



ROLE OF THERMOPHORESIS ON BINARY PHASE CHANGE MATERIALS FOR THERMAL ENERGY STORAGE

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ABSTRACT

Binary phase-change materials (PCM) used for thermal energy storage, with two phase transition temperatures or with solid nanoparticles, hold promise for improving transient performance as compared to single component materials. In these systems, small solid particles in the liquid phase are subject to thermal gradients during heat transmission. As a result, there is potential for particle migration due to thermophoresis. The impact of concentration gradient, temperature gradient, radius of nano particles and the solvent is analyzed. A mathematical model showed that thermophoresis will dominate the particle migration and there is a possibility of the development of non-uniformity in the dispersed particle in the system.

KEY WORDS: Energy Storage, Thermodynamics, Heat Transfer, Phase Change Material, Nanoparticles, Microfluidics, Thermophoresis

1. INTRODUCTION

Binary Phase Change Materials (PCM), with two phase transition temperatures or with solid nanoparticles, hold promise for improving the transient performance as compared to a single component PCM [1–7]. In these binary systems dispersed small solid particles in the liquid phase are subjected to thermal gradients during heat transmission. However, when the nano-particles are dispersed in a liquid, they might migrate under the influence of temperature gradient. This process of diffusion of particles due to temperature gradient is known as thermophoresis [8–10]. After multiple cycles of charging/discharging, a concentration gradient of the dispersed particle might develop that could negate the intended enhancement of the transient performance [11–14]. Nanoparticle migration due to thermophoresis can be nullified by the counter acting Brownian diffusion, that tends towards the uniform particle distribution. This paper examines the potential for thermophoresis to generate concentration gradients of nanoparticle in the binary PCM system. The parameters included for the analysis are: concentration gradient, radius of the particle, solvent and temperature gradient.

1.1 Summary for Performance Enhancement in PCMs

PCM has high thermal energy storage density and it is expected to utilize the entire volume of available PCM in the system. When the nanoparticles are dispersed in PCM, the enhancement is limited by the amount of loading, convection contribution migration of particles and non-uniform distribution of particles in the system. The available literature is unable to accurately predicts the performance of PCM with nanoparticles. The heat transfer performance of PCM in such system is dependent on fluid-particle interaction and not much evidence to support the mechanism is available. The development in the field of PCM with nanoparticles faces certain

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challenges like insufficient thermal conductivity enhancement, lack of agreement between experimental results, lack of a convincing theory that supports the mechanism, inhomogeneity in suspension, migration of particles, sedimentation etc. The results that support the thermal performance enhancement using nanoparticles are done by Khushnood [5], Zhang and Zhang [15], Zhou [16], Gao [17], Gurunathan [18] while there are several analysis performed by Buongiorno [9], Ho and Gao [19], Khaled and Vafai [20], Kuznetsov and Nield [21] that disagree with the performance enhancement either due to lack of convection mechanism or the lack of influence of Brownian diffusion or inconsequential Rayleigh number.

2. THERMOPHORESIS AND FACTORS AFFECTING IT

The diffusion of mass takes places under the action of concentration gradient and it is commonly known as ‘‘Fick’s Diffusion’’ or ‘‘Diffusion’’. But when suspended particles in a fluid are subjected to temperature gradient, then the diffusion of dispersed particle under the action of the temperature gradient is known as ‘‘Thermal Diffusion’’ or ‘‘Thermophoresis’’. This effect gives rise to the drift velocity given by equation 1 [14]

$$V_T = -D_T \frac{dT}{dx} \quad (1)$$

D_T is thermodiffusion coefficient and $\frac{dT}{dx}$ is the temperature gradient.

