

## Negative thermophoresis of nanoparticles in the free molecular regime

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Negative thermophoresis is a phenomenon of particle transport induced by a temperature gradient, by which small particles migrate from low to high temperatures. In gas media, it depends strongly on the gas-particle interaction and temperature. In this paper, we show that negative thermophoresis is possible in the free molecular regime and a theoretical criterion is derived. On the basis of a general gas-particle interaction potential, an empirical necessary condition for negative thermophoresis that the potential parameters should satisfy is also obtained. Finally, the temperature ranges for the occurrence of negative thermophoresis are determined for a series of gas-particle interaction parameters.

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### I. INTRODUCTION

Thermophoresis in gases is an important transport mechanism of small particles caused by temperature gradients [1]. The force acting on the particles is called the thermophoretic force, which has been widely used for manipulating particles in a variety of areas, including material synthesis, micro- and nanofabrication, and environmental science [2–5]. The direction of the thermophoretic force can be in or against the direction of the temperature gradient, depending on various parameters. Compared with the particle transport in aqueous solutions where the physics of thermophoresis is relatively known [6,7], thermophoresis in gases is far from being well understood, although extensive theoretical and experimental studies have been conducted to understand the nature of thermophoresis [8–11]. The unclear physical picture might be caused by the complexity of solving the Boltzmann transport equations and the difficulty in understanding the atomic interaction between gas molecules and particles.

In gas media, the thermophoretic force, acting on a suspended particle, depends on the flow regime, which is characterized by the Knudsen number  $\text{Kn} = \lambda/L$ , where  $\lambda$  is the mean free path of the gas and  $L$  is the characteristic length of the particle. The theoretical treatment of thermophoresis usually involves solving the Boltzmann equations. This is very difficult in the continuum ( $\text{Kn} \ll 1$ ) and transition ( $\text{Kn} \sim 1$ ) regimes where the velocity distribution of the gas molecules is greatly affected by the motion of the particle. Although a few analytical approaches have been developed based on different approximation methods [12–18], the theories in these two regimes are far from complete. In the free molecular regime ( $\text{Kn} \gg 1$ ), the problem can be greatly simplified by assuming that the presence of the particle does not affect the velocity distribution of gas molecules, and pair collisions of gas molecules dominate. In this case, the Chapman-Enskog gas kinetic theory [19,20] for dilute gases in nonequilibrium states can be used to obtain the thermophoretic force.

In the free molecular regime, it has long been assumed that the thermophoretic force is in the opposite direction of the temperature gradient, i.e., particles move from high to low temperatures, which is called positive thermophoresis. For microparticles, this has been predicted by the Waldmann equation of thermophoretic force on the basis of gas kinetic

theory. Waldmann studied the particle thermophoresis under the assumption of rigid-body collisions, i.e., the gas-particle intermolecular interactions are neglected, which is valid for microparticles, and derived the thermophoretic force  $F_T$  as [8]

$$F_T = -\frac{8}{15} \sqrt{\frac{2\pi m_g}{k_B T}} \kappa R^2 \nabla T, \quad (1)$$

where  $m_g$  is the mass of the gas molecule,  $k_B$  is the Boltzmann constant,  $\kappa$  is the thermal conductivity of the gas,  $R$  is the particle radius, and  $T$  is the temperature. Equation (1) has been confirmed by experiments [5,10,21,22], and the explanation of positive thermophoresis in Eq. (1) is that, for rigid-body collisions, the gas molecules at the hot side carry higher kinetic energy than those at the cold side, and therefore, the momentum transfer at the high temperature is larger than that at the low temperature.

Fundamentally, thermophoresis is similar to thermal diffusion. Although in the literature, thermophoresis has been frequently used as a substitute for thermal diffusion, it is well accepted, especially in gas media, that thermal diffusion is a molecular phenomenon, which describes the collective and statistical behaviors of one component in a mixture under temperature gradients, whereas, thermophoresis describes the kinetic behavior of isolated particles induced by temperature gradients in a fluid [7,23–31]. In gases, Eq. (1) predicts that micro- or larger particles can only move from high to low temperatures (positive thermophoresis). For molecules (particles of molecular size), the Chapman-Enskog theory of thermal diffusion indicates that they can transport from low to high temperatures (negative thermal diffusion) [19,20,24–26]. Therefore, as the particle size decreases from micro- to molecular scale, there exists a critical particle size, below which, negative thermophoresis becomes possible. This critical particle size might be in the nanoscale and is of great importance in practical applications. However, it is not easy to obtain the critical size because it depends on the gas-particle interaction.

