
<td>10^8</td>
</tr>
</tbody>
</table>

Thus, we seek the point where particles stop growing under the prevailing conditions. Beyond this point, spherule growth will effectively stop and 'fractal-like' aggregates will be formed. As also emphasized in the work of Lehtinen et al. (1996a) and Xing et al. (1996), this point is actually the coagulation between the characteristic coagulation and coalescence times.

We begin with a synthesis environment with decreasing temperature, i.e. \( \lambda \) in Eq. (7) is negative. Particle evolution in such case has been illustrated in Figure 1a. In Figure 7 the influence of initial temperature on particle size is shown, where the characteristic times (coagulation and coalescence) are plotted against particle size on a logarithmic scale. We see that the coagulation time is much longer than the coalescence time at small particle size, but the coalescence time quickly increases, as the particles grow. Because the slopes of the curves differ significantly at the crossover (note the logarithmic scales), i.e. \( \frac{dt_c}{d(\lambda)} > \frac{dt_{s}}{d(\lambda)} \), particle growth by coalescence effectively 'stops' beyond this crossover, after which the aggregates, not single particles, are expected. This 'stop' particle size would be the spherule size observed in experiments. From Figure 7 we see that an increase of the initial temperature from 1000 to 2000 K leads to an increase in particle diameters approximately from 30 to 400 nm, showing a significant effect of temperature.

Results at different particle loadings (10^{-3}, 10^{-2} and 10^{-1} m^3/kg-gas) are presented in Figure 8, roughly corresponding to the loading ranges in most laboratory experiments. Under conditions of an initial temperature 1500 K and a cooling rate 10^5 K/s, the spherule diameters are calculated to be 590, 270 and 58 nm, respectively. The loading of 10^{-1} m^3/kg-gas is also comparable to the industrial loading in the lower range, and we see that this loading produces a particle size also comparable to those found in commercial pigmentary powders (ca. 0.5–1 μm). Cooling rates are generally limited by flame conditions, and are found to have little apparent effects on spherule size because of the much higher rates of coagulation and coalescence.

Figure 6. Comparison of sintering times at 800 K for different particle sizes using the original surface diffusivity (Eq. (15)) and the modified diffusivity (Eq. (19)). A significant decrease in sintering time is observed using the curvature-dependent diffusion coefficient.

3.3 Predicting spherule sizes in flame particle synthesis: General cases

The particle size evolution by coagulation with the collision frequency function expressed in Eq. (2) is based on the important assumption that the coalescence rate is no longer 'instantaneous'. This assumption has been effectively used in aerosol evolution situations when the particles are sufficiently small. However, as the particles grow larger, this assumption fails, since the particle coalescence rate is no longer 'instantaneous'. Indeed, aggregates consisting of many spheres (or 'primary' particles) are commonly observed in experiments.

Figure 7. Initial temperature effects on the spherule sizes in a cooling flame with \( \phi_0 = 3 \times 10^{-2} m^3/kg \), showing the increase of 'crossover' particle size with initial temperature \( T_i \); a factor of 2 increase in \( T_i \) results in more than 10 fold increase in particle diameters. The horizontal dotted line corresponds to time scale 1 s, and an arrow indicates the crossover spherule size.

Heat ing flames are modeled as shown in Figure 1b, where the countercflow diffusion flame reactor is taken as a prototypical case (Xing et al., 1996). Under the conditions \( T_i = 500 K \) and \( \lambda = 10^5 K/s \), close to that achieved in our experiment (Xing et al., 1996), we have calculated the effect of loading level on particle size. These results are presented in Figure 9. Unlike cooling flames, in which particles are formed in the high temperature region, the reaction of precursors (e.g., trimethylaluminum for alumina) in a heating flame can also occur at a much lower temperature. Therefore, spherical diameters (7.7 and 8.3 nm, in Figure 9) are generally smaller than those found in cooling flames.

Figure 8. Particle loading effects on crossover spherule sizes in a cooling flame at \( T_i = 1500 K \) and \( \lambda = 10^5 K/s \), showing that higher loading leads to larger spherical sizes: \( \phi_0 = 10^{-3} m^3/kg \), \( \phi_0 = 10^{-2} m^3/kg \), \( \phi_0 = 10^{-1} m^3/kg \). It is interesting to note that, at the lowest considered loading, i.e. \( 10^{-3} m^3/kg \), there is no crossover between the two characteristic times, because at such low loadings, the particle coalescence rate is much
slower than the heating rate. Therefore, at any time, particles are small enough to coalesce instantaneously and always exist as isolated spherical particles. The evolution of particles is entirely controlled by coagulation in this case. On the other hand, for higher loadings in Figure 9, there is a second crossover found in the particle evolution, attributed to high temperatures (close to the bulk melting point) where the aggregates coalesce. This second crossover and its corresponding particle size should approximately correspond to the final particle sizes observed in such flames (refer to Figure 1b). However, since the coalescing particles in this calculation are assumed to be spherical (while they are actually aggregated after the first crossover), there would inevitably be a shift in the location of the second crossover in any real case. Nevertheless, this second crossover reveals a very interesting aspect of particle evolution under heating conditions, which does not appear in cooling flames. While the first crossover sets the spherical size, this second crossover marks the condition where the aggregates would collapse. To determine the second crossover more accurately one needs to address the rate of aggregate coagulation and coalescence, topics beyond the scope of this paper. Interested readers may refer to the relevant papers by Tandon and Rosner (1996), Xiong & Pratsinis (1995), Kauri et al. (1993), Sato et al. (1992), Tandon & Rosner (1995), Wu & Friedlander (1993) and Vemury & Pratsinis (1995).

3.4. Comparison with experimental results

Having generalized this approach to the prediction of particle size in cooling and heating flames, we are now in a position to apply this approach to real conditions and to compare with available experimental results. We discuss five real experimental cases in the literature (Wu et al., 1993; Xing et al., 1996; Zhu & Pratsinis, 1996; Ballou et al., 1996; Okiyama et al., 1989). Their experimental conditions are summarized in Table 4.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Tc (K)</th>
<th>λ (K/s)</th>
<th>( \phi_s ) (m^3/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Okiyama et al. (1989)</td>
<td>773</td>
<td>0</td>
<td>4.9 x 10^{-7}</td>
</tr>
<tr>
<td>Xing et al. (1996)</td>
<td>500</td>
<td>4.5 x 10^{4}</td>
<td>2.62 x 10^{-7}</td>
</tr>
<tr>
<td>Wu et al. (1993)</td>
<td>890</td>
<td>1.08 x 10^{4}</td>
<td>6.6 x 10^{-8}</td>
</tr>
<tr>
<td>Zhu &amp; Pratsinis (1996)</td>
<td>1755</td>
<td>4.0 x 10^{4}</td>
<td>2.97 x 10^{-8}</td>
</tr>
<tr>
<td>Ballou et al. (1996)</td>
<td>1000</td>
<td>5.5 x 10^{4}</td>
<td>5.67 x 10^{-8}</td>
</tr>
</tbody>
</table>

*If data not directly given, they are estimated from given information.

Table 4. Summary of experimental conditions as input in present calculations

![Figure 9. Particle loading effects on the spherical sizes in a heating flame at Tc = 500 K and λ = 10^4 K/s, showing that higher loading does not necessarily lead to larger spherical size. Also, the coagulation time curve and coalescence time curve may have one, two or no intersection(s). A second crossover is observed at a temperature close to the bulk melting point indicating ultimate collapse of the aggregates. (a) \( \phi_s = 10^{-2} \) m^3/kg, (b) \( \phi_s = 10^{-1} \) m^3/kg, (c) \( \phi_s = 10^0 \) m^3/kg.](image)

In this paper, a two-stage model is presented to describe the competition between Brownian coagulation and surface energy-driven particle coalescence in a non-isothermal environment. For this model, the absolute size of nanoparticle spheres is predicted, size and loading data are directly given in the papers. Calculated results obtained by the procedures outlined in the last section are presented in Figure 10. The model is plotted with real particle size against predicted size. In such a way perfect agreement would correspond to the 45° line, above which the experimental size is larger and below which the predicted size is larger. As can be seen, all points are close to this line (as compared to orders of magnitude differences from classical models), showing that our predictions are in good agreement with available experimental results.