Since the diffusion can take place due to the presence of thermal gradient, so the diffusion flux J_p is dependent on two terms, the particle diffusion and thermodiffusion as given by [13]

$$J_p = -D_B \frac{dc}{dx} - cD_T \frac{dT}{dx} = J_{p,c} + J_{p,T} \quad (2)$$

D_B is Brownian diffusion coefficient, $J_{p,c}$ and $J_{p,T}$ are the diffusion flux due to concentration and temperature gradient respectively. As discussed above that the ratio of thermal diffusion to Brownian diffusion gives the Soret coefficient. It is the measure of the dominant mode of diffusion, a value of $S_T > 1$ suggests that thermal diffusion is dominant while $S_T < 1$ means Brownian diffusion is more proactive. The particle diffusion under the action of temperature gradient attains a thermophoretic velocity and corresponding mass flux given by equation 3, 4 and 5 [8] [9]

$$\text{thermophoretic velocity } V_T = -\beta \frac{\mu_m}{\rho_m} \frac{1}{T} \frac{dT}{dx}, \quad (3)$$

$$\beta = 0.26 \frac{K_m}{2K_m + K_p} \quad (4)$$

$$\text{thermophoretic mass flux } J_{p,T} = -cV_T \quad (5)$$

The relative strength of Brownian diffusion to the thermal diffusion is evaluated when the particle mass flux J_p is zero then the concentration gradient along z-axis is given by [12]

$$\frac{1}{c} \frac{dc}{dz} = -\frac{D_T}{D_B} \frac{dT}{dz} \quad \text{where } S_T = \frac{D_T}{D_B} \quad (6)$$

Soret coefficient S_T is the ratio between the thermophoretic mobility and the Brownian diffusion coefficient, with the dimensions of K^{-1} . Equating equation 6, 3 and 4, we get

$$\text{thermal diffusion coefficient } D_T = \frac{\beta}{\rho_m} \frac{\mu_m}{T} \quad (7)$$

and by Einstein-Stokes's equation [9]

$$\text{Brownian diffusion coefficient } D_B = \frac{k_B T}{3\pi\mu_f d_p} \quad (8)$$

Experiments suggests thermal diffusion coefficient varies between $1 * 10^{-8} < D_T < 1 * 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1}$ [22]. From the above equations 7 and 8

$$S_T = \frac{3\pi\mu_m\mu_f d_p \beta}{\rho_m k_B T^2} \quad (9)$$

d_p is particle diameter, μ_f is the viscosity of the base fluid, μ_m is the viscosity of the nanofluid, ρ_m and ρ_p are the density of nanofluid and particle respectively, K_m and K_p are the thermal conductivity of nanofluid and particle respectively, c is concentration of particles, k_B is Boltzmann constant.

A non-dimensional form of Soret Coefficient is known as "thermal diffusion factor", α .

$$\alpha = T S_T = - \left(\frac{\frac{1}{c} \frac{\partial c}{\partial x}}{\frac{1}{T} \frac{\partial T}{\partial x}} \right)_{J_p=0} \quad (10)$$

When $\alpha < 1$, then Brownian diffusion prevents the development of concentration gradient to build up. When $\alpha > 1$ then the concentration gradient might develop to generate the migration of nano particles.

In order to understand the conditions that favor either thermal or Brownian diffusion, certain numerical models were tested. The particles of 1 nm, 5 nm and 10 nm radius of Alumina are dispersed in three different fluids: Water, Acrylic Acid and Ethylene Glycol. This system is then subjected to two conditions, either temperature gradient or concentration gradient. The results predicted by the models are discussed in this section.

The relation between the densities, viscosity and thermal conductivity of the base fluid, nano fluid and particles are given by Cho [23]

$$K_m = K_f(1 + 7.47\varphi) \quad , \quad (\text{for alumina nanoparticles}) \quad (11)$$

$$K_m = K_f(1 + 2.92\varphi - 11.99\varphi^2) \quad , \quad (\text{for titania nanoparticles}) \quad (12)$$

$$\mu_m = \mu_f(1 + 39.11\varphi + 533.9\varphi^2) \quad , \quad (\text{for alumina nanoparticles}) \quad (13)$$

$$\mu_m = \mu_f(1 + 5.45\varphi + 108.2\varphi^2) \quad , \quad (\text{for titania nanoparticles}) \quad (14)$$

$$\rho_m = \rho_p\varphi + (1 - \varphi)\rho_f \quad (15)$$

K_f is the thermal conductivity of base fluid, μ_f is the viscosity of base fluid and ρ_f is the density of the base fluid.