In this paper, we derive a theoretical criterion for the negative thermophoresis in the free molecular regime. For practical applications, an empirical necessary condition is developed on the basis of a general gas-particle interaction potential. In addition, the temperature ranges for negative thermophoresis are suggested for a series of potential parameters.

## II. CRITERION FOR NEGATIVE THERMOPHORESIS

As the particle size decreases, the molecular interactions between the gas molecules and the particle can be important, the rigid-body collision assumed by Waldmann becomes questionable, and Eq. (1) may fall apart. By considering the gas-particle intermolecular interaction, we derived the thermophoretic force for nano- and subnanoparticles based on a rigorous gas-kinetic analysis [11],

$$F_T = -\frac{8}{3} \sqrt{\frac{2\pi m_r}{k_B T}} \kappa R^2 \nabla T \left( \frac{6}{5} \Omega^{(1,2)*} - \Omega^{(1,1)*} \right), \quad (2)$$

where  $m_r = m_g m_p / (m_g + m_p)$  is the reduced mass of the gas molecule and particle,  $\Omega^{(1,1)*}$  and  $\Omega^{(1,2)*}$  are the reduced collision integrals, which depend on the temperature  $T$  and gas-particle interaction potential [11,20,23] as discussed later. For rigid-body collisions,  $\Omega^{(1,1)*} = \Omega^{(1,2)*} = 1$ , and Eq. (2) is reduced to Eq. (1), considering that  $m_p \gg m_g$ . Therefore, Eq. (1) is a special case of Eq. (2).

In Eq. (2), it is seen that the direction of the thermophoretic force depends on the value of  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*})$ . In most cases,  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*}) > 0$ , and positive thermophoresis is guaranteed. However,  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*})$  could be negative, depending on the temperature and gas-particle interaction. A general form of  $\Omega^{(1,1)*}$  and  $\Omega^{(1,2)*}$  is given by [11,23]

$$\Omega^{(1,q)*} = \frac{2 \int_0^\infty \gamma^{2q+3} e^{-\gamma^2} Q(g) d\gamma}{(1+q)! \pi R^2}, \quad q = 1, 2, \quad (3)$$

where  $g$  is the relative velocity between the gas molecules and particle,  $\gamma = g \sqrt{m_r / 2k_B T}$ , and  $Q$  is the collision cross section, which depends on how gas molecules are reflected upon collisions with the particle. Specular and diffuse scatterings are the two limiting cases [11,20]. Specular scattering has been reported to be dominant for particles smaller than a few nanometers in diameter [32,33]. For specular scattering,

$$Q_s(g) = 2\pi \int_0^\infty (1 - \cos \chi) b db, \quad (4)$$

where  $b$  is the impact parameter for gas-particle collisions and  $\chi$  is the angle of scattering (see top panel in Fig. 1) given by

$$\chi = \pi - 2b \int_{r_m}^\infty \frac{dr}{r^2 \sqrt{1 - \frac{b^2}{r^2} - \frac{2\Phi(r)}{m_r g^2}}}, \quad (5)$$

where  $r$  and  $\Phi(r)$  are the center-to-center distance and interaction potential between the gas molecules and the particle and  $r_m$  is the distance of the closest encounter.

In Eqs. (3)–(5), it is seen that  $\Omega^{(1,1)*}$  and  $\Omega^{(1,2)*}$  are complex functions of the gas-particle interaction potential  $\Phi(r)$  and temperature  $T$  [34]. Although  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*}) < 0$  represents a criterion for negative thermophoresis, it does not offer a clear picture. To fundamentally understand negative thermophoresis, we scale the temperature  $T$ , relative velocity  $g$ , and collision cross section  $Q$  by proper quantities as  $T^* = k_B T / \varepsilon$ ,  $g^{*2} = m_r g^2 / (2\varepsilon)$ , and  $Q^* = Q / (\pi R^2)$ , where  $\varepsilon$  is the gas-particle binding energy as introduced later. Using these reduced parameters, the reduced collision integrals can be expressed as

$$\Omega^{(1,1)*} = \frac{1}{T^{*3}} \int_0^\infty g^{*5} e^{-g^{*2}/T^*} Q^*(g^*) dg^* \quad \text{and}$$

