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Non-isothermal droplet evaporation and condensation in the near-continuum regime

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Abstract

The problem of non-isothermal quasi-steady state evaporation and condensation of aerosol spheres is examined to determine the rates of simultaneous heat and mass transport in the Knudsen (transition) regime. New expressions for the mass and heat fluxes are obtained that show explicitly the dependence of the rate processes on the Knudsen number, the accommodation coefficients for mass and energy transport and on the molecular weight ratio of the vapor and gas molecules. The analysis, based on the solution of the Boltzmann equation by the method of Grad for Maxwellian molecules, is shown to yield results in the continuum regime ($Kn \ll 1$) in reasonable agreement with classical methods based on continuum theory and with measured water droplet evaporation rates in dry air. Computations of heat and mass transport rates for ice sublimation for upper tropospheric and stratospheric conditions for sizes that correspond to the continuum and transition regimes show that the process is very nearly isothermal. Parametric studies explore the effects of temperature, humidity and accommodation coefficients on the heat and mass transport processes. Although the method of Grad is known to fail in the free-molecule regime, the results agree with more rigorous theoretical solutions for isothermal processes in the near-continuum regime and with an earlier solution for hard sphere molecules in the near-continuum regime. It is shown that flux-matching or resistance models used for the transition regime do not show the correct dependence on the Knudsen number and other parameters. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Accommodation coefficients; Boltzmann equation; Knudsen regime; Ice sublimation; Method of Grad; Non-isothermal transport

1. Introduction

Droplet evaporation and condensation processes have received a great deal of attention since Maxwell (1878) analyzed quasi-steady state diffusion-controlled evaporation from a wet bulb.

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Wagner (1982) and Kulmala and Vesala (1991) reviewed the literature associated with condensation in the continuum regime. Barrett and Clement (1988) reviewed the theories of heat and mass transport for the continuum and free-molecule regimes, and they proposed an interpolation formula for the intermediate or transition regime. These regimes are characterized by the Knudsen number, Kn , which is the ratio of the mean free path of the diffusing species, ℓ , to the droplet radius, R , that is, $\text{Kn} = \ell/R$. The limiting cases of continuum theory and free-molecule theory apply for $\text{Kn} \rightarrow 0$ and $\text{Kn} \rightarrow \infty$, respectively.

At normal atmospheric pressure the mean free paths of gas and vapor molecules are much smaller than a micrometer, and evaporation/condensation processes for micrometer-size aerosols are in the continuum regime. If relatively non-volatile substances are involved, the mass transport process is slow compared with the rate of heat transfer between the droplet and the surroundings. In this case the process proceeds nearly isothermally, but rapid evaporation/condensation is a non-isothermal process. At the lower pressure of the upper troposphere heat and mass transfer processes associated with micrometer-size droplets or ice particles occur in non-continuum regimes, and simultaneous heat and mass transfer processes in the transition regime are poorly understood. It is the objective of this study to apply gas kinetic theory to develop expressions for simultaneous heat and mass transfer in the transition regime.

For the mass flux of the diffusing species in the continuum approximation, j_{cont} , Maxwell's result may be written as

$$j_{\text{cont}} = -\frac{\dot{m}}{4\pi R^2} = \frac{D_{12}m_1}{R}(n_{1s} - n_{1\infty}) = \frac{D_{12}m_1}{R}\left(\frac{p_{1s}}{kT_s} - \frac{p_{1\infty}}{kT_\infty}\right) = \frac{D_{12}m_1 p_{1\infty}^0}{Rk}\left(\frac{p_{1s}}{p_{1\infty}^0} - \sigma\right), \quad (1)$$

in which \dot{m} is the rate of mass loss or gain of vapor, R is the sphere radius, D_{12} is the diffusion coefficient of vapor (species 1) in the surrounding bath gas (species 2), m_1 is the mass of a vapor molecule, n_{1s} and $n_{1\infty}$ are the number densities of vapor molecules at the droplet surface and in the bulk gas, respectively, and p_{1s} and $p_{1\infty}$ are the partial pressures of vapor at those locations. The local saturation ratio in the bulk gas, σ , is defined by $\sigma = p_{1\infty}/p_{1\infty}^0$, where $p_{1\infty}^0$ is the saturation vapor pressure at the bulk temperature, T_∞ . For an isothermal process $p_{1s} = p_{1\infty} = p_{1\infty}^0$.

In the development of Eq. (1) it is assumed that the partial pressure of the diffusing species is small compared with the total pressure, that is, the Stefan flow due to the net motion of the gas/vapor mixture is negligible. We shall make that same assumption in the analysis developed below. Wagner (1982) and Barrett and Clement (1988) presented approximate solutions taking into account Stefan flow.

In the limit $\text{Kn} \gg 1$, the so-called free molecule regime, the mass flux is described by

$$j_{\text{fm}} = \frac{1}{4}\alpha_M m_1 (\bar{c}_{1s} n_{1s} - \bar{c}_{1\infty} n_{1\infty}) \\ = \frac{m_1}{4}\alpha_M \left(\frac{\bar{c}_{1s} p_{1s}}{kT_s} - \frac{\bar{c}_{1\infty} p_{1\infty}}{kT_\infty}\right) \approx \frac{\bar{c}_1 m_1 p_{1\infty}^0}{4kT_\infty} \alpha_M \left(\frac{p_{1s} T_\infty}{p_{1\infty}^0 T_s} - \sigma\right), \quad (2)$$

where α_M is the mass accommodation coefficient, and \bar{c}_1 is the mean molecular speed of the vapor molecules defined by

$$\bar{c}_1 = \sqrt{8kT/\pi m_1}. \quad (3)$$

Eq. (2), developed from the kinetic theory of gases, is based on the assumption that the evaporation coefficient and the condensation coefficient are equal, that is, $\alpha = \alpha_e = \alpha_c$. Tompson and Loyalka (1986) applied a more rigorous analysis to analyze condensation on a sphere in the free-molecule regime.

Eqs. (1) and (2) must be coupled to appropriate energy equations, for the energy associated with the phase change at the droplet surface must be transferred to or from the surrounding gas. For the continuum regime the simplest theory for the heat flux, q , between a stagnant gas and the particle yields

$$q = -\frac{\lambda \dot{m}}{4\pi R^2} = \frac{k_2}{R}(T_s - T_\infty), \quad (4)$$

where λ is the latent heat, and k_2 is the gas thermal conductivity. Since the interfacial partial pressure is a non-linear function of the temperature, Eqs. (1) and (4) are coupled non-linearly. We have neglected radiant energy transfer, but it can be included in Eq. (4).

The special case of isothermal evaporation/condensation for the transition regime (also called the Knudsen regime) was first analyzed by Fuchs (1934) using a flux-matching approach that has the features of a resistance model. Fuchs recognized the difficulty associated with solving the Boltzmann equation to describe aerosol evaporation and condensation processes in the transition regime. He assumed that in the region near the droplet surface free-molecule theory can be applied, but beyond that region continuum theory was used. He matched the fluxes determined from the two theories at some distance of the order of the mean free path from the droplet surface. The flux-matching approach and interpolation formulas recover the limiting cases of continuum theory and free-molecule theory, but there is no fundamental reason for them to fit the transition regime. One objective of this study was to determine if flux-matching or resistance models yield a theoretically sound dependence on the Knudsen number and other system parameters.

Barrett and Clement proposed a simple interpolation formula for transport in the transition regime based on a flux-matching procedure. Their result also has the form of a resistance model that contains resistances associated with mass diffusion, mass kinetic transfer, heat conduction and energy kinetic transfer. They pointed out that for the transition regime “Accurate treatment requires solution of the Boltzmann equation which cannot be done using a Chapman–Enskog expansion as this fails at low densities”. In the limiting case of isothermal evaporation with no radiant energy transfer their equation reduces to

$$j = \frac{(1 - \sigma)}{(R/D_{12}m_1n_\infty + 4/\alpha_m \bar{c}_{1\infty}m_1n_\infty)}. \quad (5)$$

This result may be written in a more enlightening form by using kinetic theory to relate the molecular speed and the diffusivity. For example, using the result for hard spheres of uniform size, $D_{12}/\ell\bar{c} = 1/3$, and eliminating D_{12} from Eq. (5), there results

$$j = \frac{\bar{c}_{1\infty}m_1n_\infty(1 - \sigma)}{3/\text{Kn} + 4/\alpha_M} \quad \text{and} \quad \frac{j}{j_{\text{fm}}} = \frac{\text{Kn}}{(3\alpha_M/4 + \text{Kn})}, \quad (6)$$

where $\text{Kn} = \ell/a$. This equation recovers the free-molecule limit for $\text{Kn} \gg 1$ and the continuum limit for $\text{Kn} \ll 1$. As we will show, it does not represent the transition region adequately, for it

does not have the correct dependence on the Knudsen number. That is the same issue addressed by Fuchs and Sutugin (1970) when they saw that flux-matching does not yield the correct Knudsen number dependence.

Indeed, the transition regime is theoretically more difficult to analyze than the limiting cases of large and small Knudsen numbers, but there has been extensive work on the problem since Sahni (1966) developed a solution of the Boltzmann equation for neutron transport to a black sphere. The neutron transport problem is analogous to that of condensation on a sphere when the mass of the vapor molecule is small compared with the mass of a bath gas molecule. Based on Sahni's results, Fuchs and Sutugin (1970) proposed a widely used empirical correlation for isothermal evaporation/condensation that yields the correct results in the asymptotic limits of large and small Knudsen numbers and agrees with Sahni's results in the transition regime.

