

Theoretical Description of the Thermomolecular Orientation of Anisotropic Colloids

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Thermal fields bring new opportunities to manipulate colloidal suspensions. Mass anisotropy inside the colloid leads to the thermal orientation effect and to a non-monotonic dependence of the thermophoretic force with the mass of the colloid. We show here that the thermal orientation of these anisotropic colloids can be described using the von Mises probability distribution. We derive equations that link the orientation to the internal degrees of freedom of the colloid, and test these equations using both atomistic and mesoscopic stochastic rotation dynamics simulations. Our approach can be used to describe the thermophoretic response of anisotropic colloids as a function of their size and composition.

1 Introduction

Thermal gradients provide new routes to manipulate materials and complex fluids. Three key experiments involving thermal gradients were reported by Ludwig and Soret^{1,2}, who founded the area of thermodiffusion, and by Seebeck who discovered the thermoelectric effect³. These physical effects are exploited in the aerospace⁴ and car industries⁵ to make thermoelectric materials^{6,7}, as well as in medical applications⁸.

The use of thermal gradients in soft matter has attracted significant interest in recent years. Thermal fields induce thermophoretic forces on colloids, polymers and biomolecules^{9–14}. The thermophoretic forces depend on the shape of the colloids, as shown in studies of aerosols and colloidal suspensions^{15,16}. One key message from these works is that anisotropic elongated colloids feature anisotropic thermophoresis, namely, the diffusion coefficients associated to the motion along different particle axes, are different. The importance of the moment of inertia of molecules on the Soret coefficient, has also been discussed in the context of mixtures of binary fluids both experimentally^{17,18} and in computational studies¹⁹.

Recently, it was shown that the internal degrees of freedom of a colloid, *e.g.* anisotropy in mass or size, can couple with the thermal field inducing a preferred orientation in the colloid, *i.e.* a thermophoretic torque and, as a consequence, a rectification of the rotational motion of the colloid²⁰. These coupling effect result in a complex thermophoretic response, with colloids of the same shape and mass but different mass anisotropy, featuring significantly different Soret coefficient. The orientation of the colloid in a thermal field belongs to the so called "thermal orientation ef-

fect" that was demonstrated in fluids of anisotropic particles and polar fluids^{21–23}. These works have motivated a number of articles that confirmed this physical effect in other systems (see *e.g.* refs.^{24–26}), hence supporting the generality of the thermal orientation effect in a number of fluids.

The thermal orientation induced by internal mass gradients in particles might provide a new principle to control the assembly of colloids under thermal fields. Advancing in the implementation of these principles to suspensions consisting of nanometer and micrometer size colloids, requires a sound understanding of the principles determining the physical behavior of anisotropic colloids under external fields. Here we set out one step in this direction by modelling theoretically the orientational distribution function of anisotropic colloids under the influence of a thermal field. We show that the von Mises probability distribution function predicts accurately the functional dependence of the orientation of the colloids with the temperature gradient, temperature and colloid composition. The von Mises distribution has been employed before in fairly different problems, the movement of cells, cosmology, as well as in rotational diffusion studies (see refs.^{27–29} and references therein). The latter problem is of particular relevance to our work, since the presence of the thermal gradient induces the rectification of the rotational brownian motion.

We use the von Mises probability distribution to derive explicit equations for relevant properties, such as the average orientation of the colloids as a function of the thermal gradient strength, or the maximum torque induced on the colloids by a given thermal field. We examine the accuracy of the von Mises equation to describe the thermal orientation of colloids of nanometer and micrometer size. With this purpose we combine our theoretical analysis with atomistic and mesoscopic hydrodynamic computer simulations.

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2 Theoretical background

2.1 Probability distribution for the orientation

The rotational diffusion of the colloid can be described as a random walk along a circular path. We consider now the problem of an axisymmetric particle with rod or ellipsoidal like shape. The probability distribution function at a time $t + \Delta t$ for a discrete change in the angle δ and a discrete time unit Δt , is given by:

$$\begin{aligned} p(\theta_x, t + \Delta t) &= p(\theta_x - \delta, t) w^+(\theta_x - \delta) \\ &+ p(\theta_x, t) (1 - w^+(\theta_x) - w^-(\theta_x)) \\ &+ p(\theta_x + \delta, t) w^-(\theta_x + \delta) \end{aligned} \quad (1)$$

where w^+ is the probability for a step $+\delta$ and w^- is the probability for a step $-\delta$. The first term in equation (1) represents the flux from $\theta_x - \delta$, the second term corresponds to no change in angle, and the third term is the flux backwards, *i.e.* from $\theta_x + \delta$. A Taylor expansion leads to a diffusion-drift equation, the Smoluchowski or second Kolmogorov equation³⁰:

$$\frac{\partial p(\theta_x, t)}{\partial t} = -\frac{\partial}{\partial \theta_x} \left(D^{(1)} p(\theta_x, t) \right) + \frac{\partial^2}{\partial \theta_x^2} \left(D^{(2)} p(\theta_x, t) \right) \quad (2)$$

where $D^{(1)}$ represents the drift coefficient (see below for definition), and $D^{(2)}$ is the rotational diffusion coefficient. The probability flux can then be written as:

$$j(\theta_x, t) = D^{(1)} p(\theta_x, t) - \frac{\partial}{\partial \theta_x} (D^{(2)} p(\theta_x, t)) \quad (3)$$

In the forward Kolmogorov equation the probability distribution and the probability flux are periodic, hence we consider the following conditions,

$$p(0, t) = p(2\pi, t) \quad (4)$$

$$j(0, t) = j(2\pi, t) \quad (5)$$

Now, we focus on the time independent problem, *i.e.* the stationary state, for which $j(\theta_x, t) = 0$. The diffusion equation is given by:

$$\frac{\partial}{\partial \theta_x} (D^{(1)}(\theta_x) p(\theta_x)) = \frac{\partial^2}{\partial \theta_x^2} (D^{(2)}(\theta_x) p(\theta_x)) \quad (6)$$

where $p(\theta_x)$ is the probability distribution that defines the preferred orientation of the colloid in the thermal gradient. The next objective is to find a mathematical expression for this distribution. Integrating Equation (6) with respect to θ_x , and dividing both sides of the equation by $D^{(2)}(\theta_x) p(\theta_x)$, we get:

$$\frac{D^{(1)}(\theta_x)}{D^{(2)}(\theta_x)} = \frac{1}{p(\theta_x) D^{(2)}(\theta_x)} \frac{\partial}{\partial \theta_x} (D^{(2)}(\theta_x) p(\theta_x)) = \frac{\partial}{\partial \theta_x} \ln (D^{(2)}(\theta_x) p(\theta_x)) \quad (7)$$