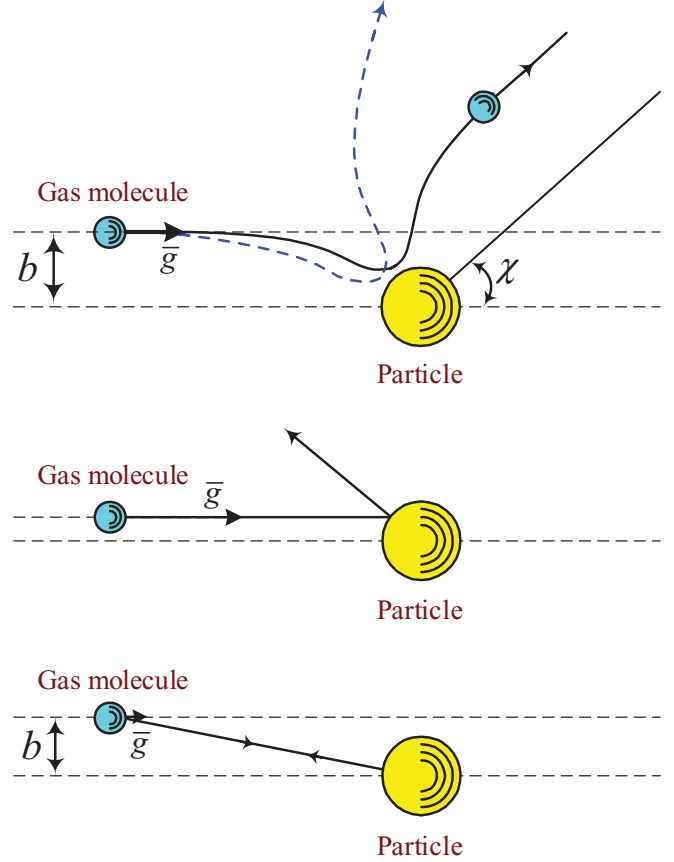


FIG. 1. (Color online) Collision scenarios between a gas molecule and a small particle. Top panel: trajectories of the gas molecule at different temperatures (the dashed line represents the case at a relatively lower temperature).  $b$  is the impact parameter,  $\chi$  is the angle of scattering, and  $\bar{g}$  is the mean relative velocity. Middle panel: a trajectory at very high temperatures where the potential is unimportant for momentum transfer. Bottom panel: a trajectory at very low temperatures where the potential is dominant in determining the trajectory of the molecule.

$$\Omega^{(1,2)*} = \frac{1}{3T^{*4}} \int_0^\infty g^{*7} e^{-g^{*2}/T^*} Q^*(g^*) dg^*. \quad (6)$$

It is easy to find that  $\Omega^{(1,1)*}$  and  $\Omega^{(1,2)*}$  can be related to each other through

$$\frac{\Omega^{(1,2)*}}{\Omega^{(1,1)*}} = 1 + \frac{1}{3} \frac{d \ln \Omega^{(1,1)*}}{d \ln T^*}, \quad (7)$$

by which  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*})$  can be written as

$$\left( \frac{6}{5} \Omega^{(1,2)*} - \Omega^{(1,1)*} \right) = \Omega^{(1,1)*} \left[ \frac{1}{5} + \frac{2}{5} \frac{d \ln \Omega^{(1,1)*}}{d \ln T^*} \right]. \quad (8)$$

Considering that  $\Omega^{(1,1)*} > 0$  [11,20], Eq. (8) suggests that negative thermophoresis requires

$$\Omega^{(1,1)*} = a(T^*)^{-s}, \quad \text{with } s > \frac{1}{2}, \quad (9)$$

where  $a$  is a constant. In Eq. (9),  $-s$  is nothing but the slope of the  $\ln \Omega^{(1,1)*}$  curve as a function of  $\ln T^*$ .

Equation (9) provides an alternative theoretical criterion for negative thermophoresis. Compared with  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*}) < 0$ , Eq. (9) reveals a clearer physical