Sahni (1980) extended his analysis to analyze droplet evaporation and condensation, and Loyalka and coworkers published a series of papers dealing with the solution of the Boltzmann equation to analyze droplet growth by condensation (Loyalka, 1973, 1982; Tompson & Loyalka, 1988; Loyalka, Hamoodi, & Tompson, 1989a, b). These solutions were for an isothermal system, but Loyalka and Park (1988) developed an approximation for non-isothermal condensation based on an extension of Mason's (1962) formula for the continuum regime. Mason's formula is based on Eqs. (1) and (4). Barrett and Clement pointed out the relevant solutions of the Boltzmann equation based on the moment method of Lees (1965) used by Sampson and Springer (1969, 1970), Shankar (1970) and Lang (1983). Moment methods were introduced by Maxwell (1879) to solve the Boltzmann equation, and many variations on that theme have been proposed. The various moments of the molecular velocity distribution function yield bulk properties of the gas.

An alternate, but less accurate solution of the Boltzmann equation, was applied by Sitariski and Nowakowski (1979) using the moment method of Grad. That method yields an equation showing explicitly the dependence of the mass flux on the vapor/gas molecular weight ratio, $z = m_1/m_2$, and the mass accommodation coefficient. Their solution for the isothermal mass flux ratio, j/j_{fm} , is

$$\frac{j}{j_{fm}} = \frac{\text{Kn}^* \left[1 + \frac{3\beta(1+z)^2}{4(3+5z)} \text{Kn}^* \right]}{\frac{4(9+10z)}{15\pi(1+z)^2} + \left[\frac{\beta(1+2z)}{\pi(3+5z)} + \frac{1}{2\beta} \right] \text{Kn}^* + \frac{9(1+z)^2}{8(3+5z)} \text{Kn}^{*2}}, \quad (7)$$

in which β is related to the accommodation coefficient (or evaporation coefficient), α , and the Knudsen number is related to the diffusivity, D_{12} , by

$$\beta = \frac{\alpha}{(2-\alpha)}, \quad \text{and} \quad \text{Kn}^* = \frac{\ell}{R} = \frac{32[1 - 1/10(1+z)] D_{12}}{3\pi(1+z) R \bar{c}_1}. \quad (8)$$

In a companion paper to this one, Qu and Davis (2001) applied the method of Grad, showing that the model of Maxwell molecules yields results effectively identical to the model of hard

spheres. Their result is

$$\frac{j}{j_{\text{fm}}} = \frac{2\text{Kn} \left[1 + \frac{8\beta(1+z)^2}{5A_1(3A_2/A_1 + 4z)}\text{Kn} \right]}{\frac{2A_1}{\pi(1+z)} + \left[\frac{1}{\beta} + \frac{16\beta(1+z)}{5\pi(3A_2/A_1 + 4z)} \right] \text{Kn} + \frac{24(1+z)^2}{5A_1(3A_2/A_1 + 4z)}\text{Kn}^2}, \quad (9)$$

where in this approximation the Knudsen number, Kn, is defined in terms of the mean free path given by

$$\text{Kn} = \frac{\ell}{R} = \frac{4A_1}{\pi(1+z)} \frac{D_{12}}{R\bar{c}_1}. \quad (10)$$

Here A_1 and A_2 have the numerical values $A_1=0.42194$ and $A_2=0.43619$ as shown by Gombosi (1994) for Maxwellian molecules. Qu and Davis pointed out that there are several definitions of the Knudsen number in the literature because of the different expressions used for the mean free path.

We note that Eq. (6) does not have the theoretical dependence on the Knudsen number shown by Eqs. (7) and (9). In addition, Qu and Davis pointed out that the Fuchs–Sutugin interpolation equation has the general form of Eqs. (7) and (9) but does not indicate the dependence on the molecular weight ratio, z . The form of these equations does not support the heuristic approach of flux-matching. Although Eqs. (7) and (9) yield results in agreement with those of Loyalka and his coworkers in the near-continuum regime, they fail to approach the correct free molecule limit. Nowakowski and Popielawski (1988) extended the analysis of Sitarski and Nowakowski to analyze non-isothermal condensation for the model of hard sphere molecules. They obtained a complicated equation for the mass flux ratio, j/j_{fm} , that is a function of the mass accommodation coefficient, α , the thermal accommodation coefficient, α_T , the molecular weight ratio, z , the gas phase thermal conductivity, the latent heat of vaporization, and the Knudsen number.

As with the solution of Sitarski and Nowakowski, the continuum limit is correctly predicted, but the correct free molecule limit is not recovered. They concluded that a more complete set of moment equations is required to analyze the non-isothermal problem. They did not apply their results to demonstrate the coupling between the mass flux and heat flux equations. It is the purpose of this paper to extend the analysis of Qu and Davis to non-isothermal evaporation/condensation in the near-continuum regime and apply the results to systems of practical importance. In addition, the results are compared with results based on the solution of Nowakowski and Popielawski.

2. Theory

Theoretical analysis of the Knudsen regime involves solution of the Boltzmann equation. For quasi-steady state and no external forces the Boltzmann equation is (Gombosi, 1994)

$$\xi_i \frac{\partial f}{\partial x_i} = \int_{\infty} d^3 \xi_2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta g s(g, \theta) (f'f'_2 - ff_2), \quad (11)$$

where $r = (x_1, x_2, x_3)$ is the position vector, ξ and ξ_2 are molecular velocities of diffusing molecules and bath molecules, respectively, f and f' are velocity distribution functions before and after collision, respectively, ϕ is the azimuthal angle, θ is the deflection angle associated with molecular collisions, $s(g, \theta)$ is the differential collision cross section, and $g = |\xi - \xi_2|$ is the relative velocity. For convenience we have neglected the subscript on the quantities associated with the vapor molecules. We shall drop the subscript '1' on the vapor molecules unless otherwise indicated.

Following Qu and Davis, we consider Maxwell molecules (Maxwell, 1879) for which the molecular interaction force takes the form $F_{12} = K_{12}r^{-5}e_r$, where r is the distance between molecules undergoing collision, and K_{12} is a constant. Gombosi has provided details of collision theory for such inverse power law interactions and other models, so we need not repeat many of his derivations and equations.

To make tractable the analysis of non-isothermal heat and mass transport in the transition regime we have made a number of assumptions: (1) quasi-steady transport with zero bath gas bulk velocity, (2) the rates of mass transport are sufficiently low such that both vapor and gas molecular velocity distributions are not far from Maxwellian, (3) the gas/vapor mixture is dilute, that is, $n = n_1 \ll n_2$, (4) the latent heat associated with the phase change is transported only in the gas phase, and (5) spherical symmetry. In addition, we must take into account the accommodation coefficients for gas and vapor. For the gas molecules we shall take $\alpha_{M2} = 0$ and $\alpha_{T2} \neq 0$, and for the vapor molecules, and for the vapor molecules α_{M1} and α_{T1} must be specified. The assumption that $\alpha_{M2} = 0$ is equivalent to saying that the gas is not absorbed by the particle.

For a dilute vapor–gas mixture the mean free paths, ℓ and ℓ_2 , of the vapor molecules and gas molecules, are, respectively

$$\ell = \frac{1}{4\pi n_2} \sqrt{\frac{8kT\mu_{12}}{\pi m K_{12}}}, \quad \text{and} \quad \ell_2 = \frac{1}{2\pi n_2} \sqrt{\frac{kT}{\pi K_{22}}}, \quad (12)$$

in which the reduced mass is $\mu_{12} = mm_2/(m + m_2)$, and the subscript "22" in K_{22} indicates that the interaction is between two approaching gas molecules.

2.1. Solution of the Boltzmann equation for the bath gas

If the bulk velocity of the gas molecules is zero, $\xi_2 = c_2$, in which c_2 is the thermal velocity, and the relevant Boltzmann equation is

$$c_{2i} \frac{\partial f_2}{\partial x_i} = \int_{\infty} d^3 \tilde{c}_2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta g_2 s(g_2, \theta) (f_2' \tilde{f}_2' - f_2 \tilde{f}_2), \quad (13)$$

where the distribution functions f_2 and \tilde{f}_2 relate to molecules prior to collision, and the primes denote post-collision distribution functions.

Following Grad (1949), we expand the distribution function in terms of Hermite polynomials, $H^{(n)}(v)$, around the local Maxwellian distribution,

$$f_2(r, c) = f_2^0(r, c) \sum_{n=0}^{\infty} a^{(n)}(r) H^{(n)}(v) / n!, \tag{14}$$

in which the Maxwellian is

$$f_2^0(r, c_2) = n_2(r) \left[\frac{m_2}{2\pi kT(r)} \right]^{3/2} \exp \left[\frac{-m_2 c_2^2}{2kT(r)} \right]. \tag{15}$$

Based on the method of Grad and using the moments of the distribution function, f_2 becomes

$$f_2 = f_2^0 \left[1 + \frac{m_2 P_{2ij}}{2 p_2 kT} c_{2i} c_{2j} - \frac{m_2 S_{2i} c_{2i}}{2 p_2 kT} \left(1 - \frac{m_2}{5kT} c_2^2 \right) \right]. \tag{16}$$

The moments of the distribution function needed to describe macroscopic properties are

$$\begin{aligned} n(r) &= \int_{\infty} f d^3c, \quad j_i(r) = m \int_{\infty} \xi_i f d^3c, \quad p_{ij}(r) = m \int_{\infty} c_i c_j f d^3c - p(r) \delta_{ij}, \\ p(r) &= \frac{1}{3} m \int_{\infty} c^2 f d^3c = n(r) kT, \quad S_{ijk}(r) = m \int_{\infty} c_i c_j c_k f d^3c, \quad S_i(r) = m \int_{\infty} c_i c^2 f d^3c. \end{aligned} \tag{17}$$

Here n is the number density of molecules, j_i is the i th component of the mass flux vector, p_{ij} is the i - j component of the pressure tensor, p is the pressure, and moments S_{ijk} and S_i are related to the heat flux as shown below.

