Rotational hot Brownian motion

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**Abstract.** We establish an effective Markov theory for the rotational Brownian motion of hot nanobeads and nanorods. Compact analytical expressions for the effective temperature and friction are derived from the fluctuating hydrodynamic equations of motion. They are verified by comparison with recent measurements and with parallel molecular dynamics simulations over a wide temperature range. This provides unique insights into the physics of hot Brownian motion and an excellent starting point for further experimental tests and applications involving laser-heated nanobeads, nanorods and Janus particles.

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1. Introduction

The popular Markovian theory of Brownian motion, as developed by Einstein, Langevin and Smoluchowski a century ago, has been the starting point and inspiration for innumerable applications [1, 2]. However, the usual convenient formulation in terms of the centre-of-mass coordinates of particles only pertains to the special case of an isolated spherical particle. In the general case of interacting and/or anisotropic particles, both translational and rotational degrees of freedom couple, calling for a more elaborate mathematical description. This is most obvious for rod-shaped particles that have different mobilities for the movement parallel and perpendicular to their long axis [3], but in fact also holds for interacting spherical particles [4]. Due to the associated technical complications, the present theoretical understanding is still relatively incomplete [6], in particular with regard to micro-swimmers and other active or self-propelled colloidal particles [7–9], for which the proper hydrodynamic description is even more subtle than for passive particles in external fields [10, 11]. The directed motion for such self-propelled particles from sperms [12] to Janus particles running on chemical fuel [13] is usually limited by (equilibrium or nonequilibrium) rotational Brownian motion. Besides, rotational Brownian motion is undoubtedly of interest for its own sake. It is accessible to spectroscopy [14] and has been the basis for the development of new microrheological techniques [15] and nanoscopic heat engines [16].

In this paper, we are concerned with a specific type of rotational Brownian motion that occurs whenever the colloidal particles have an elevated temperature with respect to their solvent. In this case, we speak of rotational hot Brownian motion, in analogy to the better understood translational case [17]. Both intended [18–22] and unintentional [23, 24] realizations of (rotational) hot Brownian motion are nowadays widespread in biophysical and nanotechnological applications, which often employ nanoparticles exposed to laser light as tracers, anchors and localized heat sources. Deliberate heating of nanoparticles is, for instance, common in photothermal therapy [25, 26], but it also helps to enhance the optical contrast for detection [27] or in photothermal correlation spectroscopy [28]. Laser-heating is also a convenient way of supplying the energy for the self-thermophoretic propulsion of anisotropic particles [18]. A quantitative theory for optical scattering from dissolved hot nanoparticles has recently become available [29, 30], paving the way for a broad range of future applications.

In the following, we show that the heating affects the rotational and translational degrees of freedom differently, which is due to the intrinsic nonequilibrium nature of the phenomenon. To this end, we perform analytical calculations based on nonequilibrium fluctuating hydrodynamics, which we compare to large-scale molecular dynamics (MD) simulations of an atomistic model of a nanoparticle dissolved in a Lennard-Jones fluid. Although, in practice, even for an isolated single colloid rotational and translational diffusion always occur simultaneously, we may focus on one or the other separately, in theory. The requirement for this considerable simplification is that the coupling only results in a superposition of the respective displacements in space and orientation. To be more specific, we assume that the conditions governing the rotational Brownian motion, i.e., the spatially heterogeneous solvent viscosity and temperature around the particle, do not depend on the translational Brownian motion.

This assumption relies on the common Brownian scale separation. Typical nanoparticle diffusivities are on the order of $10^{-11}$–$10^{-10}$ m$^2$ s$^{-1}$ while heat and vorticity diffuse at $10^{-7}$ m$^2$ s$^{-1}$. Thus, the hot Brownian motion of a single spherical nanobead constitutes a
stationary nonequilibrium process with fixed radial temperature and viscosity fields, \( T(r) \) and \( \eta(r) \), respectively, if the instantaneous particle position is taken as the origin of the coordinate system. On this basis, we construct and validate a Markov model for the rotational Langevin dynamics of a hot Brownian particle with effective temperature and friction parameters, \( T_{\text{HBM}}^\theta \) and \( \zeta_{\text{HBM}}^\theta \). While the success of this strategy has already been demonstrated for the translational motion \([17, 31, 32]\), recent experiments using heated nanorods \([24]\) and hot Janus particles \([18]\) underscore the need for a separate quantitative analysis of the rotational dynamics. Below, we derive \( T_{\text{HBM}}^\theta \) and \( \zeta_{\text{HBM}}^\theta \) for the rotational Brownian motion of a hot particle and demonstrate that they differ from their analogues for translational motion. The mathematical structure of the rotational dynamics is simpler and allows for analytical solutions where one has to resort to numerical methods in the translational case.