3.5. Applications and implications

Characteristic times are useful in describing rate processes in single or multiple phase chemically reacting systems (see, e.g., Rosner, 1986). The characteristic times presented above are just two of the many processes presented in a synthesis flame environment (Xing et al., 1996), but in many cases they are the controlling rate processes. Thus, the proposed model is applicable for fast vapor precursor reactions (e.g. Al(CH3)3, TiCl4) forming low vapor pressure materials (e.g. "refractory" ceramics such as Al₂O₃, TiO₂, etc.). For high vapor pressure materials like UO₂, evaporation-condensation mechanism may be as important as surface diffusion for the coalescence of small particles, and for slow reactions, heterogeneous processes leading to particle surface growth should be taken into account. Nevertheless, by extending our two-stage model, it should be possible to incorporate these and perhaps other complications. For example, nucleation and surface reaction have been incorporated into the coagulation equation, giving rise the so-called 'general dynamic equation' (Pratsinis, 1988). Similarly, the coalescence rate would receive contributions from each of the participating coalescence mechanisms.

Although we have focused on the synthesis of metal oxide particles in this work, the presented extended model should also be appropriate for other ceramics formed via any aerosol process, provided the above mentioned assumptions are satisfied. Since surface diffusion has been observed to be the dominant mechanism for the sintering of nanometer particles of most materials, the proposed coalescence model should also be applicable to the participation of coalescence mechanisms.
inception is the most important factor determining ultimate spherical size in both cooling- and heating-environments. This is attributed to the exponential dependence of the (surface-) diffusion-controlled coalescence rate on temperature. In a cooling environment, particle precursor loading also has a pronounced effect on ultimate spherical size, because the high initial temperature is associated with higher rates of Brownian coagulation where the coalescence rates are rapid enough to ‘keep pace’. For cooling-(quenching-) rates within the practically attainable range, the magnitude of the quench rate has little effect on ultimate spherical size because, in such an environment, the particles have already experienced peak temperature and, thus, have already reached their maximum size, with further evolution leading just to Brownian aggregation. The situation is different in heating cases, where the spheres are more likely to grow larger by the merger of adjacent spheres as the temperature increases. This will continue until their size will reduce the rate of coalescence compared to that of Brownian-motion-induced collision. Therefore, large flocular aggregates form with little further alteration of their constituent spherical sizes. In a heating environment, like that encountered on the fuel side of a laminar counterflow diffusion flame (Xing et al., 1996; Chuang & Katz, 1995; Gonzalez & Rosner, 1997), further processing often leads to the ultimate collapse of these aggregates near the bulk material melting temperature, forming much larger isolated particles (Xing et al., 1996; Zachariah & Sermcerina, 1989). Results from our modelling studies (Tandon & Rosner, 1999) suggest that lower temperature synthesis can be an effective route to smaller nanoparticles, though precursor loading in a cooling environment must also be limited. Additionally, spherical size may often be economically controlled by invoking other means to change the coalescence rate, for example, introducing ‘surface-active’ trace additives or dopants (Akhtar et al., 1992).

The extended coalescence-coagulation-rate model proposed here, which accounts for enhanced surface diffusivity on nanoparticles, enables us to satisfactorily simulate nanoparticle evolution in non-isothermal aerosol processes involving simultaneous Brownian coagulation. Predictions of absolute spherical sizes, and associated specific surface areas, are found to be in good agreement with available experimental results on pure alumina or pure titania, including our own observations of alumina nanoparticle size. Further testing and extensions of the promising, general approach outlined here are in progress. When combined with parallel studies of the joint puff of particle volume and surface area in such environments (Tandon & Rosner, 1999; Rosner & Yu, 1999), it should not only be possible to make improved Sol Reaction Engineering (SRE) predictions, but also extract valuable rate parameters from well-defined laboratory experiments on populations of coagulating, restructuring nanoparticles (Xing, 1997).

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References

PARTICLE MORPHOLOGY- AND KNUDSEN TRANSITION-EFFECTS ON THERMOPHORETICALLY DOMINATED TOTAL MASS DEPOSITION RATES FROM "COAGULATION-AGED" AEROSOL POPULATION

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Abstract: Smokes and mist of industrial and environmental interest are typically comprised of particles both large and small compared to the precursing gas mean-free-path. This fact complicates accurate predictions of, say, total mass deposition rates to cold walls or immersed cooled objects by the mechanism of particle thermophoresis (with Sc ≳ 1) across laminar or turbulence-generated or natural convection boundary layers since particle thermophoretic diffusion rates can be sensitive to the prevailing Knudsen number based on individual particle diameter. When taken into account over the entire particle size spectrum, this often reduces the contribution of the largest particles to the total deposition rate, especially if they are excellent thermal conductors (e.g., unaggregated metals). In the present paper we extend previous results from this group [Rosner 1997] on total mass deposition rates from polydispersed aerosols: A.I.Ch.E. J. 34(1), 168–177; Rosner and Toossipour 1999) to show how total mass deposition rates from a dilute flowing stream of coagulation-aged polydispersed spherical particles in the Knudsen transition regime can be conveniently predicted by systematically correcting results from the hypothetical reference case of monodispersed spheres in the free molecular limit at a single particle mass-loading. T. F. Reynolds or Grashof number and thermal conductivity ratio kₖ/kₑ. For this purpose we carry out "once-and-for-all" quadratures over the Talbot et al. 1986 "transition-regime" thermophoretic coefficient function, convolved with appropriate quasi-self-preserving particle size distribution (PSD) functions, using recent information on the effective spread of a case of these near-degenerate PSDs associated with Brownian coagulation in the transition regime (Dox et al. 1999) which lends itself to rational, "universal," deposition rate ratios correlations of the formally exact quadrature results, expressible in terms of only a prevailing Knudsen number based on mean particle size in the population, and the intrinsic thermal conductivity ratio kₑ/kₑ. The availability of these new computational results and dimensionless correlations, remarkably applicable to both laminar and turbulent boundary layer particle transport and natural or forced-convection, will dramatically simplify and accelerate such multi-scale particle thermophoretically dominated aerosol deposition rate calculations in a wide variety of engineering applications.
PARTICLE MORPHOLOGY- AND KNUDSEN TRANSITION-EFFECTS ON THERMOPHORETICALLY DOMINATED TOTAL MASS DEPOSITION RATES FROM "COAGULATION-AGED" AEROSOL POPULATION*

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Abstract—Smokes or mists of industrial and environmental interest are typically comprised of particles both large and small compared to the prevailing gas mean-free-path. This fact complicates accurate predictions of, say, total mass deposition rates to colloids or immersed cooled objects by the mechanism of particle thermophoresis (with Sc ≈ 1) across laminar or turbulent-, forced--or natural--convection boundary layers since particle thermophoretic diffusivities can be sensitive to the prevailing Knudsen number based on individual particle diameter. When taken into account over the entire particle size spectrum, this often reduces the contribution that the largest particles make to the total deposition rate, especially if they are excellent thermal conductors (e.g., unaggregated metals). In the present paper we extend previous results from this group [Rosner, 1989], [Rosner and Tassopoulos, 1989].

Total mass deposition rates from polydisperse aerosols: A.I.Ch.E. J. 35(1), 164–171; Rosner and Tassopoulos, 1989. Deposition rates from polydisperse particle populations of arbitrary spread: A.I.Ch.E. J. 35(9), 1497–1508; Rosner and Khalil, 1997. Morphology effects on polydisperse aerosol deposition rates: Trans. Amer. Inst. Chem. Eng. 77 TANSAD 75-1, 650, 425-427, to show how total mass deposition rates from a dilute flowing stream of coagulation-aged polydisperse spherical particles in the Knudsen transition regime can be conveniently predicted by systematically correcting results more easily calculated for the (hypothetical) reference case of 'monodispersed' spheres in the free-molecule limit at the same particle mass loading. AT/ub Reynolds-number channel Grashof number and thermal conductivity ratio; λT/λb. For this purpose we carry out "once-and-for-all" quadratures over the Talbot et al. (1989) "transition-regime" thermophoretic coefficient function, convoluted with appropriate quasi-self-preserving particle size distribution (PSD) functions, using recent information on the effective spreads for aerodynamic PSDs associated with Brownian coagulation in the transition regime (Otoh et al., 1984). This leads us to rational, "universal" deposition rate ratio correlations of our formally exact quadrature results, expressible in terms only of a prevailing Knudsen number based on mean particle size in the population, and the intrinsic thermal conductivity ratio: x ≡ λT/λb. The availability of these new computational results and dimensionless correlations, remarkably applicable to both laminar and turbulent boundary layer particle transport and natural or forced-convection, will dramatically simplify and accelerate such multi-size particle thermophoretically dominated aerosol deposition rate calculations in a wide variety of engineering applications. While a comprehensive theory for aggregate thermophoresis is not yet available (see, e.g., Rosner et al., 1991), provisional results are also included here for the morphologically opposite limiting case of aggregated particles (fractal morphology; not "fully dense" sphere). Our results indicate that the thermophoretic deposition rates of aggregates of conductive materials will remain high at all Knudsen numbers due to the poor effective thermal conductivity of such aggregates. © 2000 Elsevier Science Ltd. All rights reserved