Multiplying Eq. (13), successively by $m_2 c_{2i}$, $m_2 c_2^2$, $m_2 c_{2i} c_{2j}$, $m_2 c_{2i} c_2^2$ and integrating over all velocities, we obtain the sequence of the equations that must be solved to obtain the desired macroscopic quantities,

$$\frac{\partial p_{2ik}}{\partial x_k} + \frac{\partial(n_2 kT)}{\partial x_i} = 0, \quad \frac{\partial S_{2k}}{\partial x_k} = 0, \quad \frac{1}{5} \left(\frac{\partial S_{2k}}{\partial x_k} \delta_{ij} + \frac{\partial S_{2i}}{\partial x_j} + \frac{\partial S_{2j}}{\partial x_i} \right) = -\frac{3}{8} \frac{A_2}{\ell_2} \bar{c}_2 p_{2ij} \tag{18}$$

and

$$7 \frac{kT}{m_2} \frac{\partial p_{2ik}}{\partial x_k} + \frac{7k}{m_2} p_{2ik} \frac{\partial T}{\partial x_k} + \frac{5kT}{m_2} \frac{\partial p_2}{\partial x_i} + \frac{5k}{m_2} p_2 \frac{\partial T}{\partial x_i} = -\frac{A_2}{4\ell_2} \bar{c}_2 S_{2i}, \tag{19}$$

where $\bar{c}_2 = \sqrt{8kT/\pi m_2}$ is the average molecular velocity of bath gas molecules.

For this spherically symmetric system we may write vector quantities in terms of scalar functions of the distance from the origin, r , that is,

$$S_{2i}(r) = S_2(r) \frac{x_i}{r}, \quad \text{and} \quad p_{2ij}(r) = \eta_2(r) \left(\delta_{ij} - \frac{3x_i x_j}{r^2} \right). \tag{20}$$

Solving Eqs. (18) and (19), it is found that dp_2/dr is of higher order than dT/dr . Consequently, if the system is not far from isothermal, we can consider the gas pressure, p_2 , to be constant and obtain

$$S_2 = p_2 \bar{c}_{2\infty} \frac{a_1}{r^{*2}}, \quad (21)$$

$$\eta_2 = -\frac{16}{15A_2} p_2 \frac{\text{Kn}_{2\infty} a_1}{r^{*3}} \quad (22)$$

and

$$\frac{T}{T_\infty} = 1 + \frac{2A_2 a_1}{5\pi \text{Kn}_{2\infty} r^{*2}}, \quad (23)$$

where a_1 is a dimensionless constant to be determined, $r^* = r/R$ and $\text{Kn}_2 = \ell_2/R$. The subscript “ ∞ ” means the quantities are based on the ambient temperature and pressure.

2.2. Solution of the Boltzmann equation for the vapor

Changing the independent variables in the Boltzmann equation from ζ to c (Gombosi, 1994), we obtain

$$(u_i + c_i) \frac{\partial f}{\partial x_i} - (u_j + c_j) \frac{\partial u_i}{\partial x_j} \frac{\partial f}{\partial c_i} = \frac{\delta f}{\delta t}. \quad (24)$$

Multiplying this equation by any function of c , $W = W(c)$, and integrating over c , there results

$$\begin{aligned} u_i \frac{\partial \langle n \langle W \rangle \rangle}{\partial x_i} + \frac{\partial \langle n \langle W c_i \rangle \rangle}{\partial x_i} + n \langle W \rangle \frac{\partial u_i}{\partial x_i} + n u_j \frac{\partial u_i}{\partial x_j} \left\langle \frac{\partial W}{\partial c_i} \right\rangle + n \frac{\partial u_i}{\partial x_j} \left\langle c_j \frac{\partial W}{\partial c_i} \right\rangle \\ = \int_\infty d^3 c \int_\infty d^3 c_2 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta g s(g, \theta) (W' - W) f f_2. \end{aligned} \quad (25)$$

Here the average value of a quantity, W , is defined by

$$\langle W \rangle = \frac{1}{n} \int_\infty W f d^3 c \quad (26)$$

Now let $W = m, mc_k, mc^2, mc_k c_l, mc^2 c_k$, respectively, to obtain the following system of equations

$$\frac{\partial j_i}{\partial x_i} = 0, \quad \frac{\partial p_{ij}}{\partial x_j} + \frac{\partial p_1}{\partial x_i} + \rho u_j \frac{\partial u_i}{\partial x_j} = -2A_1 \pi \sqrt{K_{12} \mu_{12} n n_2} u_i, \quad (27)$$

$$\frac{\partial (u_i p_1)}{\partial x_i} + \frac{1}{3} \frac{\partial S_i}{\partial x_i} + \frac{2}{3} \frac{\partial u_i}{\partial x_j} p_{ij} + \frac{2}{3} \frac{\partial u_i}{\partial x_i} p_1 = \frac{4}{3} A_1 \pi \frac{\mu_{12}^2}{m} \left(\frac{K_{12}}{\mu_{12}} \right)^{1/2} n n_2 u^2, \quad (28)$$

$$\begin{aligned}
 & \frac{\partial(u_k p_{ij})}{\partial x_k} + \frac{1}{5} \left(\frac{\partial S_i}{\partial x_j} + \frac{\partial S_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial S_k}{\partial x_k} \right) + \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right) p_1 \\
 & \quad + p_{ik} \frac{\partial u_j}{\partial x_k} + p_{jk} \frac{\partial u_i}{\partial x_k} - \frac{2}{3} \delta_{ij} p_{kl} \frac{\partial u_k}{\partial x_l} \\
 & = \pi \frac{\mu_{12}^2}{m^2} \left(\frac{K}{\mu_{12}} \right)^{1/2} n_2 \left[mn(3A_2 - 4A_1) \left(\frac{\delta_{ij}}{3} u^2 - u_i u_j \right) - (3A_2 + 4A_1 z) p_{ij} \right] \\
 & \quad + \pi \frac{\mu_{12}}{m + m_2} \left(\frac{K}{\mu_{12}} \right)^{1/2} n(4A_1 - 3A_2) p_{2ij}
 \end{aligned} \tag{29}$$

and

$$\begin{aligned}
 & \frac{\partial(u_k S_i)}{\partial x_k} + 7 \frac{kT}{m} \frac{\partial p_{ik}}{\partial x_k} + \frac{7k}{m} p_{ik} \frac{\partial T}{\partial x_k} + 2u_l p_{ik} \frac{\partial u_k}{\partial x_l} + 5u_k p_l \frac{\partial u_i}{\partial x_k} + \frac{7}{5} S_k \frac{\partial u_i}{\partial x_k} \\
 & \quad + \frac{2}{5} S_i \frac{\partial u_k}{\partial x_k} + \frac{2}{5} S_k \frac{\partial u_i}{\partial x_k} + \frac{5kT}{m} \frac{\partial p_1}{\partial x_i} + \frac{5k}{m} p_1 \frac{\partial T}{\partial x_i} \\
 & = -v_{12} \left\{ \alpha^{(1)} S_i - \frac{mn}{m_2 n_2} \alpha^{(4)} S_{2i} + u_j \left(\alpha^{(2)} p_{ij} + \frac{2mn}{m_2 n_2} \alpha^{(4)} p_{2ij} \right) \right. \\
 & \quad \left. + u_i \left[(\alpha^{(2)} + 3\alpha^{(3)}) p_1 + 5 \frac{mn}{m_2 n_2} \alpha^{(4)} p_2 + mn \alpha^{(4)} u^2 \right] \right\},
 \end{aligned} \tag{30}$$

where the coefficients $v_{12}, \alpha^{(1)} \dots \alpha^{(4)}$ are

$$\begin{aligned}
 v_{12} &= 2\pi A_1 \frac{\mu_{12}}{m} \left(\frac{K_{12}}{\mu_{12}} \right)^{1/2} n_2, \quad \alpha^{(1)} = \frac{1}{(m + m_2)^2} \left(3m^2 + m_2^2 + 2mm_2 \frac{A_2}{A_1} \right), \\
 \alpha^{(2)} &= \frac{1}{(m + m_2)^2} \left[2(m - m_2)^2 + m_2(m - 3m_2) \frac{A_2}{A_1} \right], \\
 \alpha^{(3)} &= \frac{1}{(m + m_2)^2} \left[(m - m_2)^2 + m_2(3m + m_2) \frac{A_2}{A_1} \right], \quad \alpha^{(4)} = \frac{2m_2^2}{(m + m_2)^2} \left(2 - \frac{A_2}{A_1} \right),
 \end{aligned} \tag{31}$$

in which A_1 and A_2 are the constants given above.

For spherical symmetry the vectors j and S , and the tensor p have the forms

$$j_i(r) = j(r) \frac{x_i}{r}, \quad S_i(r) = S(r) \frac{x_i}{r}, \quad \text{and} \quad p_{ij}(r) = \eta(r) \left(\delta_{ij} - \frac{3x_i x_j}{r^2} \right), \tag{32}$$

where $j(r)$, $S(r)$ and $\eta(r)$ are scalar functions of the distance r from the center of the particle. Substituting these expressions in Eqs. (27)–(31), we obtain a set of differential equations listed in the appendix as Eqs. (A.1)–(A.4) that must be solved to obtain $j(r)$, $S(r)$ and $\eta(r)$.