Integration of equation (7) gives:

$$p(\theta_x) = A \exp \left(\int_0^{\theta_x} \frac{D^{(1)}(\theta'_x)}{D^{(2)}(\theta'_x)} d\theta'_x \right) \quad (8)$$

where A is a normalization constant. To derive the equations to describe the drift, $D^{(1)}$, and the diffusion, $D^{(2)}$, we consider now the Langevin equations for the rotational motion:

$$\begin{aligned} \frac{d\theta_x(t)}{dt} &= \omega_x(t) \\ I \frac{d\omega_x(t)}{dt} &= -\zeta \omega_x(t) - \frac{dU}{d\theta_x} + F(t) \end{aligned} \quad (9)$$

where ω_x is the angular velocity, I is the moment of inertia of the colloid, ζ is the rotational drag coefficient, $-dU/d\theta_x$ represents the force associated to the interaction of the colloid with the thermal field, and $F(t)$ is the stochastic noise term with $\langle F(t) \rangle = 0$ and $\langle F(t_1) F(t_2) \rangle = \Gamma \delta(t_1 - t_2)$, where $\Gamma = 2\zeta k_B T$ is the strength of the stochastic noise given by the thermal energy³⁰. Taking the limit of large friction, characteristic of dense fluids, $I/\zeta \rightarrow 0$, we can neglect the $d\omega_x(t)/dt$ term, obtaining:

$$\frac{d\theta_x}{dt} = -\frac{1}{\zeta} \frac{dU}{d\theta_x} + \frac{1}{\zeta} F(t) \quad (10)$$

The finite difference version of this equation can be written as³¹:

$$\Delta\theta_x = -\frac{1}{\zeta} \frac{dU}{d\theta_x} \Delta t + \frac{1}{\zeta} \Gamma^{1/2} \Delta W \quad (11)$$

where ΔW is the increment of the Wiener process, a Markovian stochastic process. The drift coefficient can be computed from its definition as the first moment of θ_x :

$$\begin{aligned} D^{(1)} &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left\langle -\frac{1}{\zeta} \frac{dU}{d\theta_x} \Delta t + \frac{1}{\zeta} \Gamma^{1/2} \Delta W \right\rangle \\ &= -\frac{1}{\zeta} \frac{dU}{d\theta_x} \end{aligned} \quad (12)$$

Similarly, the rotational diffusion coefficient can be obtained from the second moment of θ_x :

$$\begin{aligned} D^{(2)} &= \frac{1}{2} \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left\langle \left(-\frac{1}{\zeta} \frac{dU}{d\theta_x} \Delta t + \frac{1}{\zeta} \Gamma^{1/2} \Delta W \right)^2 \right\rangle \\ &= \frac{\Gamma}{2\zeta^2} = \frac{k_B T}{\zeta} \end{aligned} \quad (13)$$

where we have used $\langle \Delta W \rangle = 0$ and $\langle \Delta W^2 \rangle = \Delta t$. Equation (13) is the standard definition of the rotational diffusion coefficient. Further, assuming that $D^{(2)}$ is independent on θ_x , we get

$$p(\theta_x) = A \exp \left(-\frac{U(\theta_x)}{k_B T} \right) \quad (14)$$

The application of the thermal field leads to a potential well, $U(\theta_x)$, which imposes a preferred orientation on the colloid. We

assume that this interaction is defined by the equation:

$$U(\theta_x) = -\frac{k_E}{2} \cos(\theta_x - \theta_{x_0}) \quad (15)$$

where the "-" sign ensures the potential is a minimum at θ_{x_0} , k_E is the force constant that determines how the rotational energy changes due to changes in the orientation of the colloid, θ_{x_0} . θ_x is the angle that the colloid, c , makes with the vector defining the direction of the heat flux, J_q , namely, $\cos \theta_x = \mathbf{u}_c \cdot \mathbf{u}_{J_q}$, where $\mathbf{u}$ denote unit vectors. Our choice of this potential is motivated by the analogy between the orientation of mass dipoles in a thermal field and electric dipoles in an electrostatic field. This potential as we show below leads to the von Mises distribution, and the ensemble average results in the Langevin function, used in electrostatic problems involving dipole reorientations in electrostatic fields. We exploit this isomorphism in our work.

The probability distribution function can then be written in terms of the angular terms:

$$p(\theta_x) = A \exp\left(\frac{k_E}{2k_B T} \cos(\theta_x - \theta_{x_0})\right) \quad (16)$$

The normalization factor, A , follows from $\int_0^\pi p(\theta_x) d\theta_x = 1$, and the normalized probability distribution function becomes:

$$p(\theta_x) = \frac{\exp(\kappa \cos(\theta_x - \theta_{x_0}))}{\pi I_0(\kappa)} \quad (17)$$

where I_0 is the modified Bessel function of order 0 and $\kappa = \frac{k_E}{2k_B T}$. Eq. (17) is the von Mises distribution²⁸, an analogue to the normal distribution on a circle.

3 Non-equilibrium computer simulations approach

To test the von Mises distribution discussed in the previous section, we performed both atomistic and mesoscopic non-equilibrium computer simulations. For the mesoscopic simulations we employed the Stochastic Rotation Dynamics (SRD) algorithm introduced in reference³². We discuss below the computational details for both methods.

3.1 Atomistic simulations

The solvent and the colloid interactions were modelled using the WCA potential, *i.e.* a Lennard-Jones potential with a cutoff set to $2^{1/6}\sigma$ ³³:

$$U_{WCA}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \text{ for } r \leq 2^{1/6}\sigma \quad (18)$$

$$U_{WCA}(r) = 0 \text{ for } r > 2^{1/6}\sigma \quad (19)$$

where r is the inter-particle distance, ϵ the interaction strength and σ the particle diameter. Hereafter, we work in reduced units, and we use ϵ and σ to represent the properties of the system. We identify the reduced units by using an asterisk "*". The WCA potential has been used in a number of studies, see *e.g.*³⁴.

A simulation box with dimensions $(40, 20, 20)\sigma$ containing 16000 atoms ($\rho^* = 1.0$) was pre-equilibrated in the NVT ensemble at $T^* = 2.5$ for 10^5 timesteps, using as timestep $\delta t^* = 0.0025$. We use a high density since we are interested in describing the thermomolecular orientation of colloids suspended in dense fluid phases. In order to avoid the solid phase of the WCA fluid in the cold region, we use a high reduced temperature for our simulations.