Since thermal conductivity, viscosity and density of the base fluids are the functions of temperature then we have to incorporate its effect in the model. The property dependence of base fluid on temperature is shown in table 1. Thermal conductivity and density of the nanoparticle, alumina is our case, is considered constant.

$$K_p = 40 \text{ W/m} - K \quad , \quad \rho_p = 3950 \text{ kg/m}^3 \quad (16)$$

It can be seen from figures 1 and 2 that as the mass concentration of the particle increases, α increases, which means thermal diffusion becomes more dominant at higher concentration. In the case of Ethylene glycol figure 2, thermal diffusion is 5-8 orders of magnitude higher than Brownian diffusion. However, if we look in figure 1 then the thermal diffusion factor for low concentration (less than 5 %) is about a magnitude of order higher than Brownian diffusion.

One more thing to notice here is that as radius of particle increases thermal diffusion tends to become more dominant. It can be seen in figure 1 a, that for a particle radius of 1 nm, thermal diffusion for lower concentration is about an order of magnitude higher than Brownian diffusion. When the radius increases to 10 nm, it is 2 orders of magnitude higher than Brownian diffusion. It can also be interpreted from figures 1 and 2 that the

Table 1 Thermal properties of the base fluid [24, 25]

| Compound | Density, g/mL $AB^{-\left(1-\frac{T}{T_c}\right)^n}$ | Viscosity, cP, $\log_{10} \mu =$ $A + \frac{B}{T} + CT + DT^2$ | Thermal Conductivity, K_f (W/m-K), for organic compound $\log_{10} K =$ $A + B \left(1 - \frac{T}{C}\right)^{\frac{2}{7}}$, for inorganic $K = A + BT + CT^2$ | Melting Temperature, K |
|-----------------|---|--|--|---------------------------|
| Water | A= .34710, B= .274, n = .28571 and $T_c = 647.13$ | $A = -10.2158, B = 1.7925 * 10^3, C = 1.773 * 10^{-2}, D = -1.2631 * 10^{-5}$ | $A = -.2758, B = 4.6120 * 10^{-3}, C = -5.5391 * 10^{-6}$ | 273.16 |
| Acrylic Acid | A= .34645, B= .25822, n = .30701 and $T_c = 615$ | $A = -15.9215, B = 2.4408 * 10^3, C = 3.4383 * 10^{-2}, D = -2.7677 * 10^{-5}$ | $A = -1.6101, B = .9742, C = 615$ | 286.65 |
| Ethylene Glycol | A= .32503, B= .25499, n = .172 and $T_c = 645$ | $A = -16.97, B = 3.1886 * 10^3, C = 3.2537 * 10^{-2}, D = -2.448 * 10^{-5}$ | $A = -.5918, B = 0, C = 645$ | 260.15 |

fluid plays an important role in deciding the strength of the diffusive force. In case of ethylene glycol, thermal diffusion is more effective comparable to water and acrylic acid. Thus, nanoparticles dispersed in ethylene glycol are expected to have higher thermophoretic velocity and the migration is more prominent.

It can also be established from figure 3 that as the temperature increases, Brownian diffusion starts to become dominant. It can be seen in figure 3 that at 10 % volume fraction of nano particles at the melting point for acrylic acid (286.65K), thermal diffusion is about 2 order of magnitude higher than Brownian diffusion, while at 360 K it reduces to less than an order magnitude. If we decrease the volume fraction from 10 % to 1 %, the Brownian diffusion balances the thermal diffusion at 360 K as shown in figure 4.