These equations are still too complicated to solve directly analytically, but for most applications we can simplify the problem by expanding the moment functions in the following power series of a small parameter ε ,

$$\begin{aligned} \rho &= \rho_\infty [1 + \varepsilon\rho' + O(\varepsilon^2)], & T &= T_\infty [1 + \varepsilon\theta + O(\varepsilon^2)], & j &= \rho_\infty \left(\frac{kT_\infty}{m} \right)^{1/2} [\varepsilon j' + O(\varepsilon^2)], \\ S &= \rho_\infty \left(\frac{kT_\infty}{m} \right)^{3/2} [\varepsilon S' + O(\varepsilon^2)], & \text{and} & & \eta &= \rho_\infty \frac{kT_\infty}{m} [\varepsilon\eta' + O(\varepsilon^2)]. \end{aligned} \quad (33)$$

Provided that the condensation/evaporation process is not too fast, we can truncate these expansions, taking them to first order in ε . Comparing T/T_∞ in Eq. (33) with Eq. (23), we have

$$\varepsilon\theta = \frac{2A_2a_1}{5\pi\text{Kn}_{2\infty}r^*}. \quad (34)$$

Substituting the linearized equations into Eqs. (A.1)–(A.4) and neglecting higher order terms of ε , we obtain the modified set of equations given in the appendix as Eqs. (A.5)–(A.7). Solving these equations for the boundary conditions far from the surface, which are $\rho_\infty = \rho(r \rightarrow \infty)$ and $T_\infty = T(r \rightarrow \infty)$, we obtain

$$j = \rho_\infty \left(\frac{kT_\infty}{m} \right)^{1/2} \frac{\varepsilon a_2}{r^{*2}}, \quad S = \rho_\infty \left(\frac{kT_\infty}{m} \right)^{3/2} \frac{\varepsilon a_3}{r^{*2}}, \quad (35)$$

$$\rho = \rho_\infty + \frac{A_1\rho_\infty}{\pi(1+z)\text{Kn}_{\infty}r^*} \left[\sqrt{2\pi}\varepsilon a_2 - \frac{2A_2}{5A_1}(1+z)\gamma a_1 \right], \quad (36)$$

$$\eta = -\frac{\text{Kn}_{\infty}\rho_\infty kT_\infty/m}{(3A_2 + 4A_1z)r^{*3}} \left[\left(\frac{64}{15A_2} - \frac{1}{5} \right) \frac{za_1}{\gamma} + \sqrt{8\pi}(1+z)^2 \left(\varepsilon a_2 + \frac{\varepsilon a_3}{5} \right) \right] \quad (37)$$

and

$$\varepsilon a_3 = \frac{\sqrt{2\pi}a_1}{(3z^2 + 1 + 2zA_2/A_1)} \left[4 \left(2 - \frac{A_2}{A_1} \right) z^{3/2} + (1+z)^3 \gamma \frac{A_2}{A_1} \right], \quad (38)$$

where a_2 and a_3 are integration constants, and $\gamma = \text{Kn}_{\infty}/\text{Kn}_{2\infty}$. We may now treat εa_2 and εa_3 as new variables that need to be determined by applying the boundary conditions.

2.3. Application of the interfacial boundary conditions

If α_{T2} , the thermal accommodation coefficient for the bath gas, is the probability that a colliding gas molecule will leave with the particle surface temperature, T_s , the boundary condition at the particle surface is described as

$$S_{2i}(R) = \alpha_{T2} m_2 \left(\int_{-\infty}^0 c_{2i} c_2^2 f_2 d^3 c_2 + \int_0^{\infty} c_{2i} c_2^2 f_{2s}^0 d^3 c_2 \right), \tag{39}$$

where f_{2s}^0 denotes the Maxwellian distribution of the gas molecules at the surface temperature. Solving Eq. (39) and combining with Eqs. (21)–(23), we obtain

$$\left(\frac{1}{2\beta_{T2}} + \frac{A_2}{5\pi \text{Kn}_{2\infty}} + \frac{8\text{Kn}_{2\infty}}{5A_2} \right) a_1 = \left(1 - \frac{2A_2 a_1}{5\pi \text{Kn}_{2\infty}} \right) \left(\frac{T_s}{T_\infty} \right)^{3/2} - 1, \tag{40}$$

where $\beta_{T2} = \alpha_{T2}/(2 - \alpha_{T2})$.

Similarly, if α is the probability that an approaching vapor molecule will be absorbed on the surface, the mass flux boundary condition is

$$j_i(R) = \alpha m \left(\int_{-\infty}^0 \xi_i f d^3 c + \int_0^{\infty} \xi_i f_s^0 d^3 c \right). \tag{41}$$

Here f_s^0 denotes the Maxwellian distribution function of the vapor molecules at temperature T_s . The vapor density at the surface is the saturation value, ρ_s .

Using Eqs. (35)–(38), the constants are related by

$$E_{11} a_1 + E_{12} \varepsilon a_2 = \frac{\rho_s}{\rho_\infty} \sqrt{\frac{T_s}{T_\infty}} - 1, \tag{42}$$

where

$$E_{11} = \frac{\text{Kn}_\infty}{3A_2 + 4A_1 z} \left\{ \left(\frac{64}{15A_1} - \frac{1}{5} \right) \frac{z}{\gamma} + \frac{8\pi(1+z)^2}{5(3z^2 + 1 + 2zA_2/A_1)} \right. \\ \left. \times \left[4 \left(2 - \frac{A_2}{A_1} \right) z^{3/2} - \frac{A_2}{A_1} (1+z)^3 \gamma \right] \right\} - \frac{A_2}{5\pi \text{Kn}_{2\infty}}, \\ E_{12} = \sqrt{\frac{\pi}{2}} \left[\frac{1}{\beta} + \frac{2A_1}{\pi \text{Kn}_\infty (1+z)} + \frac{4\text{Kn}_\infty (1+z)^2}{3A_2 + 4A_1 z} \right]$$

and β is given by Eq. (6).

To calculate the constants, it is necessary to include the energy balance equation at the surface, that is,

$$\lambda j(R) + q(R) = 0, \tag{43}$$

where λ is the latent heat (J/kg), and q is heat flux. Since λ is a positive quantity, j and q have opposite signs. We have excluded the effects of radiant energy transfer to or from the droplet in the energy balance, but the radiant energy flux can be added to the heat flux to provide a more general theory.

In the absence of radiation energy transfer, the heat flux is related to S and S_2 by

$$q(R) = \frac{1}{2}[S(R) + S_2(R)]. \quad (44)$$

Because $n \ll n_2$, $S(R)$ is negligible compared with $S_2(R)$. Thus, using Eqs. (21)–(23), (43) and (44), we obtain

$$\varepsilon a_2 = E_{21} a_1 / \lambda, \quad (45)$$

where

$$E_{21} = -\sqrt{\frac{2z}{\pi}} \frac{kT_\infty}{m} \frac{p_2}{p_\infty}.$$

We now have Eqs. (40), (42) and (45) involving the unknown interfacial temperature, T_s , and the parameters a_1 and εa_2 . This system of equations can be solved easily with a numerical method such as MATLAB, but we need to input information about the vapor pressure as a function of temperature to determine the saturation density.

2.4. Additional simplification

To obtain a useful, but more restricted, expression for the condensation/evaporation rate, we can make some additional simplification. If the system is not far from isothermal, we may write

$$\frac{T_s}{T_\infty} = 1 + \theta_s, \quad (46)$$

where θ_s is a small number. Expanding related terms such $\sqrt{T_s/T_\infty}$ in power series of θ_s , and neglecting higher order terms, we obtain

$$\theta_s = F_1 a_1, \quad (47)$$

where

$$F_1 = \frac{1}{3\beta_{T_2}} + \frac{2A_2}{5\pi Kn_{2\infty}} + \frac{16Kn_{2\infty}}{15A_2}.$$

Using Eq. (47), Eq. (42) simplifies to

$$E_{12}\varepsilon a_2 + \left(E_{11} - \frac{n_s}{2n_\infty}F_1\right)a_1 = \frac{n_s}{n_\infty} - 1. \quad (48)$$

Combining this result with Eq. (45), we obtain

$$a_1 = \frac{n_s/n_\infty - 1}{E_{11} - \frac{E_{12}E_{21}}{\lambda} - \frac{n_s}{n_\infty} \frac{F_1}{2}}, \quad (49)$$

$$\varepsilon a_2 = \frac{n_s/n_\infty - 1}{E_{12} + \frac{\lambda}{E_{21}} \left(\frac{n_s}{n_\infty} \frac{F_1}{2} - E_{11} \right)}. \quad (50)$$

Note that parameters a_1 and a_2 have complicated, but explicit, dependence on the Knudsen number through the parameters E_{11} , E_{12} and F_1 . In addition, the effects of the accommodation coefficients, α and α_T , are explicit.

Finally, we obtain an expression for the evaporation/condensation rate, which is

$$\dot{m} = -4\pi R^2 j = 4\pi R^2 m \sqrt{\frac{kT_\infty}{m}} \frac{(n_\infty - n_s)}{E_{12} + \frac{\lambda}{E_{21}} \left(\frac{n_s}{n_\infty} \frac{F_1}{2} - E_{11} \right)}. \quad (51)$$

For $\text{Kn} \ll 1$, and using the approximation $\gamma = \text{Kn}_\infty/\text{Kn}_{2\infty} = 1$, Eq. (51) reduces to

$$\dot{m} = \pi^2 R^2 m \bar{c}_1 \text{Kn}_\infty \frac{(n_\infty - n_s)}{\frac{A_1}{1+z} + \frac{A_2 Q_c}{10\sqrt{z}} \left(\frac{n_s}{n_\infty} + 1 \right)} = \pi^2 R^2 \bar{c}_1 \text{Kn}_\infty \rho_s \frac{(\sigma - 1)}{\frac{A_1}{1+z} + \frac{A_2 Q_c}{10\sqrt{z}} \left(\frac{1}{\sigma} + 1 \right)}, \quad (52)$$

where Q_c is the dimensionless latent heat defined by $Q_c = p_\infty m \lambda / p_2 k T_\infty$, and σ is the saturation ratio discussed above. This parameter determines how close the simultaneous heat and mass transfer process is to isothermal.

If Q_c is sufficiently small, it can be neglected in Eq. (52). This is equivalent to isothermal behavior, and in this case Eq. (52) reduces to the classical result for the continuum regime,

$$\dot{m}_{\text{cont}} = 4\pi R D_{12} m (n_\infty - n_s) = 4\pi R D_{12} \rho_s (\sigma - 1), \quad (53)$$

where the diffusion coefficient is related to \bar{c} and ℓ_∞ by

$$\frac{D_{12}}{\bar{c}_1 \ell_\infty} = \frac{(1+z)\pi}{4A_1}. \quad (54)$$

This expression is the same as the result of Qu and Davis for the isothermal case. Writing Eq. (52) in terms of the diffusion coefficient based on Eq. (54) the evaporation/condensation rate becomes

$$\dot{m} = 4\pi R D_{12} \rho_s \frac{(\sigma - 1)}{\left[\frac{1}{10} \frac{A_2 Q_c (1+z)}{A_1 \sqrt{z}} \left(\frac{1}{\sigma} + 1 \right) + 1 \right]}. \quad (55)$$

3. Discussion of results and applications

The first observation one can make is that flux-matching and simple resistance approaches to describing simultaneous heat and mass transfer in the transition regime are overly simplistic. They do not predict the correct Knudsen number dependence and do not take into account the molecular weight ratio and the accommodation coefficients appropriately. In addition it is clear that the method of Grad used in the theoretical development is not adequate as the free-molecule regime is approached, but it should yield a good approximation in the near-continuum region.

