



MODELLING THERMOPHORESIS IN NANOFUIDS

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ABSTRACT

Nanoparticles are being used in fluids to enhance the thermal conductivity, but published results are inconsistent. A possible explanation for this inconsistency is that nanoparticles may migrate under the action of temperature gradient counteracting Brownian diffusion. This work focuses on looking at the potential for particle migration due to thermophoresis.

KEY WORDS: Thermophoresis, Nanoparticle, particle migration, Thermal Diffusion, Soret Effect, Diffusion, Nanofluids, Brownian diffusion

1. INTRODUCTION

The low thermal conductivity of traditional heat transfer fluid like water, oil and ethylene glycol reduces the effectiveness and the compactness of a heat exchanger. Nanometer size particles are added to the base fluid to enhance the overall thermal conductivity of the fluid. This increased heat transfer helps in lowering the maximum temperature of the system as well as reducing the size of the heat exchangers. This combination of base fluid and highly conductive nanoparticles is known as nanofluids and several studies have been carried out to examine the thermal conductivity of these nanofluids. However, there are discrepancies among the results published. This is due to the lack of a formidable model that can underline the physics involved with this enhancement [1–4]. Evans et al. [5] shows that the enhancement in the thermal conductivity of the nanofluid can be predicted by effective medium theory and there is no effect of Brownian diffusion. While Choi [2] claimed Brownian motion governs the thermal behavior of the nanofluid. Eastman [6] discussed the idea of ballistic transport to be the reason for thermal conductivity enhancement instead of diffusive transport. J. A. Eastman and Koblinski [7] stated particle size, particle agglomeration, particle-fluid interface and temperature as four major contributors to thermal transport in nanofluids. Thermophysical properties like viscosity can also play a significant role in the heat transfer enhancement [8, 9]. The enhancement in thermal conductivity is experimentally observed to be temperature dependent, Gao [10] showed that thermal conductivity was higher at higher temperature for the nanofluid made from n-Octadecane and Alumina. Ho and Gao [11] reported a lower heater enhancement with the increased nanoparticle mass fraction due to reduced convection. [12–15] claim that the Brownian motion plays the dominant role in thermal conductivity enhancement, while other claims that Brownian motion only affects the nanoparticles but not the heat transfer.

When particles are added to the base fluid, they move around by virtue of Brownian motion. Brownian diffusion is responsible for keeping the uniform concentration within the system, and continuously negates the formation of concentration gradient. But, when this nanofluid is exposed to the temperature gradient across the boundaries, there is diffusion due this temperature gradient. This diffusion is known as thermophoresis. This thermophoretic behavior tends to move the particles towards the cold end of the system while the Brownian diffusion tries to fight against this build up of concentration gradient. The dominant mode of diffusion will either result in uniform distribution of particle or non-uniform distribution with potential for particles to migrate towards the cold side. The analysis of the dominant mode is identified using a thermal diffusion factor.

The discrepancy between the experimental results in the thermal conductivity enhancement of the base fluid

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might be due to this migration of particles.

2. MODELLING AND FORMULATION OF THERMOPHORESIS

Heat transfer and nanoparticle transport are thermodynamically coupled.

$$\text{heat flux } J_q = L_{qq} \left(\frac{d}{dx} \frac{1}{T} \right) + L_{q\mu} \left(\frac{-1}{T} \frac{d\mu_T}{dx} \right) \quad (1)$$

$$\text{particle flux } J_p = L_{\mu q} \left(\frac{d}{dx} \frac{1}{T} \right) + L_{\mu\mu} \left(\frac{-1}{T} \frac{d\mu_T}{dx} \right) \quad (2)$$

The transport forces are thermal (T) and chemical (μ_T), The L-coefficients are known as Onsager coefficients [16–19]. Mechanisms such as sedimentation or buoyancy are not considered here. This could potentially open the gate for microgravity or space applications of nanoparticle enhanced PCMs.