NOMENCLATURE

- B, dimensionless thermophoretic "suction" Peclet number; equation (19)
- C_dav Cunningham-Millikan slip flow correction factor to Stokes’ drag; equation 3
- d, particle diameter corresponding to r
- d_p, particle diameter of "primary" particles in aggregate
- D_b, Brownian diffusion coefficient for particle of volume r
- f(λ), fractal exponent ("dimension") describing morphology of aggregate population

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Other
( ) mean value (e.g. $\bar{v} = \frac{1}{N_v} \sum_{i=1}^{N_v} v_i$)
( ) per unit rate
A change in operator: $\Delta T = T_f - T_i$
( ) argument of a function

Abbreviations/Acronyms
BL boundary layer
c continuum limit ($Kn_c < 1$)
coag pertaining to (Brownian) coagulation
C-C cluster-cluster (aggregate-aggregate)
free molecule limit ($Kn_f > 1$)
GHQ Gauss-Hermite quadrature (Section 3.5)
log logarithmic
TBL laminar boundary layer
mph gaseous molecule mean free path
TBL turbulent boundary layer
PSD particle size (volume) distribution

1. INTRODUCTION, BACKGROUND, OBJECTIVES

The fact that condensation aerosols ("smokes") of industrial interest are not comprised of dense, isolated spherical particles of only one size inevitably complicates the prediction of, say, wall deposition rates, but must, of course, be accurately taken into account. In general, we have been seeking rational yet convenient methods to take into account the systematic effects on total mass deposition rates of aerosol "polydispersity", rarefaction (Knudsen transition behavior), particle properties (e.g. thermal conductivity effects on thermophoretic deposition), and aerosol particle morphology (aggregates vs dense spheres).

In the present paper we extend previous results from this group (Rosner, 1989, 1990, b; Rosner and Tassopoulos, 1989; Rosner and Khalil, 1990) to show how thermophoretically dominated total mass deposition rates from a dilute flowing stream of coagulated polydispersed spherical particles in the Knudsen transition regime can be conveniently predicted by systematically correcting results more easily calculated for the (hypothetical) reference case of "monodispersed" spheres in the free-molecule limit at the same particle mass-loading, $\rho v m$, Reynolds- or Grashof-number and thermal conductivity ratio: $\frac{k_{pd}}{k_{pd}}$.

For this purpose we carry out "once-and-for-all" quadratures over the Talbot et al. (1980) "transition-regime" thermophoretic coefficient function, convoluted with appropriate quasi-self-perserving particle size distribution (PSD) functions, using recent information on the effective spreads ($\sigma_{efl}$) of these near-log-normal PSDs (Wu and Friedlander 1986; Tandon and Rosner, 1993) associated with Brownian coagulation in the transition regime (Otto et al., 1994). This will be shown to lead to rational, "universal" deposition rate ratio correlations of our formally exact quadrature results (Figs 4, 6), expressible in terms only of a prevailing Knudsen number based on mean particle number density and the intrinsic thermal conductivity ratio: $\frac{k_{pd}}{k_{pd}}$. The availability of these new computational results and dimensionless correlations (equations (17) and (18), applicable to both laminar and turbulent boundary layer transport in forced- or natural-convection systems, is shown to dramatically simplify and accelerate such multi-size particle thermophoretically dominated aerosol deposition rate calculations in a wide variety of engineering applications.

Provisional results are also included for aggregated particles (fractal morphology); not "fully dense"). For this latter purpose we make use of recent information: (a) the size and morphology dependence of individual particle transport properties (Garcia-Ybarra and Rosner, 1988; Rosner et al., 1991, 1992; Rosner and Tandon, 1995); (b) the spreads ($\sigma_T$) of log-normal aggregate particle size distribution (PSD) functions due to Brownian coagulation in the Knudsen and continuum regimes and (c) the fractal properties (exponent $D_f$) of the constituent multi-spherie aggregates (Megaridis and Dobbins, 1990; Koyla et al., 1995; Neirark et al., 1996). While our specific illustrations in this paper (Section 5) deal with deposition mechanism of thermophoresis, the same strategy can be successfully adapted/implemented for particle deposition by the mechanisms of convective-diffusion, gravitational sedimentation and "eddies-impaction", for laminar or turbulent flow with
particles of negligible mass fraction (Park and Rosner, 1989a, b) and not all small enough to be in the free-molecule (Kn_a ≳ 1) regime at the prevailing pressure level.

2. PRINCIPAL ASSUMPTIONS \& APPROACH

In keeping with our goal of obtaining generally applicable deposition rate results for thermophoresis from coagulation-aged polydispersed particle populations in terms of a small number of governing dimensionless groups, we explicitly make the following fundamental assumptions and idealizations:

A1: The local mainstream aerosol population is Brownian—coagulation-aged and approximately "log-normal" in terms of particle size (cf. Fig. 1).

A2: Particle volume and mass-fractal "dimension" adequately characterize the particle "state" (with D_f = 3 for dense coalesced spheres and D_f = 1.7 for "Cluster-Cluster" aggregates (Sections 3.8, 4.3)).

A3: The dominant particle deposition mechanism is thermophoretic transport to cooled solid surfaces (either immersed in or confining the hot, aerosol-containing gas).

A4: All particles in the population have the same intrinsic thermal conductivity and mass density.

A5: The suspended particle mass fraction is low (< 0.01), corresponding to even smaller volume fractions (typically of order: 0.1–10 ppm).

A6: Particles of different sizes do not appreciably interact during the transport process across laminar or turbulent BLs leading to deposition.

A7: Arriving particles are permanently captured by the cold wall with an effective capture fraction of unity.

We postpone a brief but critical examination of the limits of validity of these assumptions to Section 6, which includes explicit qualitative criteria, and suggestions or pertinent references for dealing with more complex situations (where one or more of these idealizations may require generalization).

3. FORMULATION OF DEPOSITION RATE RATIO

\[ \mathcal{R} \left( \text{Kn}_a, k_p / k_q \right) \text{ FOR } D_f \approx 3 \]

3.1. Dependence of \( \text{St}_m \) on thermophoretic coefficient; LBL or TBL when \( \text{Sc} \approx 1 \), modest temperature contrast

Mainly in the last two decades, there have been numerous theoretical studies of the laws governing thermophoretically dominated particle mass transport from flowing gases (see, e.g., Goren, 1977; Rosner and Fernandez de la Mora, 1982; Gokoglu and Rosner, 1984; Rosner and Park, 1986; Batchelor and Shen, 1985; Epstein et al., 1985; and, most recently, Garcia-Ybarra and Castillo, 1997). Most of the above deal with Sc ≳ 1 laminar forced-convection boundary layers (LBLs), but also included are natural convection, and law-of-the-wall boundary layers (TBLs). There have been fewer relevant experimental studies (Rosner and Kim, 1984; Eissner and Rosner, 1985; Makel and Kennedy, 1991; Konstandopoulos and Rosner, 1995), but it is clear from all of the above studies that there is an important domain of temperature "contrasts" (say, as measured by the departure of the absolute temperature ratio \( T_w / T_a \) from unity) in which (a) thermophoresis is the dominant particle mass transfer mechanism, and (b) the relevant mass transfer coefficient \( \text{St}_m \) is nearly linear in the dimensionless thermophoretic coefficient \( \alpha = \alpha T D_v / \nu \) discussed below.

(Section 3.2). From the usual definitions of convective mass transfer coefficient \( \text{St}_m \) and the local mainstream volume distribution function vs. log (particle volume) (cf. Rosner, 1989; Rosner and Tassopoulos, 1989).

\[ n(\nu, ...) = \frac{\int_0^{\infty} U \text{St}_m \left( \alpha, \text{Re}, \text{Pr}, ... \right) \cdot \rho_p \cdot \nu \cdot n(\nu, ...) \, d\nu,}{U}, \quad (1) \]

where, in accord with A4, all non-aggregated particles in the distribution will be assumed to have the same intrinsic mass density, \( \rho_p \), and thermal conductivity. In what follows we will combine the above mentioned linearity of \( \text{St}_m \left( \alpha, \text{Re}, \text{Pr}, ... \right) \) with respect to \( \alpha \) with the theory of the thermophoretic coefficient for dense spherical aerosol particles (Section 3.2) to carry out, once-and-for-all, a dimensionless form of this integral. In the case of aggregated particles we provide in Section 3.8 a plausible generalization to anticipate the corresponding total mass deposition rate behavior for \( D_f = 1.7 \).