3. DISCUSSION AND CONCLUSION

Nanoparticles are dispersed in the PCM to expectedly increase its thermal conductivity. When a temperature gradient is applied to this system then the particles can migrate due to thermophoresis. A non-dimensional factor, thermal diffusion factor is used to quantify the relative strength of thermal diffuse to Brownian diffusion. If this factor is greater than 1, then the particles are expected to migrate and develop a concentration gradient in the system. Alumina nanoparticles of size 1 nm, 5 nm and 10 nm were used and they were dispersed in water, acrylic acid and ethylene glycol. A mathematical model was developed to analyze the impact of concentration gradient, temperature gradient, radius of the particle and the solvent on thermal migration of particles. It is found that suspended nanoparticles migration is more prominent when the concentration is high and the radius of particle is large. As the concentration or the radius of particle decreases, tendency of particle to migrate due to thermophoresis also decreases. It was also seen that ethylene glycol has the highest tendency to support thermophoresis. It was also established that thermophoresis is more dominant near the melting point of the base fluid, when the temperature of the fluid is increased, the Brownian diffusion starts to dominate. Thus, it can be concluded that for the parameters analyzed in the model, thermophoresis is going

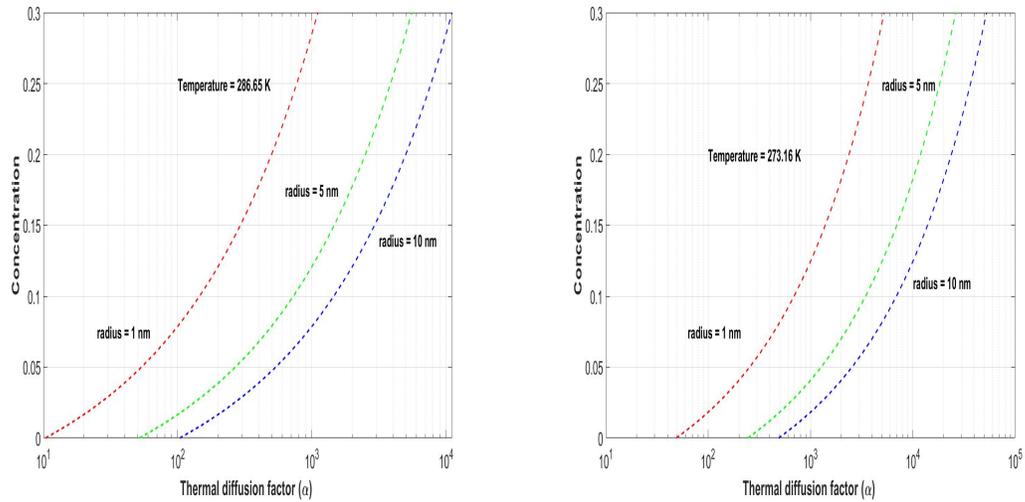


Fig. 1 Effect of Concentration on Thermal Diffusion Factor (a) Acrylic Acid and (b) Water