picture. Fundamentally,  $\Omega^{(1,1)*}$  is strongly related to the momentum transfer of gas molecules during collisions with a particle [20]. For rigid-body interactions,  $\Omega^{(1,1)*} = 1$  and  $s = 0$  for which negative thermophoresis will not occur. However, if the collisions are nonrigid,  $\Omega^{(1,1)*}$  changes with temperature  $T$ . For appropriate  $\Phi(r)$ , Eq. (9) may be satisfied in certain ranges of  $T^*$  because  $s$  basically measures how  $\Omega^{(1,1)*}$  varies with  $T^*$ . Figure 1 illustrates the collisions between a gas molecule and a small particle ( $\bar{g}$  represents the mean relative velocity corresponding to the temperature of the gas). The top panel shows two possible trajectories at different temperatures. At a relatively lower temperature (smaller  $\bar{g}$ , dashed line), the angle of scattering  $\chi$  becomes larger, which leads to a higher momentum transfer, and consequently, the force acting on the cold side of the particle is larger than that on the hot side. However, such a case is only valid in a certain range of temperatures and depends on  $\Phi(r)$ . If the temperature is very high or low, as shown in the middle and bottom panels of Fig. 1, the collisions tend to be rigid, and positive thermophoresis takes place. It is worth mentioning that the velocity of gas molecules follows a certain distribution. For a given temperature, whether negative thermophoresis occurs or not depends on the overall momentum transfer of gas molecules with velocities in a wide range. If the contribution to the momentum transfer from gas molecules experiencing the collision in the top panel of Fig. 1 dominates, negative thermophoresis will occur. At very high or low temperatures, the collision scenario in the middle or bottom panel in Fig. 1 dominates, and negative thermophoresis is not observable. Therefore, Eq. (9) and Fig. 1 suggest that it is possible to have negative thermophoresis if  $\Phi(r)$  and  $T$  are varied.

### III. NECESSARY CONDITION AND TEMPERATURE RANGES FOR NEGATIVE THERMOPHORESIS

As a quick test, we compute the collision integrals by using the simple Lennard-Jones (LJ) 12-6 potential  $\Phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ , where  $\varepsilon$  is the aforementioned binding energy and  $\sigma$  is the collision diameter. Figure 2 shows

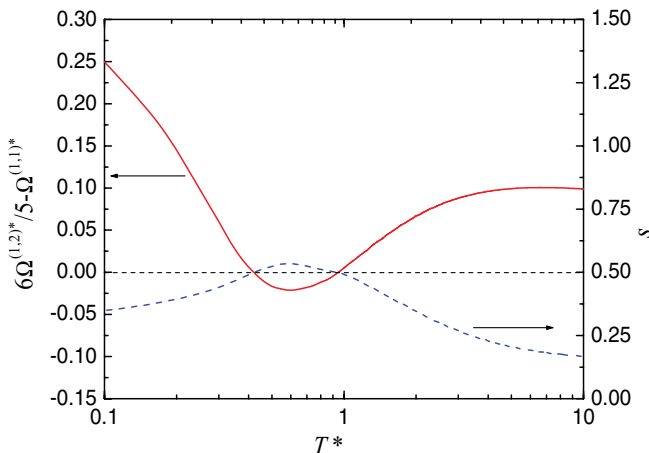


FIG. 2. (Color online) The values of  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*})$  and  $s$  as a function of the reduced temperature  $T^*$  for the LJ potential. For negative thermophoresis,  $(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*}) < 0$  is required, which is equivalent to  $s > 0.5$ .