The effective Langevin equation for the rotational dynamics of the nanoparticle orientation \( \mathbf{n} \) reads \([33]\),

\[
\dot{\zeta}_{\text{HBM}}^\theta \mathbf{n} = \xi \times \mathbf{n}.
\]

Under the presupposed nonequilibrium steady-state conditions outlined above, \( \zeta_{\text{HBM}}^\theta \) is the effective rotational friction coefficient. In the isothermal limit, \( \zeta_{\text{HBM}}^\theta \rightarrow 8\pi \eta R^3 \) for a sphere of radius \( R \) in a solvent of viscosity \( \eta \). The stochastic torque \( \xi \) is assumed to be a Gaussian random variable characterized by the moments

\[
\langle \xi(t) \rangle = 0, \quad \langle \xi_i(t) \xi_j(t') \rangle = 2k_B T_{\text{HBM}}^\theta \zeta_{\text{HBM}}^\theta \delta_{ij} \delta(t-t').
\]

The form of the noise strength amounts to the assumption that a generalized Einstein relation

\[
k_B T_{\text{HBM}}^\theta = D_{\text{HBM}}^\theta \zeta_{\text{HBM}}^\theta
\]

links the effective friction and temperature, \( \zeta_{\text{HBM}}^\theta \) and \( T_{\text{HBM}}^\theta \), to the effective rotational diffusivity \( D_{\text{HBM}}^\theta \). That the Brownian dynamics of a single heated particle is indeed constrained by this quasi-equilibrium relation is corroborated by our MD simulations, presented below.

2. Theory

The classical rotational Stokes problem is to find the friction coefficient of a steadily rotating particle in a viscous fluid of homogeneous solvent viscosity. For heated particles, the assumption of constant viscosity has to be relaxed. The general case of an arbitrarily shaped hot particle, which induces an asymmetric temperature profile in the solvent, gives rise to formidable technical complications. With the aim of deriving analytical results, we restrict our discussion to spherical beads (cf figure 1). Then the temperature can be idealized as a radial field \( T(r) \) that entails a radially varying viscosity \( \eta(r) \) via some constitutive law of the solvent, which we assume to be given. Some extensions to spheroids and slender cylinders can be discussed along the same lines if the radius \( r \) is given a slightly different interpretation, as outlined below \([34]\).

We further take the solvent to be incompressible, which is a good approximation for most common solvents, such as water, and eases the calculation. In the low Reynolds number limit, applicable to micro- and nanoparticles in solution, the solvent velocity \( \mathbf{u}(\mathbf{r}) \) follows from

\[
\nabla p = 2 \nabla \cdot \eta \Gamma = 2 \Gamma \nabla \eta + 2 \eta \nabla \cdot \Gamma, \quad \nabla \cdot \mathbf{u} = 0,
\]

with the strain rate tensor \( \Gamma \equiv (\nabla \mathbf{u} + \nabla \mathbf{u}^T)/2 \) and the pressure \( p \).
Figure 1. Artist’s conception of a hot Brownian particle, illustrating some notation.

For the purely rotational fluid motion around a steadily rotating sphere, analytical solutions can be found \[35\], as follows. The high symmetry of the velocity field \[u(r, \theta, \phi) = u_\phi e_\phi = w(r) \sin \theta e_\phi\] around the sphere entails a highly degenerate strain rate tensor. The tensor element \(\Gamma_{\theta\phi}\) contains \(u_\phi\) only in the form \(\partial_\theta (u_\phi / \sin \theta) = w_\phi(r) \sin \theta = 0\), leaving us with only a single relevant entry \(\Gamma_{\phi r}\) with

\[2\Gamma_{\phi r} = \partial_r u_\phi - u_\phi / r = (w' - w / r) \sin \theta.\]