For evaporation/sublimation processes the rates given by Eqs. (52) and (55) are always lower than the corresponding isothermal rates because the terms involving Q_c are always positive. To compare these results with previous approximations it is convenient to expand the term $(1/\sigma + 1)$ using a linearization of the Clausius–Clapeyron equation, which relates the vapor pressure to temperature. One obtains the approximation $(1/\sigma + 1) \approx \lambda m/kT_\infty$, and Eq. (55) becomes

$$\dot{m} = 4\pi R D_{12} \rho_s \frac{(\sigma - 1)}{\left[\frac{1}{10} \frac{A_2(1+z)}{A_1 \sqrt{z}} \frac{p_\infty}{p_2} \left(\frac{\lambda m}{kT_\infty} \right)^2 + 1 \right]}. \quad (56)$$

Here p_∞ is the partial pressure of vapor in the bulk gas. This result can be compared with Mason's formula for the continuum regime, which is

$$\dot{m} = 4\pi R D_{12} \rho_s \frac{(\sigma - 1)}{\left[\left(\frac{\lambda^2 D_{12} \rho_s m}{k_2 k T_\infty^2} \right) + 1 \right]}. \quad (57)$$

If kinetic theory is used to relate the gas thermal conductivity and the diffusivity to molecular parameters such as presented in Chapman and Cowling (1953) or Bird, Stewart, and Lightfoot (1960), Eqs. (56) and (57) have a similar form. This can be illustrated by introducing the Chapman–Enskog diffusivity approximation for hard spheres,

$$D_{12} = \frac{3}{8 p_2 \sigma_{12}^2} \sqrt{\frac{k^3 T_\infty^3}{2\pi \mu_{12}}} \quad (58)$$

and the approximation for the dilute gas thermal conductivity given by

$$k_2 = \frac{15}{4} \frac{k}{\pi \sigma_2^2} \sqrt{\frac{k T_\infty}{\pi m_2}}. \quad (59)$$

Here $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, where σ_1 and σ_2 are the molecular diameters of the vapor and gas molecules, respectively.

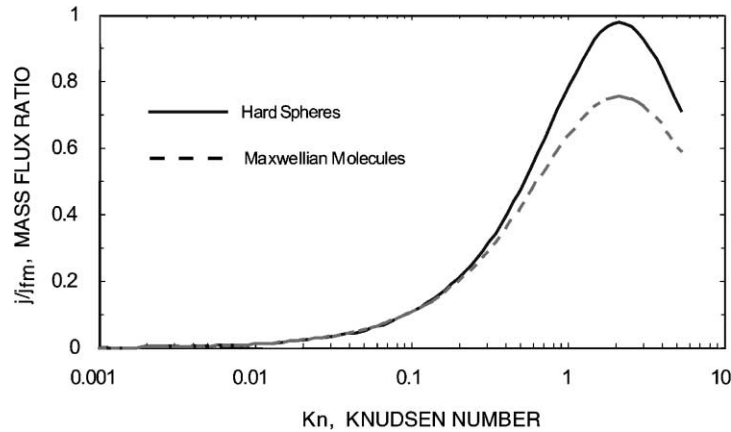


Fig. 1. Comparison between the results based on the solution of Nowakowski and Popielawski (1988) for hard spheres and this work for Maxwellian molecules for water droplet evaporation in dry nitrogen at 283.2 K and atmospheric pressure assuming $\alpha = \alpha_{T2} = 1$.

Substituting these approximations in Mason’s formula, it becomes

$$\dot{m} = 4\pi R D_{12} \rho_s \frac{(\sigma - 1)}{\left[\frac{\pi}{10\sqrt{1+z}} \left(\frac{\sigma_2}{\sigma_{12}} \right)^2 \frac{(1+z) p_s}{\sqrt{z} p_2} \left(\frac{\lambda m}{kT_\infty} \right)^2 + 1 \right]}, \tag{60}$$

which is similar in form to Eq. (56) and yields similar results.

Barrett and Clement obtained a result for the continuum regime that is more accurate than that of Mason when the gas–vapor mixture is not dilute, for they used a more accurate diffusive vapor current that becomes more important for large vapor concentrations. That is, they included the so-called Stefan flow in their expression for the vapor flux. Provided that the droplet is far from its boiling point the corrections incorporated by Barrett and Clement are very small.

3.1. Comparison with the hard sphere model

Qu and Davis showed that for isothermal processes the hard sphere and Maxwellian molecule models yield essentially identical results based on solving the Boltzmann equation by the method of Grad. Such is not the case for non-isothermal processes, and this is shown in Fig. 1. The figure presents a comparison between the results of the Maxwellian model of this paper and the hard sphere model used by Nowakowski and Popielawski. The conditions are $T_\infty = 283.2$ K, $p_\infty = 101,325$ Pa for water droplet evaporation in dry nitrogen. The mass and the thermal accommodation coefficients are both taken to be unity, and the Knudsen number indicated on the figure is the so-called standard Knudsen number, Kn_0 , defined by,

$$Kn_0 = \frac{\ell}{R} = \frac{6}{(1+z)} \frac{D_{12}}{R\bar{c}_1}. \tag{61}$$

The relationships between various Knudsen numbers were presented by Qu and Davis. The ordinate in Fig. 1 is the mass flux ratio, j/j_{fm} .

The two models yield identical results for $\text{Kn}_0 < 0.1$, but at higher Knudsen numbers the results are sensitive to the molecular interaction model used. The hard sphere model predicts higher mass flux ratios, and both fail in the free-molecule regime. Besides the model difference, there is another difference that affects the results. Nowakowski and Popielawski assumed that the bulk velocity of vapor molecules is zero, but we have relaxed this assumption to take into account the motion of vapor molecules.

The effects of the model dependence and the method of solution of the Boltzmann equation have been examined in a number of papers in which the momentum slip, thermal slip and temperature jump have been examined for the near-continuum regime. For example, if one defines a thermal slip velocity (or thermal creep velocity) by

$$v_{\text{tc}} = C_{\text{tc}} \frac{\mu}{p} \frac{k}{m} \frac{dT}{dr}, \quad (62)$$

where C_{tc} is the thermal creep coefficient, Maxwell's model yields $C_{\text{tc}} = 3/4$. Loyalka and Cipolla (1971) and others studied the problem of thermal creep. The equivalent result obtained by Loyalka and Cipolla using the BGK model of the Boltzmann equation is

$$C_{\text{tc}} = \frac{3}{2} \left(\frac{1}{2} + 0.2662\alpha_{\text{T}} \right). \quad (63)$$

Additional comparative studies of temperature jump and thermal creep were reported by Loyalka (1968, 1989). All of these investigations indicate that Maxwell's result gives lower thermal creep coefficients than other models.

3.2. Water droplet evaporation

There exists very little evaporation and condensation data obtained under precisely controlled conditions of temperature and pressure that exhibit significant non-isothermal behavior, particularly in the non-continuum regime. As indicated by Qu and Davis, there are a number of sets of evaporation rate data for low-volatility species, but these exhibit isothermal behavior. However, Taflin, Zhang, Allen, and Davis (1988) reported evaporation measurements of single water droplets that showed non-isothermal effects. They trapped single water droplets in an electrodynamic balance and made angular light scattering measurements to determine the droplet size as a function of time by comparing the data with Mie theory. The droplets were injected into bone dry air at atmospheric pressure, and a slight air flow through the balance chamber maintained the humidity at essentially zero. The rapid evaporation produced significant chilling of the droplet, which was demonstrated by comparing the evaporation rate data with theory for isothermal evaporation in the continuum regime and with analysis based on solving Eqs. (1) and (4).

Fig. 2 presents experimental data for two water droplets evaporating in dry air at bulk temperatures of 283.2 and 293.2 K, respectively. The droplet in air at 293.2 K had an initial radius of 21.9 μm , and the other droplet had an initial radius of 28.3 μm . Also shown in the figure are the solutions based on Eq. (1) assuming isothermal behavior, the solutions obtained using Eqs. (1) and (4) for non-isothermal behavior, and the results based on the solution of the

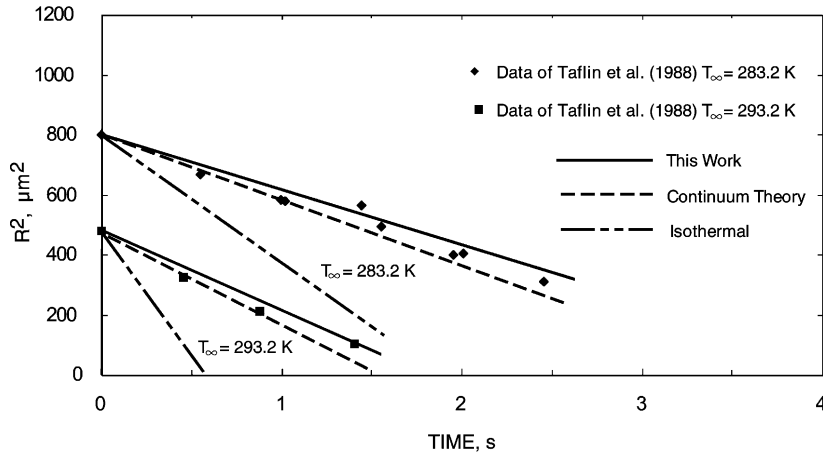


Fig. 2. Comparison between theory and experiment for water droplet evaporation at atmospheric pressure in dry air.

system of equations developed herein. We note that the smallest droplet radius was about $10\ \mu\text{m}$, so the system was in the continuum regime. The data fall between the two theories, and the new theory predicts a somewhat lower evaporation rate than the classical theory. The interfacial temperature predicted from the new theory is lower than that calculated from classical theory. For the droplet in air at $293.2\ \text{K}$ the predicted interfacial temperatures are $277.8\ \text{K}$ based on the classical solution and $273.1\ \text{K}$ based on this work. For the droplet in air at $283.2\ \text{K}$ the corresponding interfacial temperatures are 272.7 and $268.6\ \text{K}$.