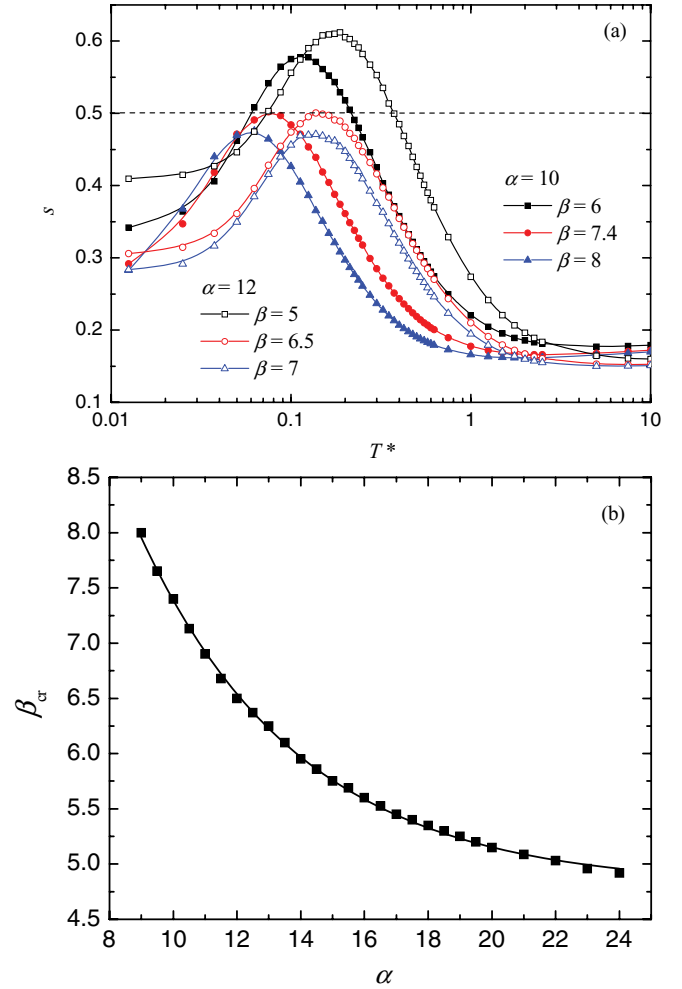


FIG. 3. (Color online) (a)  $s$  versus  $T^*$  for different  $\alpha$  and  $\beta$  values of the LJ  $\alpha - \beta$  potential. (b) The critical value of  $\beta$ ,  $\beta_{cr}$  as a function of  $\alpha$ . The solid line in (b) is the exponential fit for the data.

$(6\Omega^{(1,2)*}/5 - \Omega^{(1,1)*})$  and  $s$  as a function of  $T^*$ . It is seen that negative thermophoresis takes place when the reduced temperature  $T^*$  is roughly in the range of  $0.45 < T^* < 0.95$ , where  $s > 0.5$  as predicted by Eq. (9). The LJ potential used in Fig. 2 is well accepted for describing the van der Waals interaction of gas molecules. It may not be suitable for the interaction between gas molecules and particles. However, the gas-particle interaction can be viewed as the overall effect of the LJ interactions between the gas molecules and each constituent atom of the particle. In this sense, the gas-particle interaction potential will retain a similar shape as the LJ potential. This approach actually has been employed to develop the potentials between gas molecules and various nanomaterials and between graphitic solids [24,35,36]. Hence, the gas-particle interaction can be modeled by a general LJ type potential,

$$\Phi(r) = \varepsilon[c_1(\sigma/r)^\alpha - c_2(\sigma/r)^\beta], \quad (10)$$

where  $c_1$ ,  $c_2$ ,  $\alpha$ , and  $\beta$  are potential parameters. The format of Eq. (10) is consistent with the LJ 12-6 potential as the particle size approaches molecular scale. If  $c_1\varepsilon$  and  $\sigma$  are used to scale  $\Phi(r)$  and  $r$  [note that  $T^* = k_B T / (c_1\varepsilon)$  in this case],

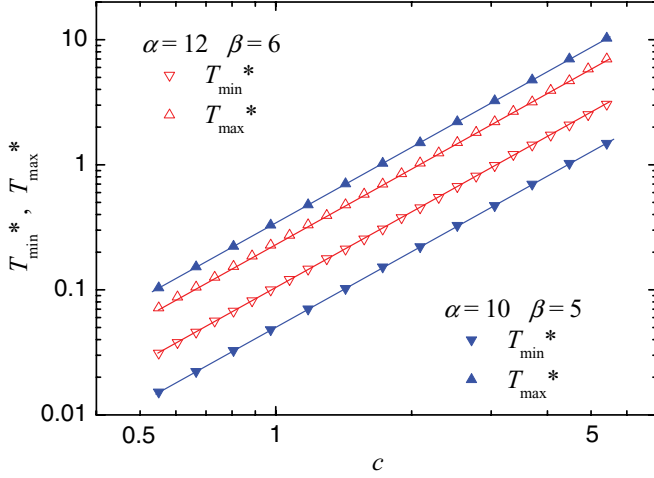


FIG. 4. (Color online) The bounds of the temperature range  $T_{\min}^*$  and  $T_{\max}^*$  as a function of  $c$  for two pairs of  $\alpha$  and  $\beta$  values. Solid lines are linear fits for the data, and their slope is equal to  $\alpha/(\alpha - \beta) = 2$ .

the dimensionless form of the potential is written as

$$\Phi^*(r^*) = (r^*)^{-\alpha} - c(r^*)^{-\beta}, \quad (11)$$

where  $\Phi^* = \Phi/(c_1\varepsilon)$ ,  $r^* = r/\sigma$ , and  $c = c_2/c_1$ . Hereafter, the potential in Eq. (11) will be referred to as the LJ  $\alpha - \beta$  potential.

