

Condensation on and evaporation from droplets by a moment method

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The moment method proposed by Lees (1959) is applied to the problem of vapour condensation on and evaporation from spherical liquid droplets when the droplet is not in equilibrium with its surrounding. Using a four-moment solution, an analytical expression is derived for the mass flux to or from the droplet surface when the droplet is surrounded by a pure vapour. By neglecting changes in temperature, an analytical solution is also obtained for the mass flux when the droplet is immersed in a vapour–gas mixture. The results of both of these analyses are applicable in the range from $\lambda/R \rightarrow 0$ to $\lambda/R \rightarrow \infty$, where λ is the mean free path and R the droplet radius, and it is shown that in the limits the results reduce to the appropriate free molecule and continuum expressions.

1. Introduction

This study is concerned with the problem of vapour condensation on or evaporation from spherical liquid droplets under non-equilibrium conditions. The existing analytical investigations of these phenomena describe the process satisfactorily over limited density ranges only. When the mean free path λ of the vapour surrounding the droplet is large compared to the droplet radius R ($\lambda/R \gg 1$), the mass flux of the vapour to or from the droplet is generally calculated by the Hertz (1882)–Knudsen (1915) formula. Under continuum conditions ($\lambda/R \ll 1$) Maxwell's relation (Fuchs 1959) is used. These formulae do not consider the mass motion of the bulk vapour and expressions which also include this effect were obtained by Schrage (1953) for $\lambda/R \gg 1$ and by Stefan (1881) for $\lambda/R \ll 1$. Recently, Kang (1967) employed Langmuir's (1915) model originally proposed for heat conduction, and calculated the droplet growth when the mean free path is comparable to the droplet radius. Kang's analysis is expected to yield reasonable results at nearly free-molecule or at nearly continuum conditions. In the present investigation a kinetic theory approach is used to calculate the mass flux. The moment method proposed by Lees (1959) is applied to the problem and closed-form solutions are derived for the mass flux for two cases: (a) when the droplet is immersed in its own vapour, and (b) when the droplet is surrounded by a gas–vapour mixture. The expressions resulting from the analyses are applicable over the entire pressure range, i.e. the range from $\lambda/R \rightarrow \infty$ to $\lambda/R \rightarrow 0$.

2. Droplet immersed in pure vapour

The problem considered here is the following. A liquid droplet (radius R) at a given temperature T_s , with corresponding saturation pressure p_s (or number density n_s), is immersed in its own vapour. The temperature T_v and pressure p_v

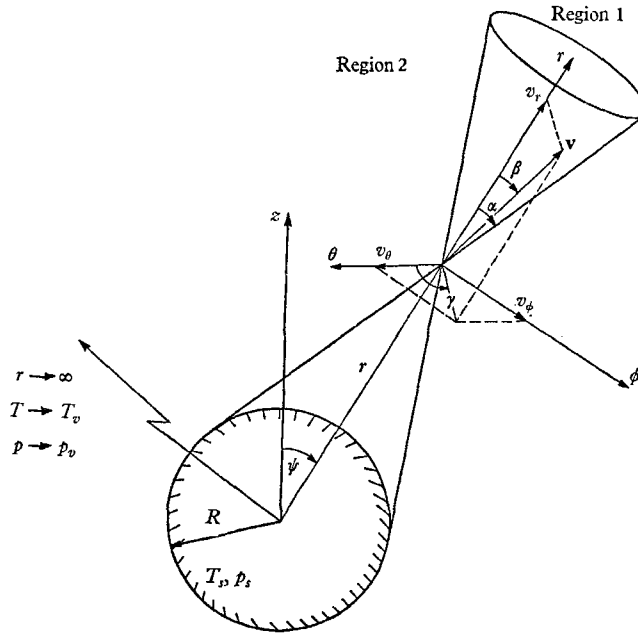


FIGURE 1. The co-ordinate system.