3.2. Dependence of thermophoretic diffusivity \( \alpha T D_v \) on \( \text{Kn}_a \) and \( k_p / k_q \)

Talbot (1980) reviewed the isolated solid sphere thermophoretic literature as of 1980 and was able to recommend a semi-theoretical/empirical formula for the dimensionless thermophoretic coefficient, \( \alpha = \alpha T D_v / \nu \), consistent with available theoretical results in the two asymptotic limits (near-continuum, and near free-molecule) as well as available experimental data on particles covering a wide range of intrinsic thermal conductivities. He recommended, in our notation

\[ \frac{\alpha T D_v}{\nu} = \frac{2.34 \left( k_p^{-1} + 4.36 \text{Kn}_a \right) - C_{\text{St}} \left( \text{Kn}_a \right)}{\left( 1 + 2 k_p^{-1} + 8.72 \text{Kn}_a \right) \left( 1 + 6.84 \text{Kn}_a \right)^{1/4}}, \quad (2) \]

We are here explicitly considering a forced-convection environment where there is an obvious physical choice of reference velocity, \( U \). However, our present formulation/results apply equally well to natural (i.e. buoyancy-induced-) convection aerosol systems, in which case \( U < \nu \) can be regarded to be \( (\gamma / \delta T / \text{Kn}_a)^{1/4} \) (see, e.g., Rosner, 1986).

---

1 Interestingly enough, this condition need not be imposed for the case of \( D_f = 1.7 \) (Section 3.8) since in that case BL coagulation would have little influence on the effective thermophoretic diffusivity and the associated mass transfer coefficient (see Fig. 6 and Park and Rosner, 1989).
where the coefficients appearing in this relation have been assigned numerical values pertinent to high effective gas/solid accommodation coefficients (see, e.g., Rosner and Papadopoulos, 1996), and $C_{	ext{slip}}$ is the familiar Cunningham–Millikan–Stokes “slip-flow” drag correction factor

$$C_{	ext{slip}}(Kn_p) = 1 + 2Kn_p(A_1 + A_2 \exp(-A_3/Kn_p)).$$

(3)

where we have used: $A_1 = 1.257$, $A_2 = 0.4$, $A_3 = 0.55$. Figure 2 shows a log-log graph of this important $\alpha$-function, revealing a $\alpha$-limit value of $0.567^9$ and the decreased thermophoretic drift of highly conductive particles as one enters the continuum regime (low Knudsen numbers based on individual particle diameter). As detailed below, this “Talbot function” is incorporated into our present dimensionless formulation of the total mass deposition rates from populations of uniformly dense spherical particles distributed with respect to size, but not thermal conductivity or density. The remarkable behavior for thermal conductivity ratios in the range: $1 < k_p/k_s < 2.12$ will prove to be important in understanding the behavior of aggregated particles, because of their low “effective” thermal conductivity (see below).

Because of their technological importance it would be valuable to have a reliable Talbot function for large “fractal” aggregates (e.g., $D_1 = 1.7$ rather than 3), as commonly observed in sooting combustors (see, e.g., Koyn et al., 1995). While no accepted theory is yet available, we have made a plausible tentative estimate of this “modified” function (Rosner, 1998) based on the “effective sphere” reasoning outlined in Section 3.8 below.

3.3. Quadrature relation for $\mathcal{R}(Kn_p, k_p/k_s, \ldots)$

Since we will be dealing with deposition from “coagulation-aged” populations (Assumption 1) it will be convenient to use appropriately rescaled dimensionless variables for the size distribution function, $\psi = \ln (n(\ldots)/N_p)$, and particle volume $\eta = \eta_v$. In our expression for the deposition rate ratio, $\mathcal{R} = \eta_v/n_{\text{free}}$, we also choose $\eta_v$ to be the thermophoretic mass deposition rate under the prevailing conditions but assuming all particles had the mean volume, and with the thermophoretic coefficient (Section 3.2) formally evaluated in the free-molecule (fm-) limit. If all particles have the same density and intrinsic thermal conductivity then the above mentioned deposition rate ratio can be conveniently expressed

in the compact quadrature form

$$\mathcal{R}(Kn_p, k_p/k_s) = \int_0^\infty \eta_v \psi(\eta; Kn_p) \, d\eta,$$

where the Knudsen number (based on mean particle size) enters both via the evaluation of the normalized thermophoretic coefficient $\alpha/\eta_v$ as a function of particle size, $\eta$, and via the spread of the “quasi-self-preserving” particle size distribution function $\psi(\eta)$ (see, e.g., Otto et al., 1994).

In what follows (Sections 3.4 and 3.5) we exploit the fact that numerically generated particle volume distribution functions $\psi(\eta)$ have been found to be well-represented by log-normal functions (i.e. they are nearly Gaussian in terms of log (volume)). This allows us to relate the median volume to the mean volume via equation (9) of Rosner and Tassopoulos (1989), i.e.

$$\theta = \eta_v \exp\left(\frac{1}{2} \ln^2 \sigma_\eta^2\right),$$

(5)

where $\sigma_\eta$ is the effective spread parameter discussed below. It also facilitates the numerical integrations themselves (Section 3.5), since efficient Gauss quadrature formulae are available for infinite domains and integrands dominated by a function of the form: $\exp \left(-x^2\right)$ (Abramowitz and Stegun, 1964).

3.4. Log-normal representation of coagulation-aged aerosol populations; spreads in the Knudsen transition regime

Well before the onset of appreciable gravitational sedimentation contributions to the coagulation rate and deposition rate, binary encounters due to isotropic particle Brownian motion will dominate the population dynamics in large, “well-mixed” volumes (Friedlander, 1977; Williams and Loyalka, 1991). For the two limiting cases (free-molecule and continuum-regime Brownian motion) log-normal representations of the corresponding self-preserving function $\eta_v(\eta)$ are comparatively well known for the $D_1 = 3$ case, and now also available for the important case of cluster–cluster fractal aggregates with $D_1 = 1.7$ (see, e.g., Wu and Friedlander, 1993; Tandon and Rosner, 1999). Recently, Otto et al. (1994) have numerically calculated the shapes of aerosol populations in the Knudsen transition regime and shown that these are also near-log-normal but with a spread which is non-monotonic in Knudsen number (based on mean size). Assembling these results leads us to introduce into equation (4) the log-normal distribution function

$$\psi(\eta) = \frac{1}{(2\pi)^{1/2} \ln \sigma_\eta} \exp\left(-\ln^2(\eta/\eta_v) / 2 \ln^2 \sigma_\eta^2\right),$$

(6)

with $\eta_v = \eta_v(\theta)$, but with the spread parameters shown in Fig. 3 over the entire Knudsen number range. Here we have modified Otto et al.'s asymptotic spreads (to give better estimates of fractional positive moments of the PSD) but adopted their transition behavior shape (and converted from their $K_{\text{nuc}}$ to our $K_{\text{nuc}}$).

3.5. Gauss–Hermite quadrature (GHQ) for numerical results

In view of equations (1) of each of the three sections above, the quantity of interest can be expressed in the "canonical" form

$$\mathcal{R}(Kn_p, k_p/k_s) = \eta_v(\pi)^{1/2} \cdot \int_{-\infty}^{\infty} f(\eta) \exp\left(-\eta^2\right) d\eta,$$

(7)

where

$$f(\eta) = \eta_v(\frac{\ln(\eta/\eta_v)}{2^{1/2} \ln \sigma_\eta}) \exp(-\frac{1}{2} \ln^2 \sigma_\eta^2),$$

(8)

and

$$\eta_v = \eta_v(\theta) \cdot \exp\left(-\frac{1}{2} \ln^2 \sigma_\eta^2\right).$$

(9)

(10)
where \( \alpha/\eta_{im} \) is evaluated at the individual particle Knudsen number: \( Kn_p \cdot \eta^{-1/3} \).

Accordingly, the integral in equation (7) can be efficiently expressed as a weighted sum (Gauss-Hermite quadrature)

\[
\int_{-\infty}^{\infty} f(x) \exp(-x^2) \, dx = \sum_{j=0}^{n} w_j f(x_j),
\]

where the associated weight factors \( w_j \) and abscissae \( x_j \) are tabulated in Abramowitz and Stegun (1964). In all cases, at least \( n = 10 \) integration formulae (corresponding to 20 quadrature points) were used, and it was verified that our results (to three significant figures) were unaltered by this choice.