A thermal gradient was set up by rescaling the velocities of the atoms, $\mathbf{v}_{new} = \mathbf{v}_{old} \sqrt{K_T/K}$, where $\mathbf{v}_{new}$ and $\mathbf{v}_{old}$ are the new and old velocities of the thermostatted particles, K is the current kinetic energy of the particles and K_T is the target kinetic energy at temperature T . The rescaling was performed every 100 timesteps and applied to specific thermostating regions in the simulation box (see Figure 1). The total linear momentum was reset to zero after each velocity rescaling, to ensure momentum conservation. The hot thermostat was located at the edges of the simulation box, while the cold thermostat was set in the centre of the box, hence creating two compartments with equal but opposite thermal gradients.

A colloid with an odd number of beads was inserted into each compartment (see Figure 1). To introduce the mass asymmetry in the colloid, we define a mass ratio $\gamma = m/m_{end}$, where m_{end} is the mass of the end bead of the colloid and m is the mass of the other beads. By setting the mass $m = 1$, the total mass of the colloid is given by $m_{total} = \gamma + N - 1$. The mass ratio γ defines the mass dipole, which quantifies the displacement of the center of mass with respect to the geometric center of the colloid, and the degree of mass anisotropy of the colloid. For our model the mass dipole has the following analytical form:

$$d = \left(\frac{\gamma - 1}{N + \gamma - 1} \right) \frac{N - 1}{2} a \quad (20)$$

where a is the diameter of the beads (set to $a = 1$ in the atomistic simulations). To prevent the thermophoretic drift of the rotating colloid, its center of mass was tethered to the center of each compartment (in the simulation box (see Figure 1), using a harmonic potential with force constant $k^* = k/\epsilon = 2 \times 10^3$. We integrated using different equations of motion both the rotational (method of quaternions) and translational (velocity Verlet) degrees of freedom.

The initial configuration was constructed by adding the colloid to a pre-equilibrated simulation cell and removing any overlaps between the colloid and the fluid. The configuration was then equilibrated for 10^6 timesteps. The orientation of the colloid along the direction of the thermal gradient was sampled every 100 timesteps for 10^7 timesteps, using 25 different initial independent configurations.

3.2 Stochastic rotation dynamics

To explore the thermal orientation in the mesoscopic regime, corresponding to very large colloid-solvent diameter ratios, we performed non-equilibrium stochastic rotation dynamics (NESRD) simulations. The non-equilibrium method exploits the boundary driven approach explained above for atomistic systems and the

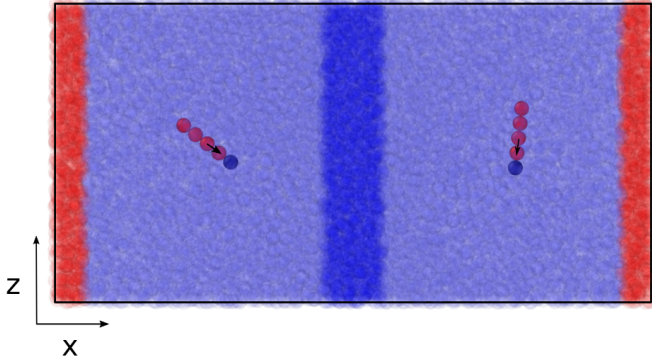


Fig. 1 Snapshot of the simulation box showing two colloids consisting of 5 beads. The rectangular regions highlighted in red and blue indicate the position of the hot and cold thermostats, respectively. The heavy bead, located at the end of the colloid, is highlighted in blue. The arrows in the colloids indicate their orientation vector, $\mathbf{u}_c$.

SRD algorithm introduced in reference³². The solvent was modelled as an ideal gas that interacts with the colloids according to predefined collision rules. One advantage of the SRD approach is that hydrodynamic effects can be included accurately³⁵. The use of hydrodynamic simulation approaches to investigate suspension under thermal gradients has been pioneered by Ripoll, Yang, Lüsebrink et al.^{16,36}, who used this method to investigate the thermophoretic drift of spherical and elongated nanoparticles. We employed in our simulations the SRD method implemented in LAMMPS³⁷.

The particles were streamed during a time-step Δt_{SRD} , updating their coordinates using the following equation of motion:

$$\mathbf{r}_i(t + \Delta t_{SRD}) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t_{SRD} \quad (21)$$

where $\mathbf{r}_i$ and $\mathbf{v}_i$ represent the position and the velocity of particle i . Following the streaming step, the box was divided into a regular cubic grid, with size $a_0 = \sigma$. The velocities of the SRD-solvent particles in each cell, were rotated relative to the centre of mass velocity of the cell:

$$\mathbf{v}_i(t + \Delta t_{SRD}) = \mathbf{v}_{cm}(t) + \mathbf{R}_\alpha(\mathbf{v}_i(t) - \mathbf{v}_{cm}(t)) \quad (22)$$

where $\mathbf{v}_{cm}$ is the centre of mass velocity of the cell, and $\mathbf{R}$ is a rotation matrix with a fixed rotation angle $\alpha = 90^\circ$, around a random axis chosen between the unit vectors in cartesian coordinates $\hat{x}$, $\hat{y}$ or $\hat{z}$ (collision model B of reference³⁸ with a fixed rotation angle). We set the number of SRD particles per cell to $n = 5$, a reduced mass density of $\rho_m = 1$, and a mass for the SRD particles of $m_{SRD} = 0.2$. For the mean free path we used $\lambda = 0.1a_0$, which renders an SRD timestep of $\Delta t_{SRD} = \lambda \sqrt{m_{SRD}/k_B T}$. Since the mean free path is smaller than the SRD cell, the same particles in the bin will undergo collisions for several timesteps, which leads to strong artificial correlations between them. This problem

is circumvented by using random shifts of the SRD cells before the collision step takes place, and by shifting the position of the cells back after the timestep has been evolved³⁹.

Following previous studies by others³⁵ we set the diameter of the colloidal particles to $a_{SRD} = 4$. This choice ensures that the hydrodynamic behavior can be resolved down to the characteristic size of the colloids. For consistency, we use $a = 4$ in Eq. (20).