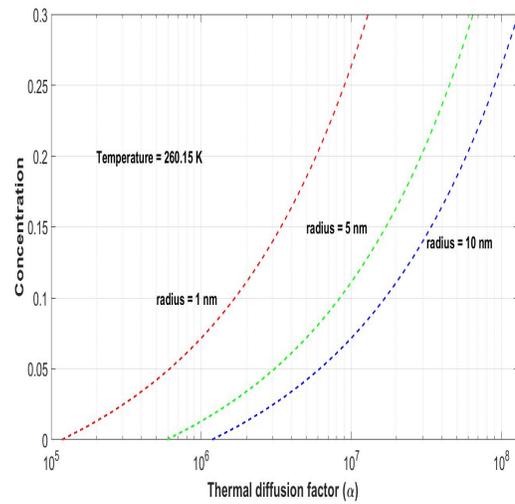


Fig. 2 Effect of Concentration on Soret Coefficient on Ethylene Glycol

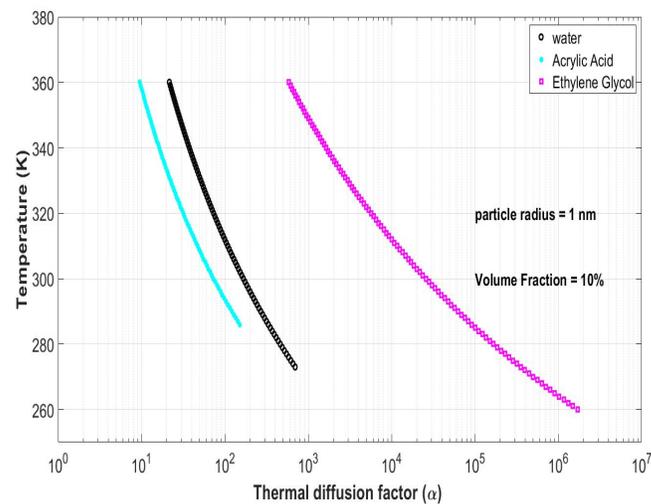


Fig. 3 Effect of temperature on Thermal Diffusion Factor, 10 % Volume Fraction

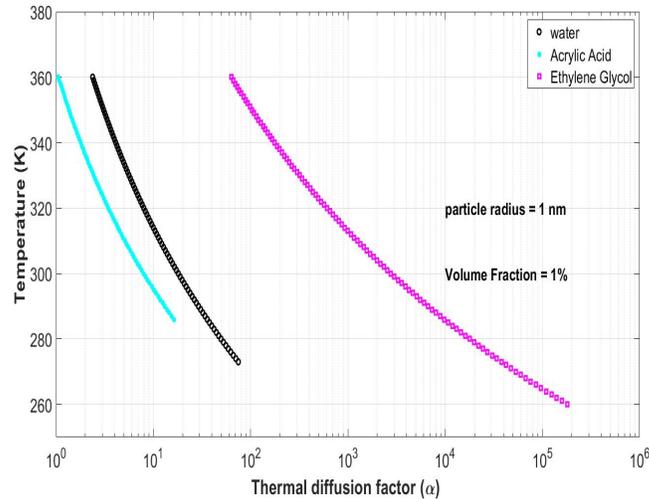


Fig. 4 Effect of temperature on Thermal Diffusion Factor, 1% Volume Fraction

to dominate and the particles are expected to migrate. This would result in the development of concentration gradient in the system and the non-uniformity of the dispersed particles.

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NOMENCLATURE

| | | | | | |
|-----------|---|-------------------------|-----------|--------------------------------|---------------------------------------|
| α | thermal diffusion factor | (-) | K_m | nanofluid thermal conductivity | (W/m-K) |
| β | non-dimensional nanofluid thermal conductivity | (-) | K_p | particle thermal conductivity | (W/m-K) |
| c | concentration | (kg/m ³) | k_B | Boltzmann Constant | (m ² kg/s ² -K) |
| D_B | Brownian diffusion coefficient | (m ² /s) | m | subscript for nanofluid | (-) |
| d_p | particle diameter | (m) | μ_m | viscosity of nanofluid | (N-s/m ²) |
| D_T | thermodiffusion coefficient | (m ² /s-K) | μ_f | viscosity of base fluid | (N-s/m ²) |
| f | subscript for base fluid | (-) | p | subscript for particle | (-) |
| J_p | mass diffusive flux | (kg-m ⁻² /s) | φ | volume fraction of particles | (kg/m ³) |
| $J_{p,c}$ | mass diffusive flux due to concentration gradient | (kg-m ⁻² /s) | ρ_f | density of base fluid | (kg/m ³) |
| $J_{p,T}$ | mass diffusive flux due to temperature gradient | (kg-m ⁻² /s) | ρ_m | density of nano fluid | (kg/m ³) |
| K_f | base fluid thermal conductivity | (W/m-K) | ρ_p | density of nanoparticle | (kg/m ³) |
| | | | S_T | Soret Coefficient | (K ⁻¹) |
| | | | T | temperature | (K) |
| | | | T_m | melting temperature | (K) |
| | | | V_T | drift velocity | (m/s) |

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