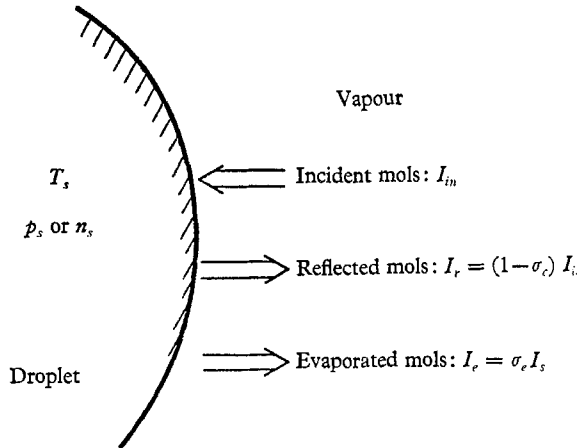


FIGURE 2. Interaction between the vapour and the droplet.

(or number density n_v) of the vapour are known at a distance far from the surface of the droplet ($r \rightarrow \infty$, see figure 1). Condensation or evaporation occurs at the surface of the droplet ($r = R$). The growth of the droplet and the change in the droplet temperature are neglected and the problem is considered to be steady,

This assumption is likely to be reasonable as long as the increase in droplet radius is small compared to R .

In order to define the process completely, the interaction between the vapour and the liquid surface must also be specified. The stream of molecules leaving the surface is composed of two parts; one due to reflexion and one due to evaporation (figure 2). It is assumed that all molecules leave the surface with a Maxwellian distribution corresponding to the temperature T_s (i.e. the thermal-accommodation coefficient is unity) with zero mean velocity. The mass flux due to the reflected molecules is related to the incident stream by the condensation coefficient σ_c , while the mass flux due to evaporation is related to the surface temperature T_s and saturation pressure p_s by the evaporation coefficient σ_e (figure 2).

The vapour is taken to be composed of monatomic molecules obeying Maxwell's inverse-fifth-power law of repulsion. The vapour will also be treated as an ideal gas with the equation of state $p = nkT$. The problem at hand is to determine the mass flux to the surface of the droplet in terms of the parameters T_s , p_s , T_v , n_v , σ_c and σ_e .

Following the suggestion of Lees (1959) the vapour molecules are divided (in velocity space) into two groups (figure 1), each of these being characterized by a Maxwellian distribution function given by

$$f_1 = n_1 \left(\frac{m}{2\pi kT_1} \right)^{\frac{3}{2}} \exp \left(-\frac{m}{2kT_1} \{ (v_r - u_1)^2 + v_\phi^2 + v_\theta^2 \} \right) \quad \text{for } 2\pi - \alpha < \beta < \alpha, \tag{1a}$$

$$f_2 = n_2 \left(\frac{m}{2\pi kT_2} \right)^{\frac{3}{2}} \exp \left(-\frac{m}{2kT_2} \{ (v_r - u_2)^2 + v_\phi^2 + v_\theta^2 \} \right) \quad \text{for } \alpha < \beta < 2\pi - \alpha. \tag{1b}$$

The angles α , β (and also γ , ψ which are to be used later) are shown in figure 1, and v_r , v_ϕ , v_θ are the components of the absolute velocity \mathbf{v} of the molecules. T_1 , T_2 , n_1 , n_2 , u_1 and u_2 are six unknown functions of the radial co-ordinate r , which have yet to be evaluated. Once these functions are known any mean quantity $\langle Q \rangle$ can be calculated from the relation

$$\langle Q \rangle = \int_0^{2\pi} \int_0^\alpha \int_0^\infty Q f_1 v^2 \sin \beta \, dv \, d\beta \, d\gamma + \int_0^{2\pi} \int_\alpha^\pi \int_0^\infty Q f_2 v^2 \sin \beta \, dv \, d\beta \, d\gamma. \tag{2}$$

The six unknowns are determined by taking moments of Maxwell's integral equation of transfer, which, for the assumptions of spherical symmetry and steady-state conditions, is (Lees 1965)

$$\begin{aligned} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \int f Q v_r \, dv \right) - \int \frac{f}{r} \left\{ (v_\phi^2 + v_\theta^2) \frac{\partial Q}{\partial r} - (v_r v_\theta) \frac{\partial Q}{\partial v_\theta} - (v_r v_\phi) \frac{\partial Q}{\partial v_\phi} \right\} dv \\ - \int \frac{f}{r} \cot \psi \left\{ v_\phi^2 \frac{\partial Q}{\partial v_\theta} - v_\theta v_\phi \frac{\partial Q}{\partial v_\phi} \right\} dv = \Delta Q, \end{aligned} \tag{3}$$