The interaction between the SRD particles and the colloid is modelled using stochastic collisions. When a fluid particle collides with the colloid, its old velocity is discarded and a new velocity is sampled from the Maxwell-Boltzmann probability distribution. The collision imparts a force and a torque on the colloid. Since our simulations involve colloids in a thermal gradient where the temperature varies spatially, we introduced a modification of the *no-slip* collision rules proposed by Inoue et al.⁴⁰. In our implementation the new velocities of a colliding SRD particle are assigned as the sum of the local velocity in the collision point, $\mathbf{v}_{local}$, and a random velocity with normal and tangential components $\mathbf{v}_n$ and $\mathbf{v}_t$, respectively. The velocities are sampled from the Maxwell-Boltzmann distributions:

$$p(v_n) = \frac{m_{SRD} v_n}{k_B T} \left(-\frac{m_{SRD} v_n^2}{2k_B T_{loc}} \right) \quad (23)$$

$$p(v_t) = \sqrt{\frac{m_{SRD}}{2\pi k_B T_{loc}}} \exp \left(-\frac{m_{SRD} v_t^2}{2k_B T_{loc}} \right) \quad (24)$$

where T_{loc} is the local temperature of the SRD cell to which the colliding solvent particle belongs to. Our implementation thus differs from existing ones^{16,36}, which compute the fluid-colloid interactions using Molecular Dynamics and Lennard-Jones pair potentials.

The temperature gradient in the SRD fluid was generated using the velocity rescaling methodology explained in the previous section, namely, resetting the velocities of the particles entering thermostating regions in the middle and at the edges of the simulation box, ensuring the momentum is conserved. We show in Figure 2 a snapshot illustrating the SRD set up, as well as representative temperature profiles for different average temperatures.

We test that our implementation reproduces the theoretical temperature profile. For an ideal gas the temperature profile can be described analytically using the equation (see Appendix for the derivation),

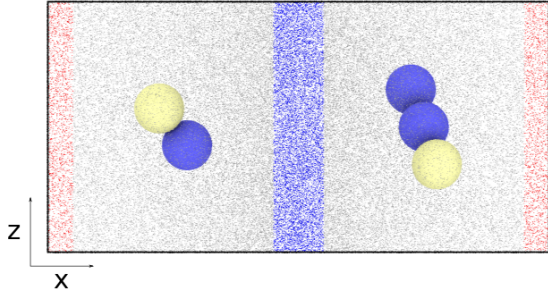
$$T(x) = \left[T_{hot}^{3/2} + \left(T_{cold}^{3/2} - T_{hot}^{3/2} \right) \frac{x}{L} \right]^{2/3} \quad (25)$$

where, T_{hot} and T_{cold} are the temperatures at positions 0 and L , respectively. We set T_{hot} and T_{cold} the temperatures at a distance of 5σ from the center of the compartment containing the pure fluid. We find that our NESRD approach is consistent with the analytical solution of the temperature profile for the ideal gas (see Figure 2).

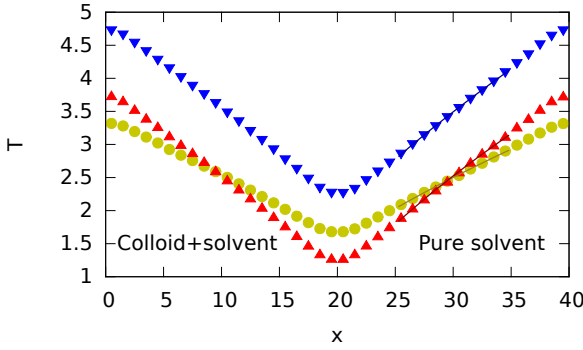
4 Results and discussion

The orientational probability distribution of the colloids in the thermal field (equation (14)) depends on the angle, θ_x , and the curvature of the potential well, κ , induced by the heat flux, which

a)



b)



c)

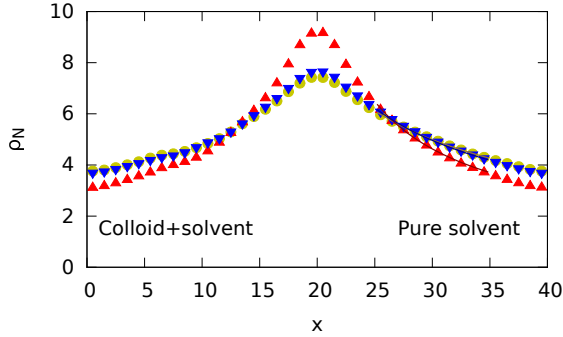


Fig. 2 a) Snapshot of the NESRD simulation set up showing a colloidal dimer (left) and trimer (right). The red and blue regions indicate the position of the hot and cold thermostats, respectively. b) Temperature profiles obtained with the NESRD method for different average temperatures. The left compartment contains a colloid (dimer), while the pure SRD fluid is in the compartment on the right. The solid lines were obtained with equation Eq. (25) using $T_{cold} = T_{x=25\sigma}$ and $T_{hot} = T_{x=35\sigma}$. Note that the temperature gradient in the region containing the colloids is slightly different to that of the pure fluid, possibly due to a change in the thermal conductivity of the suspension. c) Density profiles of the NESRD method for the temperature profiles represented in the middle panel. The solid lines represent the results obtained with the ideal gas law.

in turn depends on the mass anisotropy of the colloid, the magnitude of the thermal gradient and the temperature. In the following we examine the dependence of the probability distribution with these three variables, and propose explicit equations for κ and the average orientation in terms of the thermal gradient.

We computed the angular probability distribution of the orientation angle, θ_x , of the colloidal particles, using both the NEMD

and NESRD approaches. We first discuss results obtained with the NEMD atomistic method. These data were used to construct histograms of the angle θ_x , that the main axis of the colloid makes with the heat flux. The distributions were obtained taking into account the angular weight $\sin \theta_x$ (following from the Jacobian in spherical coordinates). The simulated histograms represent the density of states of the orientation of the colloid.

We showed recently that colloids with anisotropic mass distributions orient in the presence of a thermal field. The strength of the orientation is proportional to the mass dipole, d^{20} . A preferred orientation is reflected in a biased probability distribution, which features a maximum at a specific angle with the heat flux vector. The colloids investigated here orient in the thermal field with the heavy bead pointing towards the hot region and the maximum in the probability distribution is observed at $\theta_x = \pi$ (see Figure 3). The probability distribution does also become narrower with increasing mass asymmetry γ (see Figure 3-a).

We show in Figure-3b the probability distribution for atomistic colloids of size $N = 7$ for a mass ratio $\gamma = 15$ and $\nabla T = 0.12$, as a function of temperature. Lower temperatures lead to a stronger orientation and this is reflected in a narrower distribution. Figure-3c shows the impact of increasing the thermal gradient for a fixed mass dipole $d = 2$ and temperature, $T = 2.5$. Stronger gradients lead to a narrower distribution too. This phenomenology can be modelled accurately with the von Mises distribution discussed above (eqn. (17)). According to this distribution, κ contains all the information needed to predict the orientation of the colloids as a function of their mass anisotropy, temperature and thermal gradient. Hence, we performed additional simulations using the atomistic models, and varied the properties of the colloid systematically in order to gain insight into the dependence of κ with these variables.