Because of the complicated coupling among the equations developed here for the heat and mass fluxes it is not obvious why kinetic theory predicts a lower evaporation rate, but there are several issues that can account for it. The classical theory applied here neglects the bulk velocity of vapor, but the kinetic theory analysis takes into account such transport, so some small differences can be expected in that respect. The relatively large decrease in the interfacial temperature puts into question the assumption that the temperature does not deviate greatly from the bulk gas temperature, that is, that the perturbation θ_s defined by Eq. (47) is sufficiently small. It is also possible that the molecular model used underestimates the rate of heat transfer to the droplet thereby leading to a lower interfacial temperature. The isothermal case, which does not involve interfacial cooling, appears to be in reasonably good agreement with evaporation data for low-volatility species, as shown by Qu and Davis. Consequently, it appears that the interfacial temperature differences between continuum theory and kinetic theory are related to differences in the energy transport rates. For higher values of the relative humidity (RH) and for lower vapor pressure particles the gas kinetic theory can be expected to be a more reasonable assumption, for the thermal effects can be expected to decrease as the evaporation rate decreases.

3.3. Ice sublimation

Swanson, Bacon, Davis, and Baker (1998, 1999) and Bacon, Swanson, Baker, and Davis (1998) used electrodynamic levitation techniques to measure growth and sublimation rates and light-scattering phase functions of single ice particles having various sizes and shapes

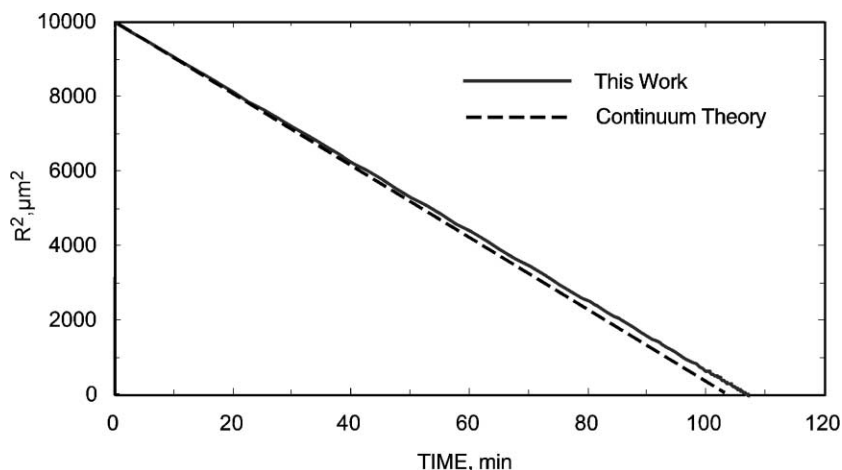


Fig. 3. Calculations of ice sublimation for upper tropospheric conditions corresponding to the continuum regime for $T_{\infty} = 223.2$ K, $p = 26,500$ Pa, $p_{\text{H}_2\text{O}} = 2.5$ Pa (RH = 64%), $\alpha_T = \alpha = 1$.

under tropospheric temperature and humidity conditions. Swanson et al. demonstrated that, under certain conditions of temperature and humidity, measurements of ice particle growth and sublimation rates of irregular frost particles and hexagonally habited ice particles are consistent with the standard quasi-steady-state model of diffusion-controlled transport for spheres, which yields the equation

$$R^2 = R_0^2 - \frac{2D_{12}\rho_1(T_{\infty})}{\rho_{\text{ice}}} \frac{(1 - \sigma)}{\left[1 + \frac{\lambda D_{12}\rho_1(T_{\infty})}{\kappa T_{\infty}} \left(\frac{\lambda}{RT_{\infty}} - 1\right)\right]} (t - t_0), \quad (64)$$

in which R_0 is the radius at time t_0 , $\rho_1(T_{\infty})$ is the vapor density at T_{∞} and ρ_{ice} is the density of ice.

Although the experimental conditions of Bacon et al. and Swanson et al. correspond to the continuum regime since they operated their chamber at atmospheric pressure, ice sublimation in the stratosphere occurs at much lower pressures. Consequently, the process is in the non-continuum regime for smaller particles. It is of considerable interest to understand such atmospheric processes. To this purpose we have applied the new theory to explore sublimation rates at the temperatures and pressures of the stratosphere. It has been traditional to apply continuum theory to such processes. In the following we consider some examples of computations using the analysis developed here.

For comparisons let us take a base case using representative conditions in the upper troposphere at 10 km above sea level where the temperature is 223.2 K and the pressure is 26,500 Pa. The partial pressure of water vapor in the surrounding air is taken to be 2.5 Pa (relative humidity, RH = 64%). The mean free path of water vapor molecules is ~ 0.4 μm under these conditions. If the initial radius of the ice particle is 100 μm , our analysis and the classical continuum theory yield the results presented in Fig. 3, a graph R^2 versus time. In this case the system is in the continuum regime over the size range shown. We have neglected the Kelvin effect in the computations since this effect is appreciable only when $R < 0.5$ μm , but it

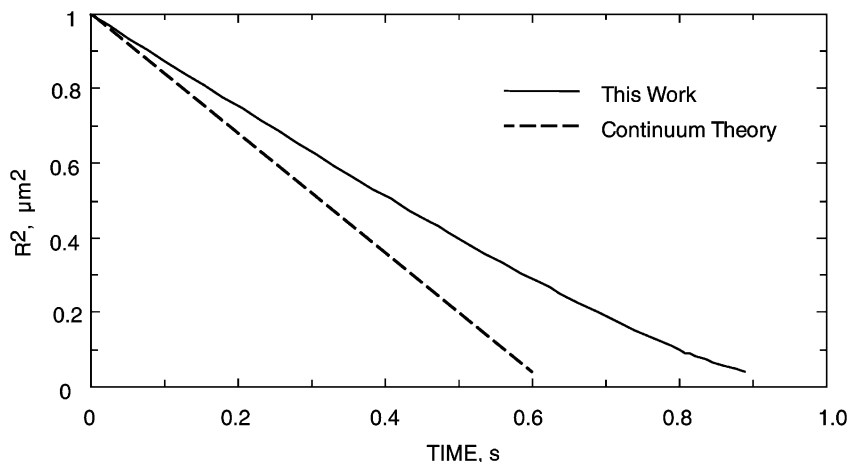


Fig. 4. Calculations of ice sublimation for upper tropospheric conditions corresponding to the non-continuum regime for $T_{\infty} = 223.2$ K, $p = 26,500$ Pa, $p_{\text{H}_2\text{O}} = 2.5$ Pa (RH = 64%), $\alpha_{\text{T}} = \alpha = 1$.

can readily be included by correcting the interfacial vapor pressure for the surface curvature. The sublimation rate is so low at 223.2 K that the system is very nearly isothermal, and the two theories yield very similar results for these conditions. However, if we consider a much smaller initial particle radius, say $1 \mu\text{m}$, under the same conditions of pressure and temperature, differences between the classical theory and our kinetic theory become significant, as shown in Fig. 4. Again we have neglected the Kelvin effect, which can be expected to increase the sublimation rate for sub-micrometer particles because of the increase in vapor pressure over the curved surface. The differences shown in the figure primarily result from non-continuum behavior at the smaller sizes, and the linear relationship between R^2 and time is not followed over the course of the sublimation.

The effect of particle size (or inverse Knudsen number) on the ‘life span’ of an ice particle is illustrated in Fig. 5 for the base case. The life span is the time required to sublime from an arbitrary initial radius (the abscissa) to zero size. Again we have neglected the Kelvin effect, but it can be expected to shorten the life span somewhat. If the initial size of the particle is sufficiently large, say $100 \mu\text{m}$, the Kelvin effect will have little effect on the life span, but for small initial sizes it should be included. There is relatively little difference between classical theory and kinetic theory for the conditions used for Fig. 5.

It is interesting to examine the effect of relative humidity on the sublimation process, and Fig. 6 shows the effect of RH on the life span of an ice crystal having an initial radius of $100 \mu\text{m}$ under the pressure and temperature conditions of the base case. There is a sharp increase in the life span predicted as the relative humidity exceeds 80%.

For the previous figures, both the mass and the thermal accommodation coefficients were assumed to be unity. Field studies show that large concentrations of small ice crystals can be found over broad regions in the upper troposphere and lower stratosphere (Heymsfield & Platt, 1984; Heymsfield, Miller, & Spinhirne, 1990; Arnott, Dong, & Hallett, 1994; Peter et al., 1994; Strom & Heintzenberg, 1994) and that these crystals are observed to persist at low relative humidities. There is considerable interest in the lifetime of ice particles when the presence of

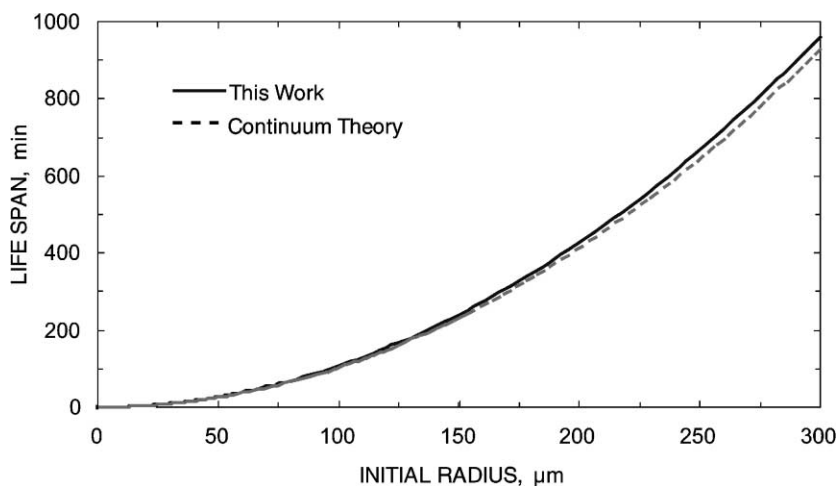


Fig. 5. The calculated life span of a subliming ice sphere for the base case, $T_{\infty} = 223.2$ K, $p = 26,500$ Pa, $p_{\text{H}_2\text{O}} = 2.5$ Pa (RH = 64%), $\alpha_{\text{T}} = \alpha = 1$.