where ΔQ represents the collision integral. By setting $Q_1 = m$, $Q_2 = mv_r$, $Q_3 = \frac{1}{2}mv^2$, $Q_4 = \frac{1}{2}mv_r v^2$, $Q_5 = mv_r^2$ and $Q_6 = mv_r^3$, six differential equations are obtained for the six unknowns (see the appendix). Since a closed-form solution

of the equations (A1)–(A6) is not feasible, the problem will be simplified by reducing the six moment equations to four by taking $u_1 = u_2 = 0$. The calculations performed recently by Shankar (1968) for condensation on infinite plane surfaces indicate that the mass flux calculated by the four and six moment equations do not differ significantly. However, in order to verify this conclusion for the spherical geometry and also to test the effects of the additional moments on the details of the flow field (e.g. density distribution) one would have to solve numerically the complete set of six moment equations.

Using Q_1, Q_2, Q_3 and Q_4 , the following dimensionless equations are obtained:

$$\text{mass} \quad \bar{n}_1 \bar{T}_1^{\frac{1}{2}} - \bar{n}_2 \bar{T}_2^{\frac{1}{2}} = -\bar{I}, \tag{4a}$$

$$r\text{-momentum} \quad \frac{d}{d\bar{r}} (\bar{n}_1 \bar{T}_1 + \bar{n}_2 \bar{T}_2) - \cos^3 \alpha \frac{d}{d\bar{r}} (\bar{n}_1 \bar{T}_1 - \bar{n}_2 \bar{T}_2) = 0, \tag{4b}$$

$$\text{energy} \quad \bar{n}_1 \bar{T}_1^{\frac{3}{2}} - \bar{n}_2 \bar{T}_2^{\frac{3}{2}} = C, \tag{4c}$$

$$\begin{aligned} \text{heat flux} \quad & \frac{d}{d\bar{r}} (\bar{n}_1 \bar{T}_1^2 + \bar{n}_2 \bar{T}_2^2) - \cos^3 \alpha \frac{d}{d\bar{r}} (\bar{n}_1 \bar{T}_1^2 - \bar{n}_2 \bar{T}_2^2) \\ & = -\frac{4}{15} \frac{C}{\lambda \bar{r}^2} \{ \bar{n}_1 (1 - \cos \alpha) + \bar{n}_2 (1 + \cos \alpha) \} - \frac{1}{5} \frac{\bar{I}}{\lambda \bar{r}^2} (\cos^3 \alpha - \cos \alpha) (\bar{n}_1 \bar{T}_1 - \bar{n}_2 \bar{T}_2). \end{aligned} \tag{4d}$$

In equations (4a)–(4d) C is an integration constant, λ is the mean free path in the vapour evaluated at $r = \infty$. \bar{I} is the dimensionless mass-transfer rate in the minus r direction

$$\bar{I} = \sqrt{\left(\frac{2\pi}{mkT_v} \right)} \frac{I}{n_v 4\pi R^2}. \tag{5}$$

\bar{n}, \bar{T} and \bar{r} are parameters normalized with respect to n_v, T_v and R . In order to establish the boundary conditions, the expressions for the mean density and mean temperature must be determined. Equations (1) and (2) yield ($u_1 = u_2 = 0$)

$$\langle \bar{n} \rangle = \frac{1}{2} \{ \bar{n}_1 (1 - \cos \alpha) + \bar{n}_2 (1 + \cos \alpha) \}, \tag{6a}$$

$$\langle \bar{T} \rangle = \frac{\bar{n}_1 \bar{T}_1 (1 - \cos \alpha) + \bar{n}_2 \bar{T}_2 (1 + \cos \alpha)}{\bar{n}_1 (1 - \cos \alpha) + \bar{n}_2 (1 + \cos \alpha)}. \tag{6b}$$