3.6. Asymptotic \( \mathcal{A} \)-results for \( D_t = 3 \), near-continuum and free-molecule regimes

Since the function \( \alpha/\eta_{im} \) possesses horizontal asymptotes (see Fig. 2 for the non-normalized Talbot function for \( D_t = 3 \)) in both extremes of Knudsen number, it is useful and straightforward to identify the associated asymptotes for the quantity of interest: \( \mathcal{A}(Kn_p, k_p/k_a) \). In the free-molecule limit we find

\[
\mathcal{A}(\infty, k_p/k_a) \equiv \mathcal{A}_{im} = \mu_1 = 1
\]

for all \( k_p/k_a \),

whereas, in the continuum limit we find

\[
\mathcal{A}(0, k_p/k_a) \equiv \mathcal{A}_c = (\alpha/\eta_{im}) \cdot \mu_1 = 2.06/[1 + (1/2)(k_p/k_a)].
\]

Indeed, a normalized version of the quantity of interest, viz. \( \log \mathcal{A}/-\log \mathcal{A}_c \) \((\log \mathcal{A}_{im} - \log \mathcal{A}_c)\) will prove useful in developing a compact correlation of our numerical results (Section 3.7). It would also be useful to have an accurate method to calculate \( \mathcal{A} \) when it is only slightly smaller than the free-molecule limit value: unity (see, e.g., Section 5.2.2), i.e.

a near-free molecule expansion for \( \mathcal{A} \) in powers of the small parameter \( \epsilon = 10(Kn_p)^{-1} \) with coefficients that depend on \( k_p/k_a \) and moments of the free-molecule near-log-normal PSD. By expanding \( \alpha/\eta_{im} \) in this manner and using equation (4) we find for the first three non-unity terms

\[
\mathcal{A} = [1 - \epsilon + 4.76[1 + (0.556/\epsilon)] \cdot \mu_{4/3} \epsilon^2 - \{17.8 + (5.66/\epsilon) + (6.06/\epsilon^2)\} \cdot \mu_{5/3} \epsilon^3 + \cdots,
\]

where the indicated moment-values can be estimated from the log-normal result

\[
\mu_k = \exp\left(\frac{1}{2}\right) (k - 1) \cdot \ln^2 a_{k,lm} \quad \text{with} \quad a_{k,lm} = 2.4.
\]

Unfortunately, the rate of convergence of this series is so slow that it is unlikely to be very useful except for very large values of the indicated Knudsen number. Interestingly enough, even the leading non-unity term is independent of the thermal conductivity ratio: \( \kappa = k_p/k_a \).

3.7. Correlation procedure for arbitrary \( Kn, k_p/k_a, D_t = 3 \)

For routine engineering calculations it would be desirable to summarize the results of our formally numerically "exact" quadratures (Sections 3.3 and 4.1) in the form of easily used, acceptably accurate formulae not limited to very large, or very small Knudsen numbers. These were obtained as follows. Based on our numerical GHQ results for \( \mathcal{A}(Kn_p, \kappa) \) it was immediately clear that this function has a "tanh" character, and this is, indeed, a convenient function to work with. By forming \( \log \mathcal{A}/\log \mathcal{A}_c \) we accomplish "normalization" on the \( \log(Kn) \) abscissa (using logs to the base 10). It remained to (a) enforce the proper location of the inflection points (i.e. the values of \( \log(Kn_p) \) where \( \mathcal{A} = (\mathcal{A}_{im} \cdot \mathcal{A}_c)^{1/2} \)) and, (b) ensure that each curve (i.e. for each \( \log(\kappa) \)) has the proper slope, \( \log \mathcal{A}/\log \mathcal{A}_c \), at this inflection point.

This was accomplished with the help of two graphs (crosplots). The first was the locus of numerically obtained inflection point locations, which conveniently agreed well with the simple fit:

\[
\log(Kn_p)_{im} = -0.9 - \{1\} \cdot \log(\kappa) \quad \text{at} \quad \mathcal{A} = (\mathcal{A}_{im} \cdot \mathcal{A}_c)^{1/2}.
\]

The second was a plot of the numerical slope: \( \log \mathcal{A}/\log \mathcal{A}_c \) vs \( \log(\kappa) \). Since this slope nearly vanishes at \( \kappa = 2.12 \) (where \( \mathcal{A}_c \) is also unity), a graph using \( \log(\kappa)/2.12 \) as the abscissa was first prepared. Fitting this graph, it was found that for \( \kappa > 2.12 \) the slope at the inflection point can be adequately described** by the equation

\[
\frac{\log \mathcal{A}_c}{\log \mathcal{A}_c(Kn_p)} \approx \left( \frac{3}{8} \right) \cdot \left\{ 1 + \left( \frac{0.365}{\kappa} \cdot 10^{(0.19 \cdot \log(\kappa)/2.12)} \right) \right\}^{-1/8}.
\]

Combining these relations led to our suggested tanh-form for estimating \( \mathcal{A}(Kn_p, \kappa) \) when \( D_t = 3 \):

\[
\log_{10}(\mathcal{A}(\kappa)) \approx \left[ 1 + \tan [m(\kappa) \cdot \log_{10}(8.19 \cdot \log(\kappa) / 2.12)] \right],
\]

where \( m(\kappa) \) is given by the product of equation (17) and \( (1/\mathcal{A}_c) \).

As will be illustrated in Section 5, equations (18) and (17) make it easy to calculate total mass deposition rates for polydispersed aerosols with any intrinsic thermal conductivity \( k_p \). Of course, if increased accuracy is required, or if the PSD is a "distorted" log-normal, it is straightforward, and not very computationally demanding, to revert to the underlying quadrature formulation, or to propose a somewhat more complicated functional form for the "curve-fit" with "optimized" coefficients.

3.8. Provisional formulation of the aggregate \( (D_t = 1.7) \) case

Even in combustion environments, most condensing materials are not able to restructure fast enough (see, e.g. Helble and Sarofim, 1989; Koch and Friedlander, 1990; Xing et al., 1997, 1999) to prevent the formation of tenuous "fractal-like" multispherule aggregates (see, e.g. Koyn et al., 1995; Neimark et al., 1996), so that the laws of particle transport must take

**This choice deliberately overcorrects the local slope somewhat to reduce overall rms deviations.
into account this morphological "fact of life". The consequences for the asymptotic spreads (with respect to aggregate mass or total sphere volume) of approximately log-normal coagulation-aged populations have recently been estimated using Monte-Carlo simulation methods for both the continuum limit (Tandon and Rosner, 1999) and the so-called "free-molecular" limit (Wu and Friedlander, 1993). If all particles in the population are assumed to have a common fractal exponent, $D_f$, and both the mobility diameter and collision diameter are assumed to scale with total aggregate volume as $(r_T)^m$, the corresponding spread results are also collected in Fig. 3, with $D_f = 3$ corresponding to the previously well-studied case of uniformly dense spheres. The systematic continuum-regime “narrowing” of the PSD-shape-preserving population (reduced $\sigma_n$ for $D_f < 3$) is taken into account in the calculations of deposition rate correction factors reported below (Fig. 6). In the absence of population spread information to the contrary, the (non-monotonic) nature of the Knudsen transition between these above mentioned asymptotes was taken to be the same as for the $D_f = 3$ case. As to our provisional estimation of the aggregate thermophoretic diffusivity, we imagine that an aggregate behaves like a homogeneous sphere with an effective mobility diameter about equal to the gyration diameter (consistent with earlier estimates of the Brownian collision rate constant), and with an effective thermal conductivity equal to that expected for the "granular medium" (of spheres) existing at the gyration radius (for details, see Tandon and Rosner, 1995; Rosner, 1998a). This introduces one new parameter which must be specified besides the aggregate fractal dimension $D_f = 1.7$ and (corresponding pre-factor, $k_B = 2.4$; Koylu et al., 1995; viz., $K_{n_1}$, the Knudsen number based on sphere diameter. 11 Accordingly, Fig. 6 (discussed below) will be constructed for the choice: $K_{n_1} = 0.3$, representative of carbonaceous soot in a high pressure (ca. 50 atm) combustor.

4. NUMERICAL RESULTS/DISCUSSION FOR $R(K_{n_1}, k_B/k_s)$

11. Equivalently, the additional parameter could have been chosen to be $\varepsilon/n_1 = \mathcal{R}$, the mean number of spheres in suspended aggregates of volume $\varepsilon$.  