We show in Figure 4 a summary of the dependence of κ with the temperature, mass dipole and thermal gradient. The von Mises parameter, κ , varies linearly with the mass dipole and the colloid length, N (see Figure 4a). N is a dominant term, as can be inferred from the almost full collapse of the data into a master curve (see Figure 4c). The linear dependence with N is reproduced for different thermal gradients and temperatures too (see Figure 4a and 4b), and the simulation data collapse into a straight line when we take into account T , ∇T and N (see Figure 4c). This results suggest that κ can be expressed as:

$$\kappa = \alpha \frac{Nd\nabla T}{T} \quad (26)$$

where α is a parameter that depends on the nature of the solvent.

Once the probability distribution is known, the average orientation of the colloids, $\cos \theta_x$, can be obtained from,

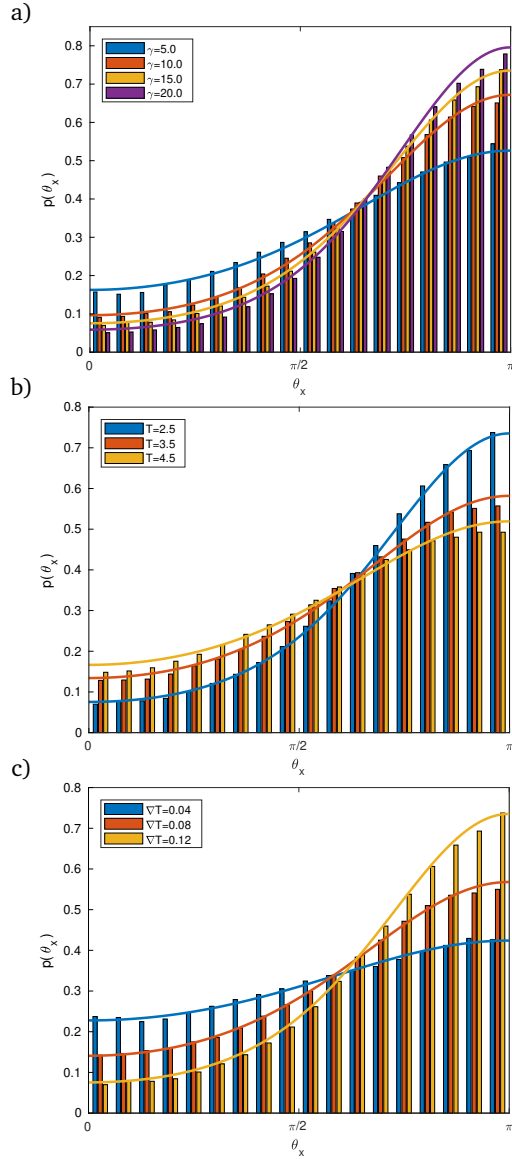


Fig. 3 a) Angular probability distribution functions of atomistic colloids of size $N = 7$ for different mass ratios, γ , and for the thermal gradient $\nabla T = 0.12$. b) Dependence of the probability distribution with temperature for $N = 7$, $d = 2$ and $\nabla T = 0.12$. c) Dependence of the probability distribution with the thermal gradient $T = 2.5$. $N = 7$ and $d = 2$. The solid lines represent a fit to the von Mises distribution (Eq. 17).

$$\begin{aligned}
 \langle \cos \theta_x \rangle &= \frac{\int_0^\pi \cos \theta_x \sin \theta_x p(\theta_x) d\theta_x}{\int_0^\pi \sin \theta_x p(\theta_x) d\theta_x} \\
 &= \frac{\int_0^\pi \cos \theta_x \sin \theta_x \exp(\kappa \cos(\theta_x - \theta_{x0})) d\theta_x}{\int_0^\pi \sin \theta_x \exp(\kappa \cos(\theta_x - \theta_{x0})) d\theta_x} \quad (27)
 \end{aligned}$$

where $\sin \theta_x$ is the angular weighting factor. By setting $\theta_{x0} = \pi$, as it can be inferred from the simulation results (see Fig. 3), the integrals in Eq. (27) can be solved easily, giving:

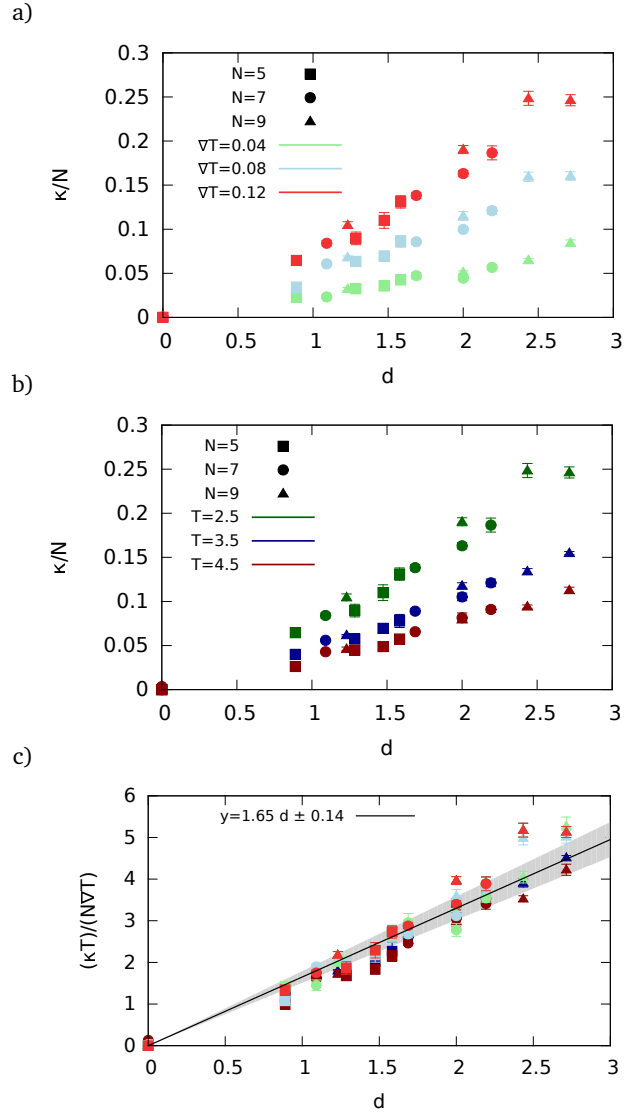


Fig. 4 Dependence of the parameter, κ , in the von Mises distribution (Eq. 17) with the mass dipole, for different colloid sizes. a) Dependence on thermal gradient for $T = 2.5$. b) Dependence on temperature for $\nabla T = 0.12$. c) Data scaled by the factor $T/(N\nabla T)$. The line represents a linear fit to all the data and the grey area shows the standard deviation of the slopes for individual fits at fixed T and ∇T .