Particle flux can be expressed in terms of gradients in temperature and concentration.

$$J_p = -\frac{L_{\mu q}}{T^2} \left(\frac{dT}{dx} \right) - \frac{L_{\mu\mu}}{T} \frac{\mu_T}{c} \left(\frac{dc}{dx} \right) \quad (3)$$

The total particle flux is given by

$$J_p = -cD_T \frac{dT}{dx} - D_B \frac{dc}{dx} = J_{p,c} + J_{p,T} \quad (4)$$

where D_B is Brownian diffusion coefficient, D_T is thermal mobility coefficient, c is concentration of particles, $J_{p,c}$ and $J_{p,T}$ are the diffusion flux due to concentration and temperature gradients, respectively. Comparing equations 3 and 4:

$$D_T = \frac{L_{\mu q}}{T^2 c} \quad - \text{ and } - \quad D_B = \frac{L_{\mu\mu}}{T} \frac{\mu_T}{c} \quad (5)$$

The relative strength of Brownian diffusion to thermal mobility is evaluated at net zero mass flux.

$$\text{at } J_p = 0 \quad , \quad \frac{1}{c} \frac{dc}{dx} = -\frac{D_T}{D_B} \frac{dT}{dx} \quad (6)$$

The Soret coefficient S_T is the ratio of thermal mobility coefficient to Brownian diffusion, $S_T = D_T/D_B$. Using Einstein-Stokes and thermal diffusion equations [20, 21], the relative effect of the thermal mobility to the Brownian diffusion can be written in the non-dimensional form as the thermal diffusion factor, which is the Soret coefficient scaled with temperature, TS_T .

$$D_T = \frac{\beta}{\rho_{nf}} \frac{\mu_{nf}}{T}; \quad D_B = \frac{k_B T}{3\pi\mu_f d_p} \quad (7)$$

$$TS_T = - \left(\frac{\frac{1}{c} \frac{\partial c}{\partial x}}{\frac{1}{T} \frac{\partial T}{\partial x}} \right)_{J_p=0} = \frac{3\pi\mu_{nf}\mu_f d_p \beta}{\rho_{nf} k_B T} \quad (8)$$

d_p is particle diameter, μ_f is the viscosity of the base fluid, ρ_p and ρ_{nf} are the density of particle and nanofluid, and k_B is Boltzmann constant. Nanofluid is the nanoparticles dispersed in base-fluid.

When $TS_T < 1$, Brownian diffusion prevents the development of a nanoparticle concentration gradient . When $TS_T > 1$, then a nanoparticle concentration gradient might develop due to thermophoresis.

We can not assume the thermal conductivity or density of the fluid to be constant over the applicable range of temperature. So it is necessary to provide these properties as a function of temperature and it is shown in table 1.

Table 1 Temperature dependent material properties [22–25]

	Ethylene Glycol	Water	Acrylic Acid	Formic Acid	Caprylic Acid	Acetic Acid	Paraffin
Density, [g/mL], $AB^{-(1-T/T_c)^n}$							
A	0.32503	0.34710	0.34645	0.36821	0.29231	0.35182	0.23837
B	0.25499	0.27400	0.25822	0.24296	0.26676	0.26954	0.25763
n	0.172	0.28571	0.30701	0.23663	0.28020	0.26843	0.274
T_c , K	645	647.13	615	580	692	592.71	745.26
Viscosity, [cP], $\log_{10} \mu = A + B/T + CT + DT^2$							
A	-16.9728	-10.2158	-15.9215	-4.2125	-10.4823	3.8937	-8.5505
$B \cdot 10^3$	3.1886	1.7925	2.4408	0.97953	2.067	.784	1.6708
$C \cdot 10^{-2}$	3.2537	1.7730	3.4383	0.552	1.8423	0.6665	1.5675
$D \cdot 10^{-5}$	-2.448	-1.2631	-2.7677	-0.57723	-1.3722	-0.75606	-1.2341
Thermal Conductivity [W/m-K]							
organic compound: $\log_{10} K = A + B \left(1 - \frac{T}{C}\right)^{2/7}$							
inorganic compound: $K = A + BT + CT^2$							
A	-0.5918	0.2758	-1.6101	-0.8626	-1.6624	-1.2836	-1.5198
B	-	4.61E-03	0.9742	0.3692	0.9819	0.5893	0.8067
C	645	-5.5391E-06	615	580	692	592.71	745.26
Specific Heat [J/mol-K], $C_p = A + BT + CT^2 + DT^3$							
A	75.878	92.053	-18.242	-16.110	70.790	-18.944	151.154
B	6.4182E-01	-3.9953E-02	1.2106	8.7229E-01	1.7647	1.0971	2.7878
$C \cdot 10^{-3}$	-1.6493	-0.21103	-3.1160	-2.3665	-4.1521	-2.8921	-6.1542
$D \cdot 10^{-6}$	1.6937	0.53469	3.1409	-2.4454	3.9451	2.9275	5.5249

Table 2 Properties of Nanoparticles [22, 25]

	Density ρ_p [kg/m ³]	Thermal Conductivity k_p [W/m-K]
Alumina	3950	50
Copper	8960	402
Gold	19300	317.422
Silver	10500	428.227
Titania	4000	11.7

3. RESULTS AND DISCUSSIONS

Five particle materials were included in this study: gold, alumina, titania, copper and silver. The density and thermal conductivity for these particles are listed in Table 2. These properties are considered constant as the variation in density and thermal conductivity at the applicable temperature is insignificant.