Equations (6a) and (6b) show that for $r \rightarrow \infty$ (i.e. $\alpha \rightarrow 0$), $\langle \bar{T} \rangle \rightarrow \bar{T}_2$ and $\langle \bar{n} \rangle \rightarrow \bar{n}_2$. Thus the boundary conditions corresponding to equations (4a)–(4d) are

$$\left. \begin{aligned} \bar{r} \rightarrow \infty: \quad & \langle \bar{T} \rangle = \bar{T}_2 = 1, \quad \langle \bar{n} \rangle = \bar{n}_2 = 1, \\ \bar{r} = 1: \quad & \bar{T}_1 = T_s/T_v; \quad -\bar{I} = \{ (1 - \sigma_c) \bar{I}_{in} + \sigma_e \bar{I}_s \} - \bar{I}_{nv}, \\ & \text{or} \quad \bar{n}_1 \bar{T}_1^{\frac{1}{2}} = (1 - \sigma_c) \bar{n}_2 \bar{T}_2^{\frac{1}{2}} + \sigma_e \bar{n}_s \bar{T}_s^{\frac{1}{2}}. \end{aligned} \right\} \tag{7}$$

Owing to the complexity of the above equations, solutions to them could be found by numerical techniques only. However, for small temperature and pressure differences ($(T_v - T_s)/T_v \ll 1$ and $(p_v - p_s)/p_v \ll 1$) one may approximate \bar{T} and \bar{n} by the expressions

$$\bar{T} = 1 + t \quad \text{and} \quad \bar{n} = 1 + N, \tag{8}$$

gas n_g is taken to be large compared to the number density of the vapour n . This condition implies that the number of collisions between vapour and gas molecules is much larger than between vapour and vapour molecules. It also assumes that the gas does not interact with the droplet surface and thus the interaction between the vapour and the droplet surface is the same as described by equation (7). To define the problem completely, one must give at $r = \infty$ the temperatures of the vapour T_v and the gas T_g , the number density of the vapour n_v and the mean free path of collisions between the vapour and gas molecules $\lambda = \lambda_{vg}$. However, based on the results of the previous section the assumption is made now that the temperatures of both the vapour and the gas remain constant, i.e.

$$T_s = T_g = T_v = T.$$

Then for the isothermal vapour with no mass motion the appropriate distribution functions are

$$f_1 = n_1 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left\{ -\frac{m}{2kT} (v_r^2 + v_\phi^2 + v_\theta^2) \right\} \quad \text{for } 2\pi - \alpha < \beta < \alpha, \quad (13a)$$

$$f_2 = n_2 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left\{ -\frac{m}{2kT} (v_r^2 + v_\phi^2 + v_\theta^2) \right\} \quad \text{for } \alpha < \beta < 2\pi - \alpha. \quad (13b)$$

In this case the only two unknown functions are n_1 and n_2 . Following the analysis of Wasserstrom, Su & Probst (1965) presented for electrostatic probes, we substitute $Q_1 = m$ and $Q_2 = mv_r$ into (3) and arrive at the following moment equations:

$$\text{continuity} \quad -\bar{I} = \left(\frac{2\pi m}{kT_v} \right)^{\frac{1}{2}} \left(\frac{r}{R} \right)^2 \frac{\langle nv_r \rangle}{n_v} = \bar{n}_1 - \bar{n}_2, \quad (14a)$$

$$r \text{ momentum} \quad \frac{d}{d\bar{r}} \{ \bar{n}_1 + \bar{n}_2 - \cos^3 \alpha (\bar{n}_1 - \bar{n}_2) \} + \frac{3}{\bar{r}} \cos \alpha \sin^2 \alpha (\bar{n}_1 - \bar{n}_2) = - \left(\frac{2Rm}{n_v kT} \right) \Delta Q. \quad (14b)$$

Due to the presence of the two separate components the collision integral ΔQ in (14b) is not zero. From Jeans (1954, equation (655))

$$\Delta Q = m_g n_g n \{ K / (m + m_g) \}^{\frac{1}{2}} A_1 (\langle v_{rg} \rangle - \langle v_r \rangle), \quad (15)$$

where A_1 and K are constants, the subscript g refers to the gas and the unsubscripted variables refer to the vapour. To preserve constant pressure, we must have (Jeans, equation (688))

$$n_g \langle v_{rg} \rangle + n \langle v_r \rangle = 0. \quad (16)$$

The diffusion coefficient for an inverse-fifth-power force law is (Jeans, equation (691))

$$D = [kT / \{ m_g m A_1 (n + n_g) \}] \{ (m + m_g) / K \}^{\frac{1}{2}}. \quad (17)$$