Since the viscosity is assumed to vary only radially, its gradient is \(\nabla \eta = \eta' e_r\), and the equation of motion, equation (4), reduces to

\[
\nabla p = [2\eta' \Gamma_{\phi r} + \eta \nabla^2 u_\phi - \eta u_\phi r^{-2} \sin^{-2} \theta] e_\phi. \tag{7}
\]

Due to the cylindrical symmetry, the pressure gradient must not contain an azimuthal component, though, i.e., \(\nabla p = 0\). This leads to the ordinary differential equation for \(w(r)\),

\[w'' + (2/r + \eta' / \eta)(w' - w / r) = 0. \tag{8}\]

For the known case of a constant viscosity \(\eta(r) = \eta_0\) one easily verifies by insertion the solution \(w = c_1 r + c_2 / r^2\) with constants \(c_1\) and \(c_2\). For an unbounded fluid \(c_1 = 0\) so that the flow field takes the familiar form \(u = \Omega \times r(R/r)^3\) for a sphere of radius \(R\) rotating at constant angular velocity \(\Omega\). A constant viscosity can be interpreted as a degenerate case (for \(n = 2\)) of the power law viscosity field

\[\eta(r) = \eta_0 (r/R)^{n-2}. \tag{9}\]

For the latter \(\eta' / \eta = (n - 2) / r\), hence equation (8) reduces to \(w'' + nw' / r - nw / r^2 = 0\), which has the general solution \(w(r) = c_1 r + c_2 r^{-n}\). Thus the flow field in an unbounded fluid with a power-law viscosity field with arbitrary \(n > 0\), reads

\[u = \Omega \times r (R/r)^{n+1}. \tag{10}\]
For more complex viscosity profiles \( \eta(r) \), the task of solving equation (8) can be reduced to an integration using the Wronskian. Knowing the particular solution \( w(r) = r \), the general solution to equation (8) is found to be

\[
w(r) = c_1 r + c_2 r \int_r^\infty \frac{1}{\eta(x)x^4} \, dx.
\]

Moreover, rewriting equation (8) in terms of \( \gamma \equiv w' - w/r \) yields

\[
\gamma' + (\ln \eta') + 3/r) \gamma = 0,
\]

which is (up to a constant factor) solved by

\[
\gamma(r) \propto (R/r)^3/\eta(r).
\]

With the solution of the Stokes problem at hand, we can explicitly calculate the effective friction coefficient \( \zeta_{\text{HBM}}^0 \) for a rotating sphere. The torque exerted by a rotating sphere on the surrounding fluid is obtained by integrating \( 2\eta \Gamma \phi \mathbf{r} \times \mathbf{e}_\phi = \eta \gamma \sin \theta \mathbf{r} \times \mathbf{e}_\phi \) over the surface of the sphere, where \( \mathbf{r} \times \mathbf{e}_\phi = -R \mathbf{e}_\theta \mathbf{r} \cos \theta - R \mathbf{e}_r \). As the \( \phi \)-integral over the \( \mathbf{e}_\rho \)-component vanishes identically, this yields

\[
2\pi \int_0^\pi R^3 \sin^3 \theta \eta(R) |\gamma(R)| = \frac{8\pi}{3} R^3 \eta(R) |\gamma(R)|,
\]

and division by \( |\Omega| \) yields the wanted effective friction coefficient. The boundary conditions \( \mathbf{u}(r) \big|_{r=R} \) and \( \lim_{r \to \infty} \mathbf{u}(r) \), and the viscosity profile \( \eta(r) \) fix the constants \( c_1 \) and \( c_2 \) in equation (11). For an unbounded medium, \( w(r \to \infty) = 0 \) implies \( c_1 = 0 \), and \( w(r = R) = \Omega R \) fixes \( c_2 \). Collecting results, we find the known friction coefficient [35]

\[
\left( \zeta_{\text{HBM}}^0 \right)^{-1} = \frac{3}{8\pi} \int_R^\infty \frac{1}{\eta(r)r^4} \, dr,
\]

which indeed attains the isothermal value \( 1/(8\pi \eta_0 R^2) \) for \( \eta(r) = \eta_0 \).