4.1. Results for $D_f = 3$: $R(K_{n_1}, k_B/k_s)$

In Fig. 4 we plot (using log-log coordinates) our GHQ-computed $R$-values (solid contours) over the important range of intrinsic thermal conductivity ratios up to 10,000. (On the same scale we show (dashed) the corresponding $R$-results formally computed from our recommended correlation formula (equations (17) and (18); this comparison is briefly discussed in Section 4.2). We illustrate in Section 5.2.1 below how such $R$-results can be used to predict thermophoretically dominated deposition rates in engineering devices (e.g., those operating at very high pressures), provided the conditions outlined in Section 2 are satisfied (see, also, the critical discussion in Section 6, along with possible extensions). Remarkably, these results apply to either laminar or turbulent boundary layer situations, and for either "forced"- or "natural"-convection systems. Moreover, the strategy and procedure we have used here to generate these deposition rate ratio results for the $D_f = 3$ case (uniformly dense particles) carry over to our plausible quantitative treatment of the important $D_f = 1.7$ case (aggregated "soot"), as demonstrated in Section 4.3 below.

4.2. Success of proposed correlation

The convenient correlation formulae developed/presented in Section 3.7, which were used to generate the (dashed) contours shown in Fig. 4, will be adequate for many engineering mass-deposition rate estimates, since the rms errors for predicting $R$ over this entire range are found to be less than about 3% in the important $k_B/k_s$ range below 10,000. A second type of plot was also used to test the accuracy of this correlation formula, viz: a normalized linear plot of exact vs correlation-values of $\log(R/R_0)/\log(1/R_0)$. One such plot (Fig. 5) exhibits only modest deviations from the 45° straight line corresponding to perfect agreement, and shows the success of equation (16) in tracking the inflection point locations (the point $\frac{1}{2}$, $\frac{1}{2}$ on these coordinates) for all values of $k_B/k_s$. Of course, if much greater accuracy is required, the numerical calculation of $R$ for any desired combination of $K_{n_1}$ and $k_B/k_s$ would be quite efficient/straightforward using the above mentioned Gauss–Hermite quadrature procedure.

4.3. Provisional $R(K_{n_1}, k_B/k_s)$-results for $D_f = 1.7$

To illustrate the likely consequences of dealing with thermophoretically dominated deposition from a coagulation-aged population of aggregated particles, we have prepared Fig. 6, covering the same range of Knudsen numbers, $K_{n_1}$, and intrinsic thermal conductivity ratios $k_B/k_s$, but for the particular case of $K_{n_1} = 0.3$ (roughly corresponding to organic soot in a combustor at near 50 atm pressure). What is most noteworthy about these
aggregate results is the rather modest departures from $\Psi = 1$ even at very high intrinsic thermal conductivity ratios (e.g., near 1000) and low Knudsen numbers based on mean aggregate size (i.e., in the near-continuum regime). Moreover, since the relevant effective thermal conductivity ratios often fall in the range: $1 < k_e/k_a < 2.12$, this approach leads to $\alpha$- and $\Psi$-values exceeding unity. These (and similar) preliminary results provide the basis of the instructive numerical example discussed in Section 5.2.1 below, dealing with anticipated soot deposition rates from very high pressure combustors.

5. PROCEDURE FOR PRACTICAL USE

5.1. Steps

Thermophoretically dominated total mass deposition rates from flowing polydisperse aerosol populations can now be be conveniently calculated by sequentially following these tractable steps:

S1. First calculate "reference mass deposition rate" which would prevail due to thermophoresis in the same flow environment if all suspended particles had the mean size: $\overline{r} = \Phi/N_p$, but using the size-independent Waldmann free-molecule limit value ($\overline{\Psi}_0 = 0.53852 ~ T_p/n$) for the particle thermophoretic diffusivity (see, e.g., Rosner, 1980; Garcia-Ybarra and Rosner, 1986; García-Ybarra and Castillo, 1997)

S2. Correct this "reference rate" by the dimensionless factor $\Psi$ calculated (correlated here "once- and-for-all") (Fig. 4, equations (18) and (17), and Fig. 6) over the entire parameter range of practical interest (with $\text{Kn}$ based on the length scale $(6/n)^{1/2}$)

This "two-step" strategy leads us to rational, efficient correlation formulae for $\Psi$ in all cases treated here; i.e., for all combinations of Knudsen number (based on mean size), thermal conductivity ratio, and for both extreme suspended particle morphologies ($D_i = 3$ or 1.7). Remarkably, these results apply to either laminar or turbulent boundary layer situations, and for either "forced"- or "natural"-convection systems.

Some important applications are briefly illustrated below.

5.2. Illustrative numerical calculations and implications

5.2.1. Soot deposition rates from high-pressure combustors. A technologically important application of our present methods is the prediction of soot deposition rates from very high-pressure hydrocarbon fuel/air combustors. As reported earlier, all published laboratory studies of soot deposition were carried out with laminar boundary layers at $1 \text{ atm}$, and few studies of soot production itself have been carried out much above atmospheric pressure. However, based on the available work of Miller (1979) (up to 50 atm) and Flower and Bowman (1986) (up to 20 atm), we will assume for purposes of illustration$^{8}$ that the diffusion flame soot mass fraction remains constant at a value near 0.5 ppt (corresponding to soot volume fractions which increase linearly with pressure from ca. 0.8 ppm). Because high-pressure soot morphology studies do not appear to be available, we will provisionally assume that pressure level does not appreciably change the soot sphere diameter (near 30 nm) or the average number of spheres per aggregate (near 300). Now suppose that soot deposition rates could be measured downstream of a combustor like that operated at 1 atm. by Makel and Kennedy, 1991, and consider the deposition rates that would be expected at pressures up to, say, 1000 atm. for turbulent boundary layer flows of soot-laden combustion products past a cooled solid surface. Also suppose that this surface is maintained at $T_{so} / T_{jet} = 0.8$ and configured such that the wall shear rate at 1 atm is kept below $\approx 8 \text{s}^{-1}$, to rule out soot re-entrainment ("rip-off") even at 1000 atm. In the calculations below all deposition rates will be expressed in multiples of the actual deposition rate at 1 atm., and the intrinsic carbon sphere thermal conductivity will be taken as $\approx 1000$ times that of the background gas (based on the thermal conductivity of pyrolytic graphite in the direction ("AB") of the graphite sheets).

In the language of Sections 3.3 and 5.1, we first calculate the "reference" rates that would be expected in the same environment if all aggregates had the free-molecule thermophoretic diffusivity, $0.53852$. In Fig. 7 this is plotted as a straight line of slope 0.8 (on equal cycle size log-log paper), corresponding to a reference deposition rate which increase as the 0.8 power of the pressure level. Moreover, at 1 atm the reference rate would be indistinguishable from the observed rate because $\text{Kn}_s$ is about 0.67 and $\text{Kn}_f \approx 11.4$ (cf. Fig. 6). In accord with the present formulation (Step 2, Section 5.1) actual aggregated soot deposition rates will be estimated by multiplying the reference rate (above) by the function $\Psi (\text{Kn}_p, k_e/k_a, D_i, \text{Kn}_f)$ (again, see Fig. 6) evaluated at $D_i = 1.7, k_e/k_a = 1000$, for the prevailing values of the arguments $\text{Kn}_p$ and $\text{Kn}_f$ (these shrink, respectively, to $0.67 \times 10^{-3}$ and $0.0114$ at 1000 atm).

$^8$If the soot mass fraction, sphere size, and mean number of spheres per aggregate were subsequently found to have a non-negligible pressure dependence, this information could easily be incorporated.
The resulting predicted deposition rates are shown in Fig. 7 as the dashed curve marked: AGG ("predicted aggregate deposition rate"). Finally, it is interesting to consider the hypothetical soot deposition rate if aggregation were somehow prevented, or if the aggregates were somehow broken up prior to the deposition process. This curve, marked: "spherule deposition rate", is calculated by simply multiplying the reference rate by the term \( k_{\text{ref}} / k_{\text{agg}} = 1000 \), for the prevailing values of Kn or Fig. 2. It is remarkable that at 1000 atmosphere the spherule rate would be only about \( \frac{1}{4} \) the reference rate, whereas the predicted aggregate rate would be fully ca. 137 pct of the reference rate, which is 251 times that achieved at 1 atm. Thus, while our aggregate thermophoretic diffusion estimates are provisional, our two principal conclusions, expected to be "robust", are that:

C1: Actual large soot aggregate (say, \( N > 30 \)) deposition rates at very high pressures will be perceptibly (but not appreciably) different from the rates formally expected using the free-molecule isolated sphere thermophoretic diffusivity.

C2: If aggregates could be prevented from forming, or broken up prior to thermophoretic deposition, then, apart from considerations of shear-induced removal, appreciable soot deposition rate reductions could be realized at very high pressures.