For the assumption of $n/n_g \ll 1$, equations (14a) and (15)–(17) yield

$$\Delta Q = - \frac{kT}{2m} \left(\frac{2kT}{\pi m} \right)^{\frac{1}{2}} \frac{1}{D} \sin^2 \alpha (n_1 - n_2). \quad (18)$$

For simplicity we replace the diffusion coefficient with the expression computed for hard-sphere molecules

$$D = \lambda \langle c \rangle / 4, \quad (19)$$

where $\langle c \rangle$ is the mean molecular speed and $\lambda = \lambda_{vy}$. Equations (14*b*), (18) and (19) give the second moment equation

$$\frac{d}{d\bar{r}} \{ (\bar{n}_1 + \bar{n}_2) - \cos^3 \alpha (\bar{n}_1 - \bar{n}_2) \} + \frac{3}{\bar{r}} \cos \alpha \sin^2 \alpha (\bar{n}_1 - \bar{n}_2) = - \frac{2R}{\lambda} \sin^2 \alpha (\bar{n}_1 - \bar{n}_2). \quad (20)$$

The boundary conditions corresponding to (14*a*) and (20) are (see equations (7))

$$\left. \begin{aligned} \bar{r} \rightarrow \infty: \quad \langle \bar{n} \rangle &= \bar{n}_2 = 1, \\ \bar{r} = 1: \quad \bar{n}_1 &= (1 - \sigma_c) \bar{n}_2 + \sigma_e \bar{n}_s. \end{aligned} \right\} \quad (21)$$

The solution of equations (14*a*) and (20) for the above boundary conditions gives the mass flux of the vapour at the droplet surface ($r = R$)

$$-i = \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} \frac{(\sigma_e/\sigma_c) p_s - p_v}{(1/\sigma_c) + (R/\lambda)}. \quad (22)$$

It can be seen that in the free-molecule limit for $\sigma_e = \sigma_c = 1$ equation (22) results in the same mass flux as the analysis described in §2 (equation (11)). In the continuum limit ($\lambda/R \rightarrow 0$), equation (22) becomes ($\sigma_e = \sigma_c$)

$$-i = \frac{m}{kT} \frac{D}{R} (p_s - p_v), \quad (23)$$

which is exactly Maxwell's equation (Fuchs 1959).

The fact that the analyses for both the pure vapour (equation (11)) and the vapour-gas mixture (equation (22)) yield the appropriate free molecule and continuum expressions lends confidence to the results. A more critical evaluation of the results would require a comparison between the theoretical expressions and experimental data. Although numerous experiments have been performed on the condensation or evaporation phenomena for droplets, unfortunately the authors were unable to find data that were reported in sufficient detail so as to allow a meaningful comparison between theory and data.

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Appendix—the six moment equations

The following six equations were obtained by substituting the distribution functions f_1 and f_2 (equations (1*a*), (1*b*)) into Maxwell's integral equation of transfer (equation (3)), by setting $Q = m, mv_r, \frac{1}{2}m\mathbf{v}^2, \frac{1}{2}mv_r\mathbf{v}^2, mv_r^2, mv_r^3$ and by assuming low mean-flow velocities and neglecting terms of order $(m/2kT)^2 u^2$.

$$\frac{d}{dr} \left[\left(\frac{mk}{2\pi} \right)^{\frac{1}{2}} rx^2(A_1 - A_2) + \frac{1}{2}mr^2\{B_1(1 - y^3) + B_2(1 + y^3)\} \right] = 0, \quad (A 1)$$

$$\frac{1}{2}k \left\{ (1 - y^3) \frac{dD_1}{dr} + (1 + y^3) \frac{dD_2}{dr} \right\} + \left(\frac{2mk}{\pi} \right)^{\frac{1}{2}} \left[\left\{ (1 - y^4) \frac{d}{dr} (E_1 - E_2) \right\} + \frac{E_1 - E_2}{r} \{ 2x^2 - (1 - y^4) \} \right] = 0, \quad (A 2)$$

$$\left(\frac{2k^3}{\pi m} \right)^{\frac{1}{2}} x^2 \frac{d}{dr} (F_1 - F_2) + \left(\frac{1}{2}\pi \right)^{\frac{1}{2}} k \left\{ (1 - y^3) \frac{dG_1}{dr} + (1 + y^3) \frac{dG_2}{dr} + \frac{G_1}{r} (2 - 3y + y^3) + \frac{G_2}{r} (2 + 3y - y^3) \right\} = 0, \quad (A 3)$$