Six types of PCMs were studied. These were modeled only in the liquid phase without solidification. The base fluids are acetic acid, acrylic acid, caprylic acid, ethylene glycol, formic acid and water. Nanoparticles of the five materials listed earlier were paired with these fluids with varying particle size and volume fraction. The potential for particles to migrate or remain uniformly distributed depends on the size of nanoparticles, volume fraction, particle type, fluid, and operating temperature range.

3.1 Impact of Particle Size and Temperature

Variations in thermal diffusion factor with temperature for copper particles of diameter 2, 5 and 20 nm at 5% volume fraction in all six fluids are shown in Fig 1. There is potential for more uniformly distributed particles at 2 nm as compared to 20 nm. This observation aligns with the results reported by Lüsebrink and Ripoll [26]. The TSt curves shift to large values as particle size increases indicating Brownian diffusion is dominant relative to thermophoresis. Nevertheless, caprylic acid and ethylene glycol always have some potential for particle migration.

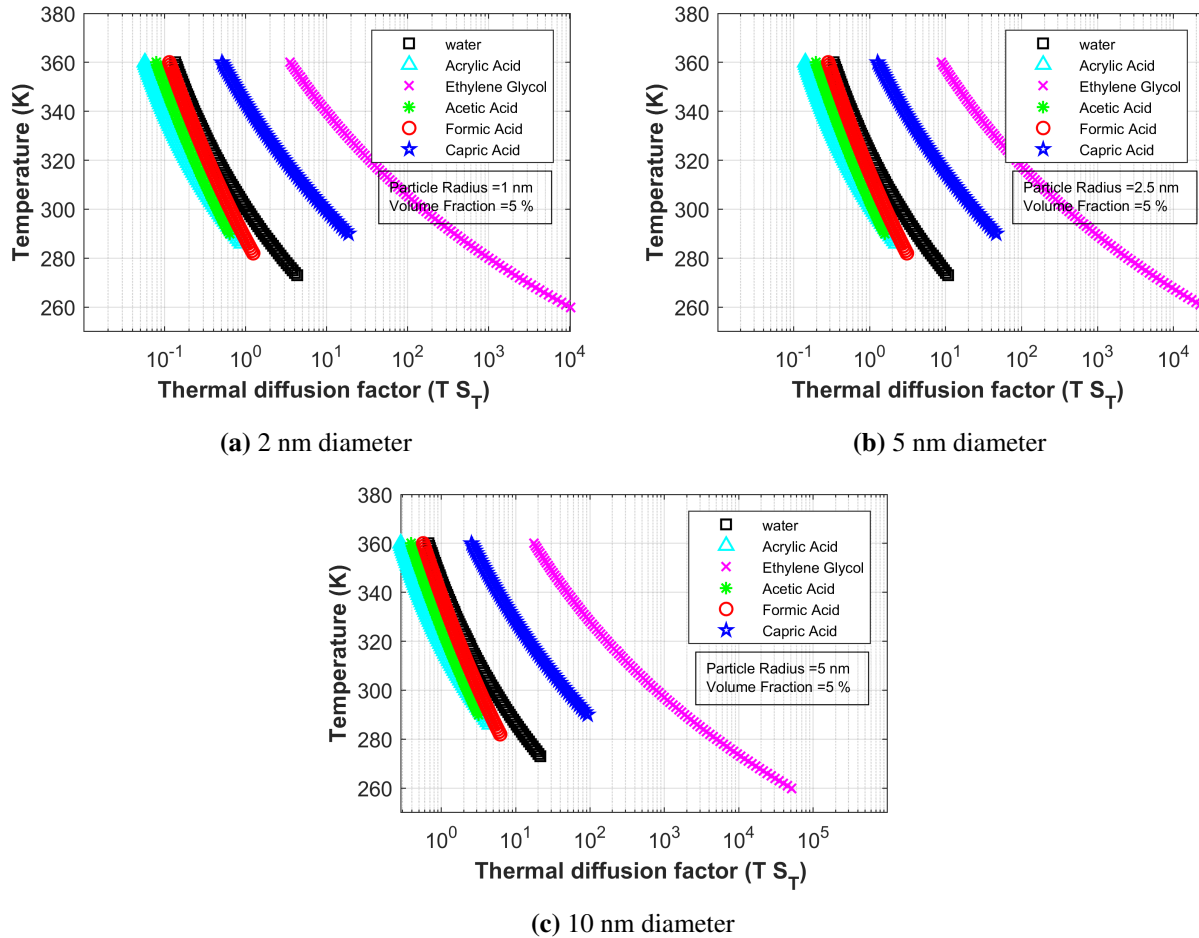


Fig. 1 Temperature vs Thermal Diffusion Factor with Copper Particles

We can also see from these figures, that particles are expected to be more uniformly distributed at higher temperatures and thus, the migration towards cold end. This result is supported by experimental and molecular dynamic simulation results of Galliero and Volz [27], Duhr and Braun [28].

3.2 Impact of Particle Type

Nanoparticles of alumina, copper, silver, titania and gold were studied for 5 nm diameter and 2% volume fraction. Alumina (Fig 2a) and titania (Fig 2b) particles have potential for thermophoresis over the entire range of temperatures. While Brownian diffusion is dominant at temperatures greater than 300 K for gold (Fig 2c) and silver (Fig 2d) particles in water, acrylic acid, formic acid and acetic acid.

The variation in thermal conductivity between different types of particles affect the migration potential. Alumina and titania have relatively low thermal conductivity as compared to silver, gold, and copper. While particle density also plays a role, its effect is minor due to the minimal change in nanofluid density caused by the addition of nanoparticles. The results indicate that to offset the lower thermal conductivity of alumina and