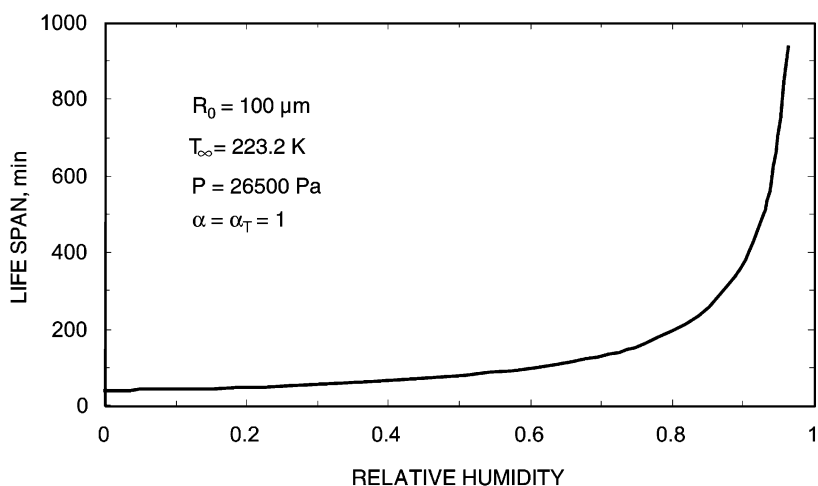


Fig. 6. The effect of relative humidity on the lifespan of a subliming ice particle for $T_{\infty} = 223.2$ K, $p = 26,500$ Pa, and $\alpha_{\text{T}} = \alpha = 1$.

organic and inorganic surface coatings may effectively lower the accommodation coefficients, thereby slowing the sublimation rate (Peter, Müller, Crutzen, & Deshler, 1994; Peter & Baker, 1996). Fig. 7 shows the effect of accommodation coefficients on the life span of an ice particle for the base case conditions of temperature and pressure. Decreasing the accommodation coefficients has relatively little effect on the life span for α and $\alpha_{\text{T}2}$ greater than 0.01, but for smaller values of α the life span is significantly increased. The mass accommodation coefficient has a larger effect on the transport processes than the thermal accommodation coefficient.

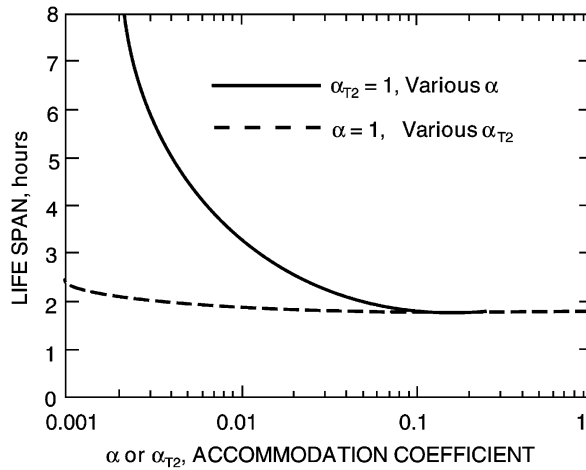


Fig. 7. The effect of the accommodation coefficients for vapor and bath gas on the lifespan of a subliming ice particle for the base case.

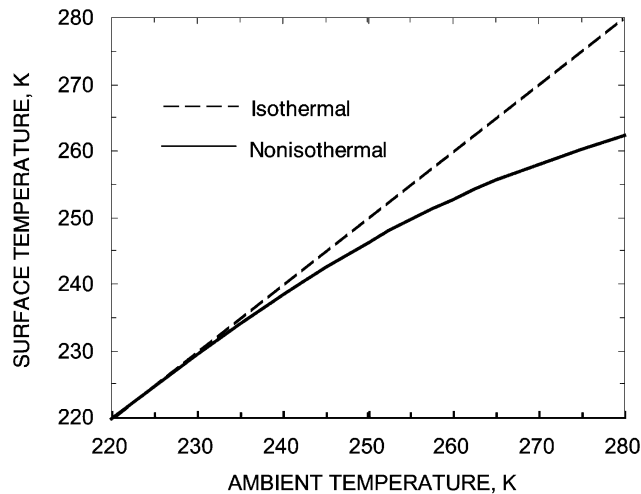


Fig. 8. The effect of the ambient temperature on sublimation of an ice sphere for $p = 54,048$ Pa, $RH = 0\%$, and $\alpha_T = \alpha = 1$.

At the low temperatures of the upper atmosphere the ice sublimation process is very nearly isothermal, but at lower altitudes and higher temperatures the process becomes non-isothermal. To illustrate the effect of the ambient temperature on the sublimation process let us change the parameters to represent the conditions at 5 km above sea level where the air pressure is 54,048 Pa, varying the ambient temperature. Fig. 8 shows the ice particle surface temperature as function of the ambient air temperature for sublimation in bone dry air. The radius of the ice particle is taken to be 20 μm , and we assume $\alpha = \alpha_{T2} = 1$. As expected, the higher the ambient temperature, the faster the sublimation, and the larger the temperature difference. When the ambient temperature is about 250 K, the temperature difference exceeds 3 K, which can be

considered to be non-isothermal. When the ambient temperature is the typical air temperature at 5 km above sea level, 255.7 K, the temperature difference is 5.6 K. Since the vapor pressure is strongly dependent on the surface temperature, the sublimation rate is significantly altered by a change of 5.6 K.

4. Summary

The method of Grad has been applied to investigate non-isothermal evaporation/condensation and sublimation processes in the near-continuum regime. Although the results for isothermal processes are relatively insensitive to the molecular interaction model used, non-isothermal processes appear to depend on the model used in the solution of the Boltzmann equation. Evaporation rates predicted here are in reasonable agreement with water droplet evaporation measurements for the continuum regime, and illustrative calculations of ice sublimation in the upper atmosphere indicate that both non-continuum behavior and non-isothermal behavior can occur under some conditions of temperature and pressure. From a theoretical point of view this analysis shows that flux-matching approaches and resistance models for simultaneous heat and mass transfer in the transition regime are not adequate to predict the Knudsen number dependence and the dependence on the molecular weight ratio.

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Appendix

The equations describing the scalar functions $j(r)$, $S(r)$ and $\eta(r)$:

$$\frac{dj}{dr} + \frac{2j}{r} = 0, \quad -2\frac{d\eta}{dr} - \frac{6\eta}{r} + \frac{dp_1}{dr} + \frac{j}{\rho} \frac{dj}{dr} - \frac{j^2}{\rho^2} \frac{d\rho}{dr} = -2A_1\pi\sqrt{K_{12}\mu_{12}} \frac{n_2j}{m}, \quad (\text{A.1})$$

$$\begin{aligned} & \frac{(5p_1 - 4\eta)}{\rho} \left(\frac{dj}{dr} - \frac{j}{\rho} \frac{d\rho}{dr} \right) + \frac{3j}{\rho} \frac{dp_1}{dr} + \frac{(10p_1 + 4\eta)j}{\rho r} + \frac{dS}{dr} + \frac{2S}{r} \\ & = 4A_1\pi \frac{\mu_{12}^2}{m^2} \left(\frac{K_{12}}{\mu_{12}} \right)^{1/2} n_2 \frac{j^2}{\rho}, \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} & \frac{j}{\rho} \frac{d\eta}{dr} + \left(\frac{7}{3}\eta - \frac{2}{3}p_1 \right) \frac{1}{\rho} \left(\frac{dj}{dr} - \frac{j}{\rho} \frac{d\rho}{dr} \right) + \left(\frac{8}{3}\eta + \frac{2}{3}p_1 \right) \frac{j}{\rho r} + \frac{2}{15} \left(\frac{S}{r} - \frac{dS}{dr} \right) \\ & = \pi A_1 \frac{\mu_{12}^2}{m} \left(\frac{K_{12}}{\mu_{12}} \right)^{1/2} \left[nm_2 \left(\frac{A_2}{A_1} - \frac{4}{3} \right) \frac{j^2}{\rho^2} - \left(\frac{3A_2}{A_1} + 4z \right) \frac{n_2\eta}{m} + \left(4 - \frac{3A_2}{A_1} \right) \frac{n\eta_2}{m_2} \right] \end{aligned} \quad (\text{A.3})$$

and

$$\begin{aligned} & \frac{1}{\rho} \left(\frac{16}{5} S - \frac{4j\eta}{\rho} \right) \left(\frac{dj}{dr} - \frac{j}{\rho} \frac{d\rho}{dr} \right) + \frac{j}{\rho} \frac{dS}{dr} + \frac{14}{5} \frac{jS}{\rho r} - \frac{14kT}{m} \left(\frac{d\eta}{dr} + \frac{3\eta}{r} \right) \\ & + \frac{5kT}{m} \frac{dp_1}{dr} + (5p_1 - 14\eta) \frac{k}{m} \frac{dT}{dr} \\ & = -v_{12} \left[\alpha^{(1)} S - \frac{\rho}{m_2 n_2} \alpha^{(4)} S_2 - 2\alpha^{(2)} \frac{j\eta}{\rho} - \frac{4\alpha^{(4)} j\eta_2}{m_2 n_2} \right. \\ & \quad \left. + (\alpha^{(2)} + 3\alpha^{(3)}) \frac{jkT}{m} + 5\alpha^{(4)} \frac{jkT}{m_2} + \alpha^{(4)} \frac{j^3}{\rho^2} \right]. \end{aligned} \quad (\text{A.4})$$

Again we point out that un-subscripted parameters and variables such as S , j , n , ρ , and η refer to the vapor, and the subscript 2 refers to the bath gas.