Following the derivations in [32], the second important parameter of a hot Brownian particle, its effective Brownian temperature \( T_{\text{HBM}}^\theta \), is given by

\[
T_{\text{HBM}}^\theta = \frac{\int_{\Gamma} T(r) \phi(r) \, d^3r}{\int_{\Gamma} \phi(r) \, d^3r}.
\]

(Depending on the type of motion of the particle, the result gives the translational/rotational effective temperature \( T_{\text{HBM}}^{\theta,\text{HBM}} \). It can explicitly be determined by integration once the dissipation function \( \phi \equiv \eta \Gamma : \Gamma/2 \) is known. For the rotational flow field in equation (5),

\[
\phi = \eta \left( w' - w/r \right)^2 \sin^2 \theta \equiv \eta \gamma^2 \sin^2 \theta,
\]

from which we get

\[
T_{\text{HBM}}^\theta = \frac{\int_R^\infty T(r) \eta^{-1}(r)r^{-4} \, dr}{\int_R^\infty \eta^{-1}(r)r^{-4} \, dr}.
\]

Together with equation (15), this completes our formal derivation of the effective friction and temperature parameters characterizing the rotational hot Brownian motion of a sphere. They can explicitly be evaluated and used in the effective Langevin equations (1) and (2), provided that the temperature dependence \( \eta(T) \) of the solvent viscosity and the temperature profile \( T(r) \)
Figure 2. Left: Effective temperature of rotational hot Brownian motion. The simulation results for $T_{\text{HBM}}^\theta$ (●) were deduced from the numerically measured $\zeta_{\text{HBM}}^\theta$ and $D_{\text{HBM}}^\theta$ using the generalized Einstein relation (3). An alternative estimation of $T_{\text{HBM}}^\theta$ (□) was obtained from the Boltzmann distribution of the inclination angle $\theta$ in a harmonic angular confinement (right panel). The theoretical prediction (solid line) was evaluated within the idealized theory for an incompressible fluid via equation (18), using the radial viscosity and temperature profiles $\eta(r)$ and $T(r)$, determined in the MD simulation. For comparison, the effective temperature $T_{\text{HBM}}^\rho$ for the translational degrees of freedom (dot-dashed line) and the solvent temperature at the particle surface (dotted line) are shown. Right: The measured distribution of the inclination angle $\theta$ in a harmonic angular confinement potential for nanoparticle temperatures $T_p = 0.8 \varepsilon / k_B$ (●), $1.25 \varepsilon / k_B$ (■) and the corresponding distribution $p(\theta) \sim e^{-\beta V(\theta)}$ with $\beta^{-1} = k_B T_{\text{HBM}}^\rho$ depicted by the solid lines.

around the nanoparticle are known. For the practically important special case that the solvent is water, which is well characterized by

$$\eta(T) = \eta_\infty e^{A/\left(T - T_{\text{VF}}\right)} \text{ and } T(r) = T_0 + \Delta T R/r,$$

the convenient approximation (accurate to within 2% for $\Delta T \lesssim T_0$)

$$T_{\text{HBM}}^\theta \approx T_0 + \frac{3}{4} \Delta T$$

is obtained by neglecting the temperature dependence of the viscosity, i.e., by setting $\eta(r) = \text{constant}$, in equation (18).

For the example of a Lennard-Jones fluid with an immersed hot nanobead, we have evaluated equation (18) numerically, based on the temperature and viscosity profiles obtained from our simulations. Care has been taken to include the density variations and finite size effects correctly, as detailed in [32]. In figure 2, we compare the predicted $T_{\text{HBM}}^\theta$ to the effective temperature deduced from the directly measured friction $\zeta_{\text{HBM}}^\theta$ and diffusivity $D_{\text{HBM}}^\theta$ via the generalized Einstein relation (3). (A brief description of the MD simulations can be found further below.)

Beyond the above limiting results for spherical particles, analytical estimates for the rotational hot Brownian motion of anisotropic particles can readily be obtained in the slender
rod limit. To find the friction coefficient per unit length for an infinitely long hot cylinder, equation (4) has to be extended by adding Oseen’s term \( \rho \mathbf{U} \cdot \nabla \mathbf{u} \) to the force on the right hand side [36]. The effective friction coefficient for stationary translation along the main axis can then be calculated as

\[
\tilde{c}_HBM^\parallel = 2\pi \left( \int_R^\infty \frac{e^{-j_r \pi \eta(r) dr}}{\eta(r) r} \right)^{-1},
\]

where the radius \( r^* \) now denotes the distance to the symmetry axis of the cylinder. Exploiting the formal analogy between the Reynolds number \( \rho U R/\eta(R) \) and the aspect ratio \( L/(2R) \) in cutting off the hydrodynamic divergences under isothermal conditions, we arrive at a plausible estimate for the friction coefficient of a slender cylinder of finite length \( L \) and radius \( R \), namely,

\[
\tilde{c}_HBM^\parallel = 2\pi \eta(R) (\ln[\eta(R)L/(2\eta_0 R)] - \gamma)^{-1}.
\]