Apart from the fact that the reference deposition rate "line" for laminar boundary layer transport would have a slope of 0.5 rather than 0.8 (Fig. 7) these conclusions would carry over to fully LBL cases (if transition to turbulence did not occur at 1000 atm due, say, to small dimensions). Incidentally, an interesting experimental corollary of our present findings is that, in contrast to the fortunate situation at 1 atm (Rosner et al., 1991; Dobbs and Meganidis, 1987), thermophoretic sampling of intrinsically conductive materials (including carbon) at very high pressures would be "biased" (against small aggregates and isolated spherules), again, apart from considerations of shear-induced removal.

5.2.2. Applications to interpretation/design of laboratory experiments involving the thermophoretic deposition of particle populations. An interesting class of applications of the present formulation/results is in the design/interpretation of laboratory experiments involving thermophoretic deposition from particle populations. In our own group such experiments have been of two types, considered sequentially below. The first category are experimental methods to study local soot concentration and morphology in atmospheric pressure flames by exploiting the laws of soot thermophoresis (Eisner and Rosner, 1986; McEnally et al., 1997; Koylu et al., 1997). In implementing these ideas it was assumed that even though the soot is comprised of aggregated spherules the free-molecule limit-laws were valid even though some aggregates in the suspension inevitably had overall dimensions comparable to or larger than the prevailing mean-free-path. Whether this produces any appreciable error in, say, the inferred soot volume fraction can not be easily estimated based on our present results—we need only compare the calculated \( \Delta r \)-value (at the prevailing mean Kn or \( D_{\text{agg}}/D_{\text{ref}} \)) with unity (the \( \Delta r \)-value of \( \Delta r \)). In the above mentioned experiments we can estimate typical values of these parameters as: \( \text{Kn} = 2.6 \), \( k_{\text{agg}}/k_{\text{ref}} = 800 \) (upper limit at the prevailing gas temperature), \( D_{\text{agg}}/D_{\text{ref}} = 1.7 \), and \( \text{Kn} = 0.20 \). Under these conditions one immediately sees from Fig. 6 (and even Fig. 4) that \( R \) is indeed near unity under the conditions studied by these authors. In the second category are experimental methods to study the laws governing thermophoretic particle deposition—such as the recent example being that of Konstandopoulos and Rosner, 1995, who worked with a narrow distribution of spray-pyrolysis-formed MgO particles centered about a diameter of 0.8 \( \mu \text{m} \). In this case we estimate \( \text{Kn} = 0.5 \), \( k_{\text{agg}}/k_{\text{ref}} = 30 \) (upper limit) and (based on TEM-images) \( D_{\text{agg}}/D = 3 \). Reference to Fig. 4 suggests that for these parameters a coagulation-aged population would deposit with \( \text{Kn} = 0.93 \), or some 10% less than that expected using the free-molecule value of the thermophoretic coefficient: \( r_{\text{agg}}/r_{\text{ref}} \). Interestingly enough, it was reported that about a 7% reduction gave best overall agreement with the measured particle deposition rates at \( T_{\text{agg}}/T \) near 0.8. Considering the fact that Fig. 4 is constructed for a broader (fully

"coagulation-aged") spread near \( \text{Kn} = 2.1 \) (Fig. 3) at this \( \text{Kn} \) rather than that reported (1.2) \( = 1.7 \), this agreement with our \( a \) posteriori "expectation" is encouraging.

Somewhat less directly related are estimates of the thermophoretic coefficient of suspended particles based on the observed location of thermophoretically created "particle stagnation planes" in atmospheric pressure laminar counterflow diffusion flames (Gomez and Rosner, 1993). While these inferences are not made based on total mass deposition rates to an immersed solid surface, it can be concluded that the flame-generated titania particle experiments of Gomez and Rosner were indeed run under conditions of negligible departure from the free-molecule limit value, whereas those of Nishioka et al. (1991) (using elutriated titania particles of mean diameter near 1 \( \mu \text{m} \)) were not. Since their averaged Kn-values were near 0.5, this is probably one of the reasons the latter investigators inferred \( k_{\text{agg}}/k_{\text{ref}} \)-values nearly half of the \( \Delta r \)-limit theoretical value for a sphere (cf., Gomez and Rosner, 1993).

In the highest-pressure laboratory studies of flame-generated soot (see, e.g. Flower and Bowman, 1986; Miller, 1978), Knudsen numbers based on average aggregate mobility diameter are as small as 0.1, corresponding to \( \text{Kn} \approx 0(1) \)-values. Under these conditions (cf. Fig. 6) despite the high intrinsic thermal conductivity ratio for this system, we would expect noticeable but not dramatic departures from \( \Delta r \)-limit behavior for the aggregate thermophoretic diffusivity, and, hence, inferred volume fractions (McEnally, et al., 1997; Koylu et al., 1997) or predicted mass deposition rates. The latter conclusion will be of special interest for anticipating/controlling soot deposition in (downstream of high pressure airpropulsion combustors (Section 5.2.1). Ironically, our reasoning also leads us to expect (see also, Fig. 7) that, if aggregation of soot spherules could be prevented, or the aggregates could be broken up into sufficiently small "fragments", soot deposition rates at very high pressures but modest shear rates would be appreciably reduced (see Fig. 7, curve marked: "aggregate deposition, \( D_{\text{agg}} = 3 \))."

6. DISCUSSION OF ASSUMPTIONS; GENERALIZATIONS

It would be useful and prudent to at least outline the basis for our present idealizations (Assumptions 1–7, Section 2), and briefly present quantitative criteria for their validity in any new situation. In some cases due to space limitations, we can direct the reader to more detailed treatments that transcend these simplifications. The accuracy of our treatment of fractal aggregate thermophoresis (Sections 3.8 and 4.3) will have to remain for future research to determine—which accounts for our repeated use of the descriptor: provisionally to describe our predictions for the case: \( D_{\text{agg}} = 1.7 \).

"Coagulation aged" aerosol populations? The depositing population will be accurately described using this concept provided enough time has elapsed between particle inception (and any appreciable growth from the vapor) and arrival at the deposition location. If \( \beta(\text{Kn}, \Psi) \) is the coagulation coefficient for two particles of size \( \Psi \) then this condition will be satisfied if the elapsed time is an adequate multiple of the characteristic coagulation time: \( \frac{\beta(\text{Kn}, \Psi)}{D_{\text{agg}}/D_{\text{ref}}} \) \( \text{Kn} \) \( \Psi \). This required multiple is dependent on the spread of the post-molecular number size distribution and the prevailing Knudsen number (see, e.g. Vemury et al., 1994) but is of the order of 12 for an initially "monodispersed" aerosol in the continuum limit. Coagulation-aged populations are known to be "single mode" and nearly log-normal (only slightly negatively "skewed") and effective geometric mean spreads, \( \sigma_{\Psi} \), can be chosen to adequately retrieve the lower dimensionless moments needed for most deposition analyses (Rosner, 1989).

Definition of particle "state">. The adequacy of particle volume and fractal dimension to define the size and morphology of a particle in the depositing population depends on the

\[ \text{It is noteworthy that our present deposition rate results (Figs 4 and 6) for arbitrary Kn cannot be compactly expressed in terms of appropriate fractional moments of the log-normal PSD (cf. Rosner, 1989, 1998; Rosner and Tatsopoulos, 1989). However, in the near-\( \Delta r \)-limit, note the presence of } \mu_{3,\Psi} \text{ and } \mu_{4,\Psi} \text{ in the truncated expression (14).} \]
possible deposition rate importance of other uncorrelated morphological variables, such as particle surface area (see, e.g. Koch and Frießland, 1990; Tandon and Rosner, 1998). We may consider the present analysis adequate in the two well-understood limiting cases of rapid- or slow-coalescence rates. This can be quantified in terms of the ratio of the above-mentioned characteristic coagulation time, and the characteristic time associated with surface-energy-driven sphere coalescence in the prevailing environment (Tandon and Rosner, 1998), which can either be very large (leading to $D_1 = 3$) or very small (leading to $D_1 = 1$).