$$\begin{aligned} & \left(\frac{1}{2}\pi\right)^{\frac{1}{2}} \frac{k^2}{m} \left\{ \frac{d}{dr} (H_1 + H_2) - y^3 \frac{d}{dr} (H_1 - H_2) \right\} + \left(\frac{18k^3}{\pi m} \right)^{\frac{1}{2}} \left[(1 - y^4) \frac{d}{dr} (K_1 - K_2) \right. \\ & \quad \left. + \frac{K_1 - K_2}{r} \{2x^2 - (1 - y^4)\} \right] = \left\{ \frac{\langle n \rangle}{n_v \lambda} \left(\frac{\pi k T_v}{2m} \right)^{\frac{1}{2}} \right\} \\ & \quad \times \left[- \left(\frac{8k^3}{9\pi m} \right)^{\frac{1}{2}} x^2 (F_1 - F_2) - \frac{5}{8} k \{y^3 (G_2 - G_1) + (G_1 + G_2)\} \right. \\ & \quad \left. + \langle v_r \rangle \left\{ \frac{1}{2} k (y^3 - y) (D_1 - D_2) + \left(\frac{mk}{2\pi} \right)^{\frac{1}{2}} (E_1 - E_2) (2y^4 - 2 + \frac{8}{3} x^2) \right\} \right], \quad (A 4) \end{aligned}$$

$$\begin{aligned} & \frac{3}{2} k \left\{ (1 - y^5) \frac{dG_1}{dr} + (1 + y^5) \frac{dG_2}{dr} \right\} + \left(\frac{2k^3}{\pi m} \right)^{\frac{1}{2}} (1 - y^4) \frac{d}{dr} (F_1 - F_2) \\ & \quad + \frac{k}{2r} \{G_1 (2 - 5y^3 + 3y^5) + G_2 (2 + 5y^3 - 3y^5)\} \\ & = \frac{\langle n \rangle}{n_v \lambda} \left(\frac{\pi k T_v}{2m} \right)^{\frac{1}{2}} \left[\frac{1}{2} k (y^3 - y) (D_1 - D_2) + \left(\frac{2mk}{\pi} \right)^{\frac{1}{2}} \{(E_1 - E_2) (y^4 - 1 + \frac{4}{3} x^2)\} \right], \quad (A 5) \end{aligned}$$

$$\begin{aligned} & \frac{3k^2}{2m} \left\{ (1 - y^5) \frac{dH_1}{dr} + (1 + y^5) \frac{dH_2}{dr} \right\} + \left(\frac{32k^3}{\pi m} \right)^{\frac{1}{2}} \\ & \quad \times \left[(1 - y^6) \frac{d}{dr} (K_1 - K_2) + \frac{K_1 - K_2}{r} \{y^6 - 1 + \frac{3}{2} (1 - y^4)\} \right] = \left\{ \frac{\langle n \rangle}{n_v \lambda} \left(\frac{\pi k T_v}{2m} \right)^{\frac{1}{2}} \right\} \\ & \quad \times \left[-\frac{1}{3} k \langle v_r \rangle \left\{ D_1 (1 - y^3) + D_2 (1 + y^3) + \left(\frac{8mk}{\pi} \right)^{\frac{1}{2}} (E_1 - E_2) (1 - y^4 - 2x^2) \right\} \right. \\ & \quad \left. + \frac{1}{2} mk (y^3 - y^5) (G_1 - G_2) + \left(\frac{2k^3}{9\pi m} \right)^{\frac{1}{2}} (1 - y^4) (F_1 - F_2) \right], \quad (A 6) \end{aligned}$$

where $A_i = n_i T_i^{\frac{1}{2}}$, $B_i = n_i u_i$, $D_i = n_i T_i$, $E_i = n_i u_i T_i^{\frac{1}{2}}$, $F_i = n_i T_i^{\frac{3}{2}}$, $G_i = n_i u_i T_i$, $H_i = n_i T_i^2$, $K_i = n_i u_i T_i^{\frac{3}{2}}$, ($i = 1, 2$), $x = \sin \alpha$, $y = \cos \alpha$, and the symbol $\langle \rangle$ is defined by equation (2).

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