$$\langle \cos \theta_x \rangle = \frac{1}{\kappa} - \coth(\kappa) \quad (28)$$

which is the well known Langevin function, first derived by Paul Langevin in his theory of paramagnetism⁴¹, and later by Onsager in the context of the electric moments of molecules in liquids⁴². We have checked the accuracy of Eq. (28) in predicting the orientation of the colloids as a function of their mass asymmetry, by using for κ in equation (26) $\alpha = 1.65 \pm 0.14$. We show in Figure 5 the dependence of the orientation with the mass asymmetry for colloids of different lengths. The orientation increases with the colloid length and mass asymmetry. Equations (28) and (26) reproduce accurately the simulation results. Further, the equations predict the behavior of long colloids $N = 11$ very well too (see Figure 5). We note that the fitting for α was performed includ-

ing data for colloids with size $N \leq 9$ only. Hence the results from equations (26) and (28) for $N = 11$ are predictions obtained with our model. Overall, the agreement between the predicted orientation using Eqs. (28) and (26) and the simulation results is in all cases satisfactory, supporting our conclusion that the von Mises distribution describes accurately the orientational probability of the colloid in the thermal field.

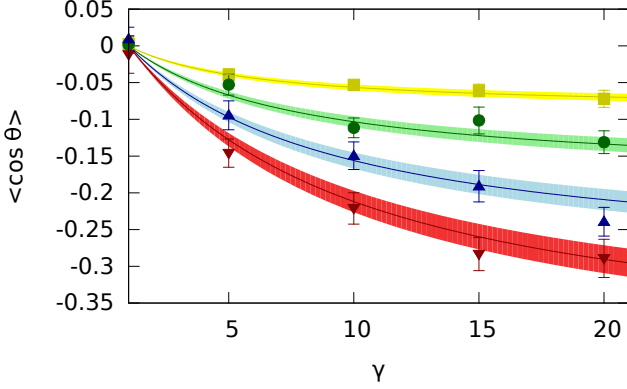


Fig. 5 Average orientation of the colloids as a function of the heavy mass, γ , for different colloid sizes and $T = 2.5$ and $\nabla T = 0.04$. The solid lines represent the prediction using Eq. (28) and equation (26), and the simulation results are shown as points. The shadowed region represents the uncertainty in the prediction associated to α . The lines represent results for different colloid sizes. From top to bottom: $N=5, 7, 9$, and 11 .

The functional form derived above for κ (equation (26)), was obtained using data of colloids in an atomistic solvent. We have investigated the applicability of this equation to a large colloid/solvent size ratio. With this purpose we analyzed the dependence of κ with the mass dipole, temperature, and temperature gradient, of the SRD model, focusing initially on colloidal dimers. Consistently with the atomistic simulations, the SRD computations predict a linear dependence of κ with the mass dipole for different thermal gradient and temperatures (see Fig. 6).

Our results also collapse into a master curve (see Figure 6), although the slope $\alpha = 5.91 \pm 0.30$ in equation (25) is different from that obtained in the atomistic case. This result indicates a dependence of the force constant, κ with the type of model employed and possibly the simulation method. We show in Fig. 7 the predictions of equation (28) and equation (26) for the colloids, dimer and trimers, in the SRD simulations. The data for SRD trimers, $N = 3$, were predicted using the α value fitted to the results for dimers. The excellent agreement between the predicted and the computed results indicates again that the von Mises probability distribution in conjunction with equation (25) provides a useful approach to predict the thermal orientation of colloids across scales, from nano to micron-size.

Once the functional form for the orientational probability distribution is known, it is possible to obtain the free energy of the colloids as a function of their orientation, as well as the rotational torque, from the free energy. We define the free energy in the thermal field as,

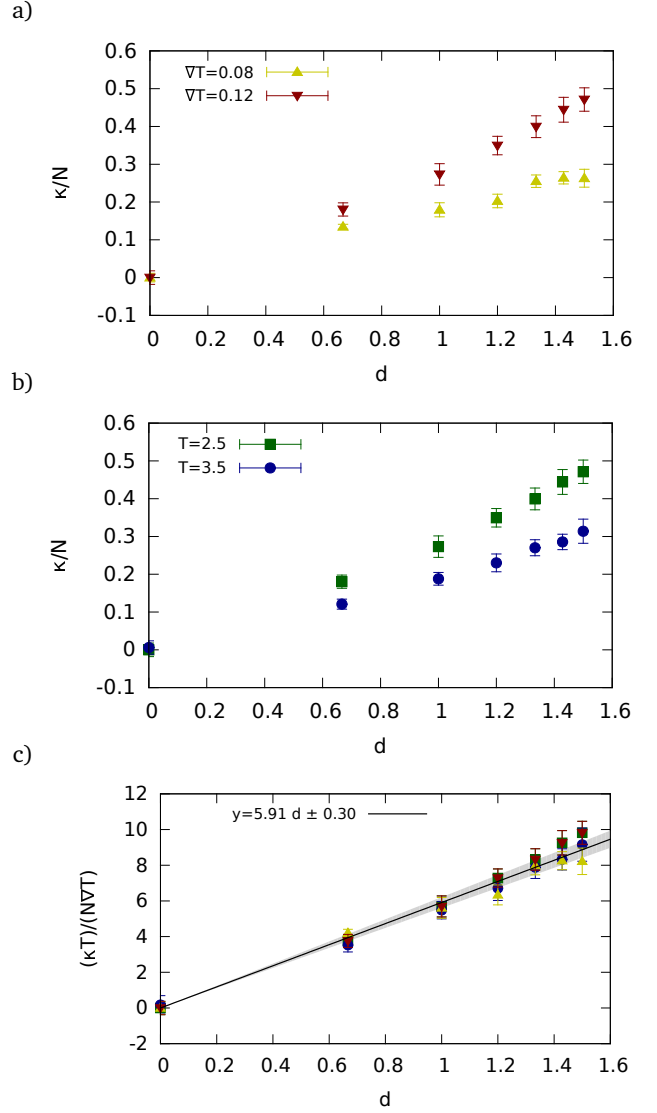


Fig. 6 Dependence of κ with the mass dipole, d , for colloid sizes $N = 2$ using SRD simulations. The panels a) and b) illustrate the dependence of κ with d for different temperature gradients and temperatures, respectively. Panel (c) illustrates the collapse of the data when these are rescaled by T , N and ∇T . The line represents a linear fit to all the data and the grey area is the standard deviation of the slope, α .