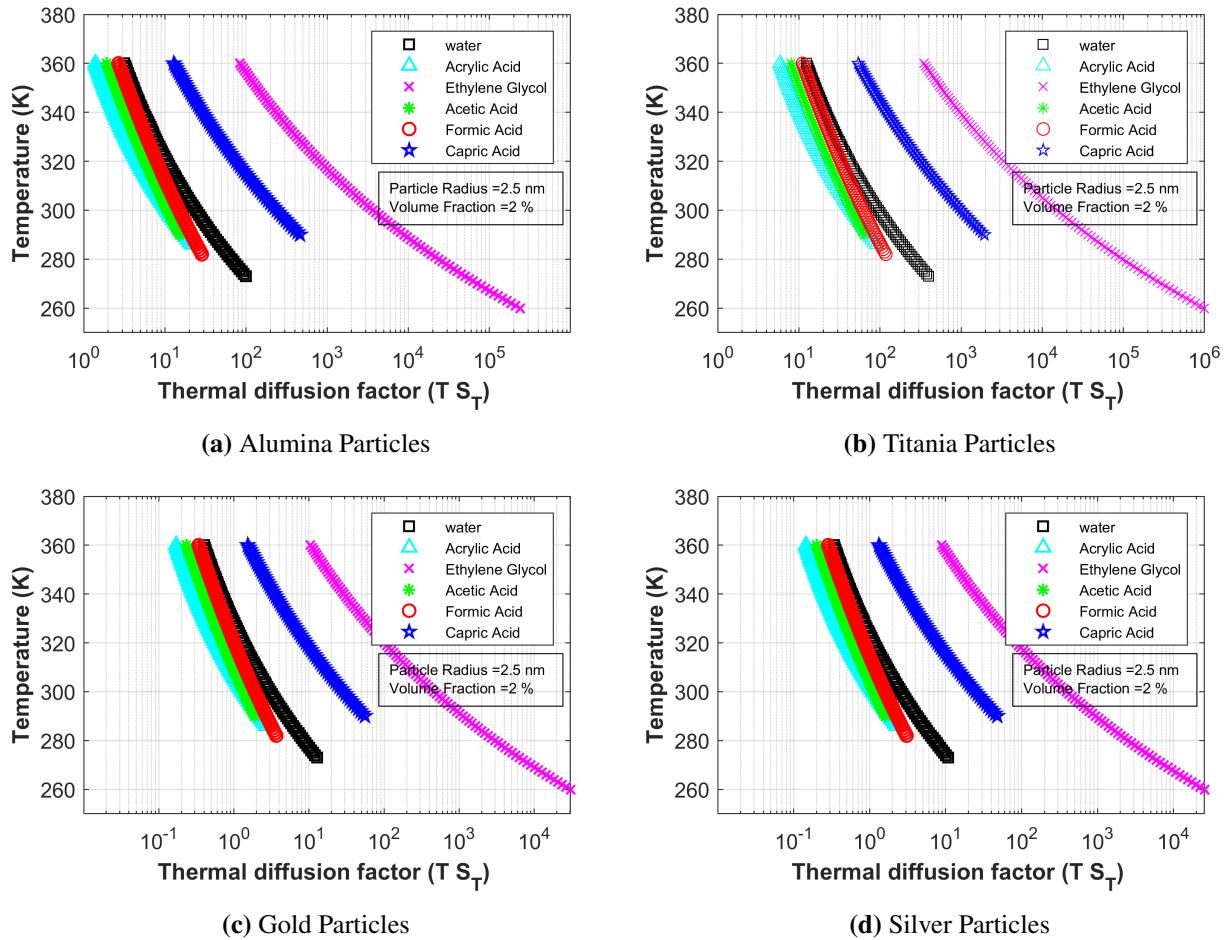


Fig. 2 Comparison of particle materials at 5 nm diameter.

achieve the same thermal diffusion as copper, its density would need to be increased by 117 times. However, the impact of density remains insignificant because it changes proportionally with the particle fraction so the fluid density is primary in determining nanofluid density.

3.3 Impact of Volume Fraction

The effect of volume fraction is not insignificant. Figure 3 shows the change in thermal diffusion factor for a range of volume fractions up to 5%. Only copper particles at 360 k are shown. Results are similar for other particle types and temperatures.

3.4 Comparison with Reported Published Data

Figure 4 illustrates the trends in $T S_T$ for a few select particle-fluid pairs. All combination except for acetic acid with 2.5 nm copper particles have thermal diffusion factors greater than one, indicating a potential for non-uniform particle distributions due to thermophoresis. Figure 4 also includes