The linearized equations:

$$\frac{dj'}{dr^*} + \frac{2j'}{r^*} = 0, \quad \frac{d\eta'}{dr^*} + 3\frac{\eta'}{r^*} - \frac{1}{2} \frac{d\rho'}{dr^*} - \frac{1}{2} \frac{d\theta}{dr^*} = \frac{A_1}{\sqrt{2\pi}} \frac{\mu_{12}}{m} \frac{j'}{\text{Kn}}, \quad \frac{dS'}{dr^*} + \frac{2S'}{r^*} = 0, \quad (\text{A.5})$$

$$\begin{aligned} & \frac{2}{3} \left(\frac{j'}{r^*} - \frac{dj'}{dr^*} \right) + \frac{2}{15} \left(\frac{S'}{r^*} - \frac{dS'}{dr^*} \right) \\ & = -\frac{\mu_{12}^2}{m^2} \frac{1}{\sqrt{2\pi} \text{Kn}_\infty} \left[(3A_2 + 4A_{1z}) \eta' + \left(\frac{64}{15A_2} - \frac{1}{5} \right) \frac{z \text{Kn}_{2\infty} a_1}{\epsilon r^{*3}} \right] \end{aligned} \quad (\text{A.6})$$

and

$$\begin{aligned} & 5 \frac{d\rho'}{dr^*} + 10 \frac{d\theta}{dr^*} - 14 \left(\frac{d\eta'}{dr^*} + 3 \frac{\eta'}{r^*} \right) \\ & = -\sqrt{\frac{2}{\pi}} \frac{A_1 \mu_{12}}{\text{Kn}_\infty m} \left[\alpha^{(1)} S' + (\alpha^{(2)} + 3\alpha^{(3)} + 5z\alpha^{(4)}) j' - \sqrt{\frac{8}{\pi}} \alpha^{(4)} z^{3/2} \frac{a_1}{\epsilon r^{*2}} \right]. \end{aligned} \quad (\text{A.7})$$

References

- Arnott, W., Dong, Y., & Hallett, J. (1994). Role of small ice crystals in radiative properties of cirrus: A case study. FIRE II. *Journal of Geophysical Research*, 99, 1371–1381.
- Bacon, N. J., Swanson, B. D., Baker, M. B., & Davis, E. J. (1998). Laboratory measurements of light scattering by single ice particles. *Journal of Aerosol Science*, 29, S1317–S1318.
- Barrett, J. C., & Clement, C. F. (1988). Growth rates for liquid drops. *Journal of Aerosol Science*, 19, 223–242.
- Bird, R. B., Stewart, W. E., & Lightfoot, L. N. (1960). *Transport phenomena*. New York: Wiley.
- Chapman, S., & Cowling, T. G. (1953). *Mathematical theory of non-uniform gases*. Cambridge: Cambridge University Press.
- Fuchs, N. A. (1934). Über die Verdampfungsgeschwindigkeit Kleiner Tröpfchen in Einer Gasatmosphäre. *Physikalische Zeitschrift der Sowjetunion*, 6, 225–243.
- Fuchs, N. A., & Sutugin, A. G. (1970). *Highly dispersed aerosols*. Ann Arbor, MI: Ann Arbor Science Publishing.
- Gombosi, T. I. (1994). *Gaskinetic theory*. Cambridge: Cambridge University Press.

- Grad, H. (1949). On the kinetic theory of rarefied gas. *Communications on Pure and Applied Mathematics*, 2, 331–407.
- Heymsfield, A., Miller, K., & Spinhirne, J. (1990). The 27–28 October, 1986 FIRE IFO cirrus case study: cloud microstructure. *Monthly Weather Review*, 118, 2313–2328.
- Heymsfield, A., & Platt, C. (1984). A parameterization of the particle size spectrum of ice clouds in terms of the ambient temperature and the ice water content. *Journal of Atmospheric Science*, 41, 846–855.
- Kulmala, M., & Vesala, T. (1991). Condensation in the continuum regime. *Journal of Aerosol Science*, 22, 337–346.
- Lang, H. (1983). Heat and mass exchange of a droplet in a polyatomic gas. *Physics of Fluids*, 26, 2109–2114.
- Lees, L. (1965). Kinetic theory description of rarefied gas flow. *Journal of the Society for Industrial and Applied Mathematics*, 13, 278–311.
- Loyalka, S. K. (1968). Momentum and temperature-slip coefficients with arbitrary accommodation at the surface. *Journal of Chemical Physics*, 48, 5432–5436.
- Loyalka, S. K. (1973). Condensation on a spherical droplet. *Journal of Chemical Physics*, 58, 354–356.
- Loyalka, S. K. (1982). Condensation on a spherical droplet, II. *Journal of Colloid and Interface Science*, 87, 216–224.
- Loyalka, S. K. (1989). Temperature jump and thermal creep: Rigid sphere gas. *Physics of Fluids A*, 1, 403–408.
- Loyalka, S. K., & Cipolla Jr., J. W. (1971). Thermal creep slip with arbitrary accommodation at the surface. *Physics of Fluids*, 14, 1656–1661.
- Loyalka, S. K., Hamoodi, S. A., & Tompson, R. V. (1989a). Isothermal condensation on a spherical particle. *Physics of Fluids A*, 1, 358–362.
- Loyalka, S. K., Hamoodi, S. A., & Tompson, R. V. (1989b). Isothermal condensation on a spherical particle. *Physics of Fluids A*, 1, 358–362.
- Loyalka, S. K., & Park, J. W. (1988). Aerosol growth by condensation: A generalization of Mason's formula. *Journal of Colloid and Interface Science*, 125, 712–716.
- Mason, R. J. (1962). *Clouds, rain and rainmaking*. Cambridge: Cambridge University Press.
- Maxwell, J. C. (1878). Diffusion. In *Encyclopaedia Britannica*, London Vol. 7 (9th ed.) (pp. 214–221).
- Maxwell, J. C. (1879). On stresses in rarefied gases arising from inequalities of temperature. *Philosophical Transactions of the Royal Society*.
- Nowakowski, B., & Popielawski, J. (1988). Nonisothermal condensation on spherical aerosol particles from the Grad solution of the Boltzmann equation. *Journal of Colloid and Interface Science*, 122, 299–307.
- Peter, Th., & Baker, M. (1996). Lifetimes of ice crystals in the upper troposphere and stratosphere. In P. J. Crutzen, V. Ramanathan (Eds.), *Clouds, chemistry and climate*, NATO ASI Series, Heidelberg: Springer.
- Peter, Th., Müller, R., Crutzen, P. J., & Deshler, T. (1994). The lifetime of leewave-induced ice particles in the atmosphere. II. Stabilization due to NAT-coating. *Geophysical Research Letters*, 21, 1331–1334.
- Qu, X., & Davis, E. J. (2001). Droplet evaporation and condensation in the near-continuum regime. *Journal of Aerosol Science*, 32, 1–5.
- Sahni, D. C. (1966). The effect of a black sphere on the flux distribution in an infinite moderator. *Journal of Nuclear Energy*, 20, 915–920.
- Sahni, D. C. (1980). Evaporation and condensational growth of tiny droplets. *Journal of Aerosol Science*, 11, 293–304.
- Sampson, R. E., & Springer, G. S. (1969). Condensation on and evaporation from droplets by a moment method. *Journal of Fluid Mechanics*, 36, 577–584.
- Sampson, R. E., & Springer, G. S. (1970). Condensation on and evaporation from droplets by a moment method. *Journal of Fluid Mechanics*, 40, 859–861.
- Shankar, P. N. (1970). A kinetic theory of steady condensation. *Journal of Fluid Mechanics*, 40, 395–400.
- Sitarski, M., & Nowakowski, B. (1979). Condensation rate of trace vapor on Knudsen aerosols from the solution of the Boltzmann equation. *Journal of Colloid and Interface Science*, 72, 113–122.
- Strom, J., & Heintzenberg, J. (1994). Water vapor, condensed water and crystal concentration in orographically influenced cirrus clouds. *Journal of Atmospheric Science*, 51, 2368–2383.
- Swanson, B. D., Bacon, N., Davis, E. J., & Baker, M. B. (1998). Levitated ice crystals: Laboratory measurements of ice particle breakup and growth/sublimation rates. *Proceedings of the AMS conference on cloud physics*, Everett, Washington, USA.

- Swanson, B. D., Bacon, N., Davis, E. J., & Baker, M. B. (1999). Electrodynamic trapping and manipulation of ice crystals. *Quarterly Journal of the Royal Meteorological Society*, *125*, 1039–1058.
- Taffin, D. C., Zhang, S. H., Allen, T., & Davis, E. J. (1988). Measurement of droplet interfacial phenomena by light-scattering techniques. *A.I.Ch.E. Journal*, *34*, 1310–1320.
- Tompson, R. V., & Loyalka, S. K. (1986). Condensational growth of a spherical droplet: free molecule limit. *Journal of Aerosol Science*, *17*, 723–728.
- Tompson, R. V., & Loyalka, S. K. (1988). Condensation on a spherical droplet III. *Journal of Aerosol Science*, *19*, 287–293.
- Wagner, P. E. (1982). Aerosol growth by condensation. In: Marlow, W.H. (Ed.) *Aerosol Microphysics II. Chemical physics of microparticles*, Vol. 29 (pp. 129–178). Berlin: Springer.