$$F(\theta_x, \kappa) = -k_B \bar{T} \ln p(\theta_x, \kappa) \quad (29)$$

where $\bar{T}$ represents the local average temperature corresponding to the position of the center of mass of the colloid. The torque is given by,

$$\tau(\theta_x, \kappa) = -\frac{\partial F(\theta_x, \kappa)}{\partial \theta_x} = k_B \bar{T} \kappa \sin(\theta_x) \quad (30)$$

Equation (30) predicts a maximum torque corresponding to the orientation perpendicular to the direction of the heat flux, namely, $\theta_x = \pi/2$,

$$\tau_{max} = k_B \bar{T} \kappa \quad (31)$$

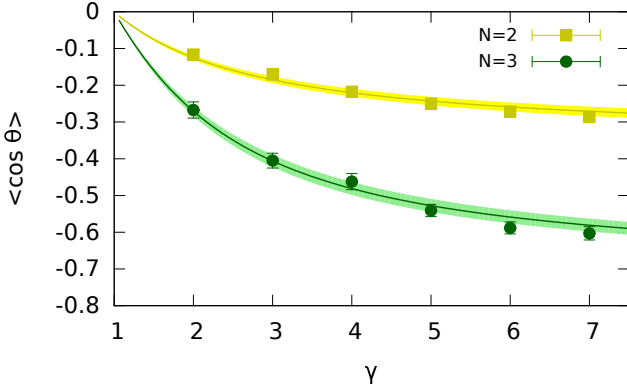


Fig. 7 Average orientation of SRD colloids as a function of the heavy mass, γ , at $T = 2.5$ and $\nabla T = 0.12$. The symbols represent data from computer simulations and the solid lines prediction using Equations (28) and (26). The shadowed regions correspond to the uncertainty in the prediction associated to the standard deviation of α .

Equation (31) shows that the maximum torque is proportional to κ and the temperature. Since κ is inversely proportional to the temperature, we expect that the maximum thermophoretic force, for a given mass dipole d , colloid size N and temperature gradient ∇T , should be independent on the temperature of the system, since the temperature factors appearing in equation (26) and (32) compensate each other, giving,

$$\tau_{max} = \alpha N d \nabla T \quad (32)$$

This equation can be used to estimate the torque induced by the thermal field. Considering $\alpha = 1.65 \pm 0.14$ for the atomistic simulations, and large thermal gradients achievable in experimental settings, 10^8 K/m,⁴³ ($\nabla T \sim 10^{-4}$, assuming a characteristic energy scale of $\varepsilon/k_B \sim 10^2$ K and a length scale of ~ 0.3 nm), considering a dipole $d \sim 1$, corresponding to $\gamma = 3.86 - 3.06$ for colloids of size $N = 10 - 100$, the maximum torque would change as $\tau_{max} \sim 10^{-4} N$, hence increasing linearly with the length of the rod, N . For the colloid sizes investigated in this work, the expected torque on a single particle would be of the order of $10^{-3} - 10^{-2}$ pN nm. The measurement of the maximum thermophoretic torque should yield information on the angular probability distribution by means of equations (17), (30) and (31).

We have established above that the von Mises distribution describes accurately the orientational probability distribution of rotating colloids in a thermal field. The results compare well with the simulation data. One question relevant to the simulation approach is whether finite size effects have a significant impact on the data and on the conclusions of our analysis.

To address this question we have explored the impact of finite size effects using both atomistic and the mesoscale simulations. We performed additional simulations computing the average orientation of the colloid in a larger simulation box with size $(60, 30, 30)\sigma$. In both cases, atomistic and mesoscopic, we computed $\langle \cos \theta \rangle$ as a function of the mass of the heavy bead, for a temperature $T = 2.5$ and thermal gradient $\nabla T = 0.04$ (atomistic) and $\nabla T = 0.08$ (mesoscopic). Fig. 8a shows that the average ori-

entation in the atomistic fluid does not significantly depend on system size. However, for the SRD case, we do find a difference in the average orientation between both system sizes. Specifically, the average orientation increases its magnitude for smaller simulation boxes (see Fig. 8b).

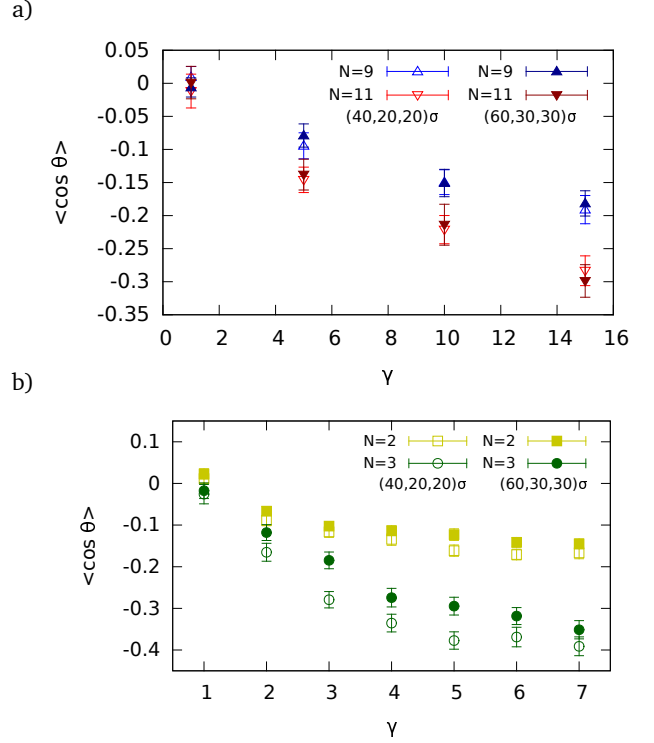


Fig. 8 Average orientation of the colloid as a function of the mass of the heavy bead at $T = 2.5$ and $\nabla T = 0.04$ (atomistic), $\nabla T = 0.08$ (mesoscopic), for two box sizes in a) atomistic simulations and b) SRD simulations.

To analyze the system size dependence in the SRD case, we computed the von Mises parameter κ for colloids with a mass ratio $\gamma = 5.0$ and size $N = 2, 3$, as a function of the simulation box size. Fig. 9 shows that the von Mises parameter decreases and converges to lower values with increasing system size. This result resembles previous SRD simulations of the thermophoretic force^{36,44}, where a significant dependence of the thermophoretic force (increasing with decreasing system size) was reported. Here we demonstrate that finite size effects do also affect the thermophoretic torque. The strong finite size effects observed in the SRD case are connected to the modification of the fluid flow, which changes with system size. Our results also show that the finite size dependence scales with the rod size. By taking this dependence into account using $\kappa/(Nd)$ we recover a general dependence of the von Mises parameter with the system size. This result indicates that although finite size effects are indeed affecting the magnitude of the orientation, they are not modifying the main physics of the problem.