selected test conditions (square symbols) from studies on thermal conductivity enhancement of phase change materials [3, 29–32]. Data from Iyahraja1 and Rajadurai [29] and Kang et al. [31] (black and blue symbols, respectively) align with the predicted trend lines that indicate an increase in the size of silver nanoparticles dispersed in water increases the potential for thermophoretic migration. Also, when particles of lower thermal conductivity like alumina are used, as shown by red square [30], there is a shift towards higher thermophoretic potential. The fluid viscosity has the most prominent impact on particle migration as can be seen from the dashed green trend line, with test conditions from Eastman et al. [3] (green square). The thermophoretic potential is 1000 times greater than Brownian diffusion even though the particle is only 4 nm radius. The most commonly used PCM, paraffin,

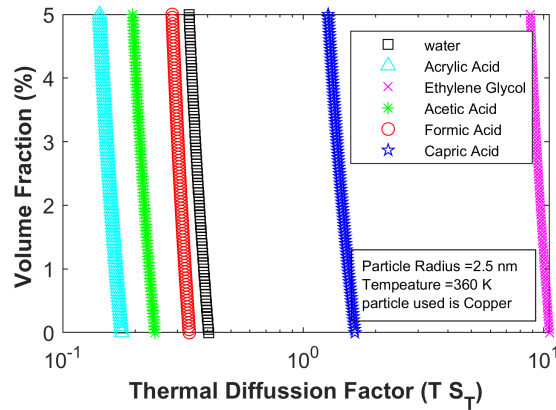


Fig. 3 TSt dependency on volume fraction for 5 nm copper particles at 360 K.