Using the LJ  $\alpha - \beta$  potential, we calculate the exponent  $s$  in Eq. (9). For  $c = 1$ , the values of  $s$  are depicted in Fig. 3(a). It is seen that negative thermophoresis does depend on the potential parameters. For a given  $\alpha$ , there exists a critical value of  $\beta$ ,  $\beta_{\text{cr}}$ , below which, negative thermophoresis becomes possible and takes place in a range of temperatures. The term involving  $\beta$  in Eq. (11) corresponds to the attractive interaction, which is dominant for  $r^* \gg 1$  (usually  $\alpha > \beta$ ). As  $\beta$  is increased, the attractive interaction weakens, and the potential approaches the rigid-body collision for which, negative thermophoresis is not observable as predicted by Eq. (1). It is noted that  $\beta_{\text{cr}}$  is independent of  $c$ . This is because the potential  $\Phi(r)$  in Eq. (10) can be reduced to a  $c$ -independent format  $\Phi^*(r^*) = (r^*)^{-\alpha} - (r^*)^{-\beta}$  if  $\Phi(r)$  and  $r$  are scaled by  $\varepsilon c_1 c^{\alpha/(\alpha-\beta)}$  and  $\sigma c^{1/(\beta-\alpha)}$ , respectively. In Fig. 3(b),  $\beta_{\text{cr}}$  is plotted as a function of  $\alpha$ , which suggests a necessary condition for the occurrence of negative thermophoresis,

$$\beta < 4.8 + 18.8 \exp(-\alpha/5.05), \quad \alpha \in (9, 24). \quad (12)$$

If Eq. (12) is satisfied, negative thermophoresis is expected to occur in a certain temperature range ( $T_{\min}^*$ ,  $T_{\max}^*$ ). Figure 4 depicts the bounds of the temperature range  $T_{\min}^*$  and  $T_{\max}^*$  for different  $\alpha$  and  $\beta$  values as a function of  $c$ . It is found that the temperature bounds are linearly related to  $c$  in the logarithmic

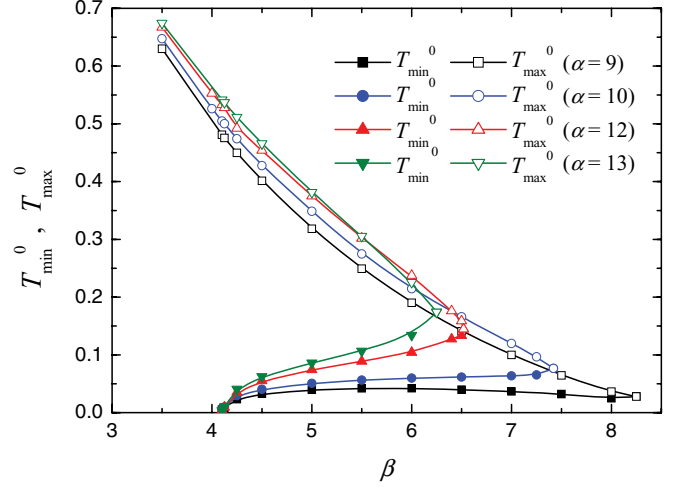


FIG. 5. (Color online)  $T_{\min}^0$  and  $T_{\max}^0$  as a function of  $\beta$  for different  $\alpha$  values. Solid lines are guides to the eye.

plot, and extensive investigations show that  $T_{\min}^*$  and  $T_{\max}^*$  can be expressed as

$$T_{\min(\max)}^* = T_{\min(\max)}^0 c^{\alpha/(\alpha-\beta)}. \quad (13)$$

Therefore, the temperature range for negative thermophoresis can be determined using Eq. (13) if the coefficients  $T_{\min}^0$  and  $T_{\max}^0$  are known. Due to the complexity of the intermolecular interaction, it is not easy to find simple expressions for  $T_{\min}^0$  and  $T_{\max}^0$ . By varying the values of  $\alpha$  and  $\beta$  under the condition of Eq. (12), we obtain  $T_{\min}^0$  and  $T_{\max}^0$ . Figure 5 illustrates their values as a function of  $\beta$  for several values of  $\alpha$ . With the help of Fig. 5, for a given gas-particle interaction, whether negative thermophoresis will occur or not can be predicted using Eqs. (12) and (13).

#### IV. CONCLUSIONS

To summarize, we have studied the negative thermophoresis of small particles in dilute gases. Based on the previous theoretical analysis, a criterion for negative thermophoresis is proposed. By using a general format of the gas-particle interaction potential, an empirical necessary condition for the occurrence of negative thermophoresis is developed. Finally, the temperature ranges for negative thermophoresis are suggested for a series of potential parameters.

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