The results reported above do also reveal differences between the atomistic and mesoscopic simulations. The lack of finite size dependence obtained in our atomistic simulation is compatible with a behavior dominated by Brownian rotation, where the fluid flow plays a minor role. The SRD fluid models conditions where

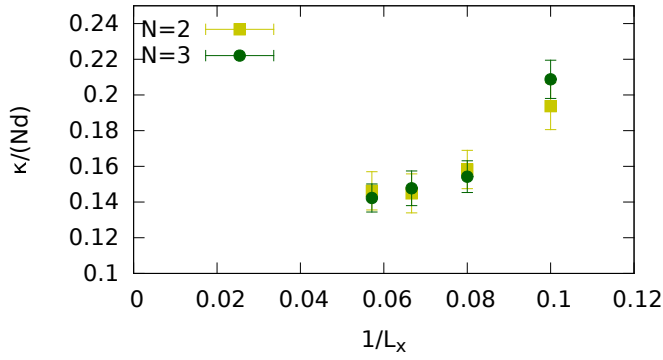


Fig. 9 von Mises parameter κ as a function of $1/L_x$ for colloids of size $N = 2, 3$ with heavy mass $\gamma = 5.0$, at $T = 2.5$ and $\nabla T = 0.08$.

fluid flow effects become more important, adding additional contributions to the thermal orientation of the colloids. Notwithstanding, the theoretical approach presented here describes the orientation response to the thermal gradient in both cases, atomistic and mesoscopic.

5 Conclusions

We have derived theoretical expressions to describe the orientation induced by thermal fields on axially symmetric colloids featuring an internal anisotropic mass distribution. The internal degrees of freedom couple with the thermal fields and the colloids feature a thermophoretic torque, which induces their orientation in the direction of the field.

The orientational probability distribution can be accurately described with the von Mises function. This function is defined by a Boltzmann factor that includes an angular potential, whose force constant, κ , depends on the thermal gradient (∇T), temperature (T), mass dipole (d) and colloid length (N). We used atomistic and mesoscopic (stochastic rotation dynamics) non-equilibrium computer simulations to inform the theory and to identify the leading dependence of the force constant and the thermophoretic torque in terms of (∇T), (T), (d) and (N). Using Boltzmann averaging we showed that the average orientation of the colloid is given by the Langevin function. This function connects the thermal orientation effect to the force constant of the angular potential induced by the thermal gradient. Hence, the thermal orientation can be added to the list of other physical phenomena, *e.g.* paramagnetism, or polar fluids under electrostatic fields, which can be described using the Langevin function. We have tested the applicability of our theoretical approach in a wide range of length-scales, from the small colloidal domain, to large colloid/solvent size ratios, characteristic of micrometer colloids.

Finite size effects are found to be negligible in the atomistic simulations, indicating that the rotation in these systems is dominated by the Brownian regime. However, we have demonstrated that in mesoscopic simulations finite size effects are important, and the thermal orientation is found to increase when the system size decreases. These finite size effects, however, do not change the main physics of thermal orientation, which can be described

accurately using the von Mises distribution. Overall, our results highlight important differences between the conditions simulated with atomistic and mesoscopic methods, which deserve further investigation.

The work presented here provides a theoretical framework to describe thermal orientation effects and possibly a route to experimentalists and simulators to estimate thermophoretic torques of anisotropic colloids by measuring/computing probability distributions. Further extensions of this work should target other colloidal compositions in order to assess the generality of the approach. In particular, systematic investigations to investigate the impact that the type of internal mass distribution has on the thermal orientation would be highly interesting. The concept of mass dipole provides a route to address such problem, and this will be reported in a future work.

Conflicts of interest

There are no conflicts to declare.

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Appendix

Derivation of the Smoluchowski equation The term on the left can be written using a Taylor expansion to the first degree in Δt , giving:

$$\begin{aligned} \Delta t \frac{\partial f}{\partial t}(\theta, t) = & f(\theta - \delta, t)p(\theta - \delta) - f(\theta, t)p(\theta) \\ & + f(\theta + \delta, t)p(\theta + \delta) - f(\theta, t)p(\theta) \end{aligned} \quad (33)$$

Using a Taylor expansion to the second order on θ gives:

$$\begin{aligned} \Delta t \frac{\partial f}{\partial t} = & \left(-\delta f \frac{\partial p}{\partial \theta} - \delta p \frac{\partial f}{\partial \theta} \right) \\ & + \left(\delta f \frac{\partial q}{\partial \theta} + \delta q \frac{\partial f}{\partial \theta} \right) \\ & + \left(\frac{\delta^2}{2} f \frac{\partial^2 p}{\partial \theta^2} + \delta^2 \frac{\partial f}{\partial \theta} \frac{\partial p}{\partial \theta} + \frac{\delta^2}{2} p \frac{\partial^2 f}{\partial \theta^2} \right) \\ & + \left(\frac{\delta^2}{2} f \frac{\partial^2 q}{\partial \theta^2} + \delta^2 \frac{\partial f}{\partial \theta} \frac{\partial q}{\partial \theta} + \frac{\delta^2}{2} q \frac{\partial^2 f}{\partial \theta^2} \right) \\ = & \delta \frac{\partial}{\partial \theta} (f(q - p)) + \frac{\delta^2}{2} \frac{\partial^2}{\partial \theta^2} (f(p + q)) \end{aligned} \quad (34)$$

Temperature profile for an SRD fluid The thermal conductivity of the ideal gas depends on the temperature as $\lambda = \beta \sqrt{T}$, where β is a constant. Fourier's law gives:

$$J_q = -\lambda \frac{dT}{dx} \quad (35)$$

where J_q is the heat flux. Integrating Fourier's equation from 0 to x and from x to L , gives:

$$J_q x = -\beta \frac{2}{3} (T_x^{3/2} - T_0^{3/2}) \quad (36)$$

where T_0 is the temperature at $x = 0$.

$$J_q (L - x) = -\beta \frac{2}{3} (T_1^{3/2} - T_x^{3/2}) \quad (37)$$

where T_1 is the temperature at $x = L$.

Dividing Eq. (36) by (37) gives:

$$(L - x) (T_x^{3/2} - T_0^{3/2}) = x (T_1^{3/2} - T_x^{3/2}) \quad (38)$$

Solving for T_x gives:

$$T_x = \left[T_0^{3/2} + \left(T_1^{3/2} - T_0^{3/2} \right) \frac{x}{L} \right]^{2/3} \quad (39)$$

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