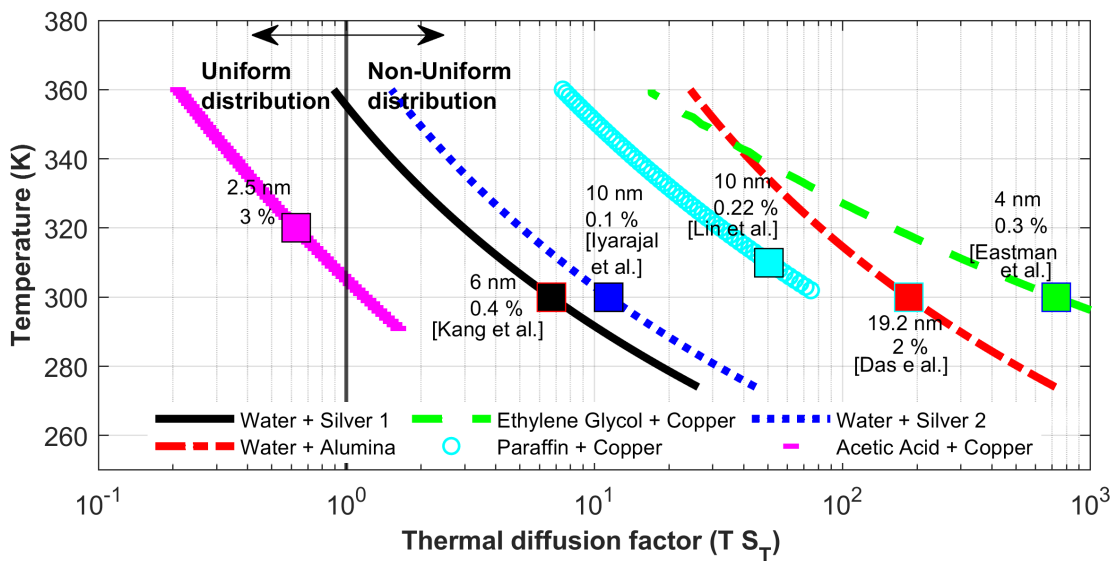


Fig. 4 TSt dependency on particle radius, particle-fluid pair, volume fraction, and temperature.

also shows that the dispersion of copper nanoparticles may result in thermophoretic migration with a particle radius of 10 nm [32].

The experimental data shown in Figure 4 all have potential for thermophoretic migration except for the scenario of dispersed copper nanoparticles of 5 nm diameter in acetic acid shown by the magenta square. This combination of particle size, material, and base fluid at 320 K is dominated by Brownian diffusion and ought to remain uniformly distributed. Choosing the appropriate combination of PCM and nanoparticle might avoid the development of concentration gradients. Though such concentration gradients have not been reported, most thermal conductivity studies are not cycled in the same manner as PCM energy storage systems. PCM thermal storage systems have much longer operational times and particle concentrations become locked between cycles due to solidification.

4. SUMMARY

The analysis reported herein has accounted for the experimentally verified empirical relations and considers the nanoparticle and fluid as a continuum. Values of thermal diffusion coefficient D_T are determined from previously validated equations 7 and thermophoretic force F_T that match well with experimental values of Semenov and Schimpf [33], Ramachandran et al. [34]. The work presented here shows that depending on the range of temperature, particle size, type of fluid and type of particle, the dispersed nanoparticles have the

potential for migration. Nanoparticles will likely be more uniformly distributed at large temperature gradients or high viscosity base fluids.

This work looks at the nanoparticles dispersed in PCM in a single phase liquid model. This will be extended to include the phase transition effect going forward. During the phase transition, the PCM will have certain interfacial velocity which can be compared to the thermophoretic velocity. This could reveal if the particles will lag, or always lead the interface leading to the sticking condition at that interface.

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NOMENCLATURE

β	non-dimensional nanofluid thermal conductivity	(-)
c	concentration	kg/m ³
D_B	Brownian diffusion coefficient	m ² /s
d_p	particle diameter	m
D_T	thermodiffusion coefficient	m ² /s-K
f	subscript for base fluid	-
F_T	thermophoretic force	N
J_p	mass diffusive flux	kg/m ² /s
$J_{p,c}$	mass diffusive flux due to concentration gradient	kg/m ² /s
$J_{p,T}$	mass diffusive flux due to temperature gradient	kg/m ² /s
k_B	Boltzmann Constant	m ² kg/s ² -K
k_f	base fluid thermal conductivity	W/m-K
k_{nf}	nanofluid thermal conductivity	W/m-K
k_p	particle thermal conductivity	W/m-K
$L_{\mu\mu}$	Onsager coefficient	-
μ_{nf}	viscosity of nanofluid	N-s/m ²
μ_f	viscosity of base fluid	N-s/m ²
nf	subscript for nanofluid	-
p	subscript for particle	-
φ	volume fraction of particles	-
φ_e	equivalent volume fraction of particles	-
r_p	radius of particle	nm
ρ_f	density of base fluid	kg/m ³
ρ_{nf}	density of nano fluid	kg/m ³
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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