Thermophoretic domination. In earlier work we have shown that particle transport by thermophoresis will dominate Brownian diffusion whenever the dimensionless parameter $B_1$ defined below is large compared to unity (see, e.g. Rosner et al., 1992).

$$B_1 = (s_2D_1/v)\left(\frac{\Delta T}{T_{av}}\right)\left(Pr\right)^{-1/2} (Sc)^{1/2}.$$  \hspace{1cm} (19)

But, since the "property" factors $s_2D_1/v$ and $Pr$ are each of order unity, and, for aerosol systems $Sc > 1$, the temperature contrast parameter, $\Delta T/T_{av}$, would have to be exceedingly small for convective-diffusion to play a non-negligible role in determining particle deposition rates, especially if the suspended particles were near the free-molecule extreme or relatively non-conducting. For much larger particles in turbulent thermal boundary layers we must consider the onset of "eddy impaction" effects which could ultimately become important enough to "compete" with thermophoresis. This is a particle inertia-sensitive process which would only become important when the particle stopping time, $t_{sp}$, exceeds the product $\left(1/B_1\right)(\delta_{a}d_{s}/k_{a})$, where $\delta_{a} = (L/Nu_{a})$ is the mass transfer BL thickness in the absence of thermophoresis or particle inertia, and $d_{s} = (C_{1}/2)U_{a}$ is the so-called "friction velocity" (see, e.g. Rosner and Fernandez de la Mora, 1982; Rosner, 1986; Rosner and Tassopoulos, 1989). On inspection of the above mentioned criteria, it is interesting to observe that the difference in applicability of our present deposition rate treatment is even broader for the fractal aggregate case (slow coalescence), than for the dense spherical particle case.

Also, since the particle sedimentation speed can be written: $g_{ts}$, thermophoresis will dominate gravitational sedimentation whenever $t_{sp}$ is much smaller than the product $s_2D_1/v\left(\Delta T/T_{av}\right)$, or $\delta_{a}$ is the prevailing thermal BL thickness, $L/Nu_{a}$, at the deposition location.

Dependence of mass transfer coefficient on $s_2D_1/v$. The condition $B_1 \gg 1$ above is necessary but not sufficient for the mass transfer coefficient to vary nearly linearly on $s_2D_1/v$. From the viewpoint of Gokoglu and Rosner (1984) it is also necessary that particle mass fraction reduction across the BL (outside the thin Brownian diffusion sublayer) be negligible, which leads to the additional condition: $(s_2D_1/v)\left(Pr\right)(\Delta T/T_{av}) \ll 1$. This additional condition will normally be satisfied when the absolute temperature ratio $T_{2a}/T_{av}$ does not fall much below about 0.8. When wall cooling is much more severe there would be an associated reduction in the sensitivity of the mass transfer coefficient to $s_2D_1/v$, which should be taken into account in our quadratures, especially for the smallest particles in the population. However, this observation also suggests that the insensitivity of total aggregate mass deposition rate to the population-averaged Knudsen number, irrespective of $k_{p}/k_{q}$ (Section 4.3 and Fig. 6) will be even more accurate for highly cooled walls.

Uniformity of intrinsic particle thermal conductivity and density. It seems likely that if the aerosol population is "coagulation-aged" (in the sense above) at the site of deposition, it will also be nearly physically "well mixed". This implies that the prevailing particle thermal conductivity and density at the deposition site will be that expected by physically "blending"-coalescing the initial populations. More quantitative validity criteria will be possible based on multi-variate aerosol coagulation research in progress (e.g. Tandon and Rosner, 1998), but single chemical substance aerosol is ubiquitous and justify our present emphasis on this situation, especially in view of our stated objectives.

Neglect of high particle-mass-loading effects. This situation has been dealt with in our earlier research on the industrially significant deposition process of optical wave-guide manufacture (see, e.g. Rosner and Park, 1988; Rosner, 1997). Particle volume fractions in many environmentally significant aerosol applications are small enough (often below 0.1% ppm) to allow these complications to be safely neglected.

Neglect of BL coagulation effects: Low particle volume fractions are also consistent with the neglect of particle-particle interactions within the mass transport BL. Moreover, except for the case of thermally conductive particles in the Knudsen transition regime, even if Brownian coagulation did occur within the thermal BL, it would not modify the operative thermophoretically dominated mass transfer coefficient (Park and Rosner, 1988). In any case, a sufficient condition for the neglect of Brownian coagulation effects will be that the above mentioned coagulation time be long on the time scale:

$$(s_2D_1/v)\left(\Delta T/T_{av}\right)^{-1}(Pr)^{-1/2} (Sc)^{-1/2}d_{s}.$$  \hspace{1cm} (20)

where $d_{s}$ is the gas mixture thermal diffusivity.

Irreversible particle capture by the wall: Threshold velocities for particle/surface "rebonding" (see, e.g. Konstandopoulos and Rosner, 1997; Rosner et al., 1994; Rosner and Tandon, 1995) from a clean cold solid typically far exceed those associated with thermophoretic drift—i.e. $(s_2D_1/v)(Pr)(\Delta T/T_{av})d_{s}/k_{a}$). Accordingly, irreversible particle "trapping" by the cold solid surface is fully consistent with the abovementioned physical model, unless the shear stress at the gas/depot interface is large enough to overcome the adhesive forces holding spheres to one another, and/or to the underlying target. In the 1 atm. ethylene/air source deposition experiments of Makel and Kennedy (1991), this occurred at shear rates of the order of 2000 s$^{-1}$. We conclude from these considerations that the mathematical model investigated here (Section 2) has a broad domain of applicability even for aerosols comprised of dense spherical particles ($D_1 = 3$). Ironically, we expect the domain of validity to be increased (without the need to specify many additional dimensionless parameters) for cases involving suspended aggregates (with $D_1 = 1.7$), with the principal remaining uncertainty being the absolute accuracy of our evaluation of $s_2D_1$ for such particles (Section 3.8).

7. CONCLUSIONS; CURRENT/FUTURE WORK

Previous papers from this group (Rosner, 1989, 1998; Rosner and Tassopoulos, 1989, 1991, 1992) have shown that total mass deposition rates from a stream containing coagulation-aged polydispersed aggregated particles can be predicted by systematically correcting (for polydispersity) results first calculated for the (hypothetical) case of monodispersed particles (with the same volume fraction, $N_{v}$) in the same environment. This "first step" result (Section 5.1) is then corrected for polydispersity by using the $s$-factors calculated/displayed here (Fig. 4 (or correlation equations (17) and (18), Fig. 6) for the particular case of deposition by the non-power-law mechanism of thermophoresis (e.g., isothermal convection-diffusion, gravitational sedimentation, or "eddy impaction"), for lamina or turbulent, forced- or free-convective flow of suspended particles in the Knudsen regime. Using this convenient but rational formalism above, we have also estimated how suspended particle morphology (i.e. the presence of unfractured "fractal aggregates" with $D_1 = 1.7$) would influence thermophoretically dominated mass transfer rates, concluding that, irrespective of intrinsic thermal conductivity, thermophoretically dominated deposition rates would be remarkably insensitive to Knudsen number (corresponding to surprisingly large aggregate deposition rates (e.g. carbonaceous soot) in the high pressure (continuum) limit. We illustrated in Section 5 the extent to which this strategy/set of results simplifies engineering calculations of mass deposition rates from polydispersed aerosol populations. We also note that the laws underlying our calculations (Section 3) have been rather well established based on both earlier theoretical analysis (see, e.g. Rosner and Fernandez de la Mora, 1982; Garcia-Ybarra and Castillo, 1993), and laboratory experiments by Rosner and Kim, 1986; Makel and Kennedy, 1991; Gomez and Rosner, 1993; Konstandopoulos and Rosner, 1995). Thus, if the validity criteria discussed in Section 6 are indeed met, the results reported here can be used with considerable confidence.
even in the absence of further "direct" validation. Ironically, the domain of validity is expected to be greater for suspended aggregates (Df = 1.7) than for the more familiar case of spherical particles (Df = 3), however our procedure for estimating fractal aggregate thermophoretic diffusivities (Section 3.8) must be regarded as provisional, and may require systematic corrections.

Deposition rates from aggregated particle populations (Sections 3.8 and 4.3) can change not only due to coagulation but also due to finite-rate aggregate restructuring processes—e.g. those brought about by surface-energy driven sintering at high temperatures (Xing et al., 1997, 1999; Tandon and Rosner, 1996, 1999) or, say, aggregate-induced vapor capillary condensation. The implications of such finite-rate restructuring for particle deposition rates are currently being considered in the light of the formalism above and recent Monte-Carlo coagulation-coalescence simulations of spatially uniform particle populations (dos Santos and Tandon, 1996). The latter, despite its neglect of inter-particle and particle surface area (Tandon and Rosner, 1998). Merely considering Figs 4 and 6, respectively, to the limiting cases Df = 3 and 1.7, reveals the maximum extent to which a sintering will reduce the rate of thermophoretic deposition from populations of conductive particles, and, perhaps more surprisingly, (b) aggregation is now expected to increase the rate of thermophoretic deposition in high pressure but low shear rate, non-isothermal systems (e.g. ordinary carbonaceous soot in downstream of high-pressure combustors).

It is anticipated that these new deposition rate methods, results, correlations and conjectures will prove useful to simplify and enhance existing software (often large and complex codes containing arguable deposition-rate subroutines) developed in recent decades for specific industries.

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