For transverse and rotational motion, expressions corresponding to equation (21) are more complicated to calculate, due to the lower symmetry of the temperature and fluid velocity fields. However, simple estimates for the effective transverse and rotational friction coefficients are readily obtained if one neglects a potential dependence of the ratios of the various friction coefficients on the heating, namely,

\[
\tilde{c}_HBM^{\perp} \approx 2\tilde{c}_HBM^\parallel \quad \text{and} \quad \tilde{c}_HBM^\theta \approx (L^2/12)\tilde{c}_HBM^\perp.
\]

The result for \( \tilde{c}_HBM^\parallel \), normalized to its isothermal limit, is depicted in the left panel of figure 3, for various aspect ratios. For aspect ratios that are large enough to admit the slender-rod approximation, the temperature dependence of the expression (22), normalized to its isothermal limit, is close to the normalized rotational friction coefficient of a sphere.

A practical estimate for \( T_{HBM}^\theta \) of a hot rotating rod is obtained to first order in \( \Delta T \) by ignoring the temperature dependence of the viscosity and treating the rod as a prolate spheroid. In this case, the flow field \( \mathbf{u}(r) \) is known analytically [37]. It is constructed by a line distribution of some moments of the fundamental solutions to the Stokes equations under different singular forcings, so-called stresslets, rotlets and potential quadrupoles. From \( \mathbf{u}(r) \), a straightforward calculation yields the ‘radial’ dissipation function \( \phi(\tau) \) from which \( T_{HBM}^\theta \) is calculated for a given temperature field \( T(r) \) around the spheroid. In spheroidal coordinates, \( (\tau, \xi, \phi) \), where \( x = c\tau \xi, y = c\sqrt{(\tau^2 - 1)(1 - \xi^2)} \cos \phi, z = c\sqrt{(\tau^2 - 1)(1 - \xi^2)} \sin \phi \), the temperature field

\[
T(\tau) = T_0 + \Delta T \arccoth \tau/\arccoth \tau_0
\]

obtained from Fourier’s law for constant heat conductivity only depends on the ‘radius’ \( \tau \) and the eccentricity \( \tau_0^{-1} = [1 - (2R/L)^2]^{1/2} \) of the particle. Using it together with the isothermal \( \phi(\tau) \) in equation (16), we obtain the first order term of the series expansion of \( T_{HBM}^\theta \) for slender particles in powers of \( \Delta T \). Its coefficient \( (T_{HBM}^\theta - T_0)/\Delta T \) is plotted in figure 3. Substantial deviations from the value \( 3/4 \) for a sphere, equation (20), only become apparent for eccentricities \( \tau_0^{-1} \gtrsim 0.95 \), corresponding to extreme aspect ratios \( L/(2R) \gtrsim 3.5 \).

Note that the high power of the radial distance \( r \) in the denominator under the integral in equations (15) and (18) suggests that the effective rotational temperature and friction should

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3 The calculation essentially parallels the one detailed in section 2 for the rotational motion of a sphere—but now in cylindrical coordinates and purely axial flow. The quantity \( U \) denotes the absolute value of the particle velocity \( \mathbf{U} \) relative to the distant fluid at rest.
Figure 3. Left: Effective friction coefficient $\zeta_{\text{HBM}}$ of a hot nanoparticle in water (normalized to the isothermal limiting value) as a function of the temperature increment $\Delta T$ above the ambient temperature $T_0 = 298$ K. The analytical predictions for a spherical bead of radius $R$ from equation (15) and [31] are represented by solid and dot-dashed lines for rotational and translational motion, respectively. Note that they differ by a heating-dependent kinematic factor, an effect that we neglect in the estimate equation (23), for slender rods. Dashed lines represent the effective longitudinal friction coefficient $\zeta_{\parallel \text{HBM}}$ of a hot slender rod according to equation (22), for the aspect ratios $L/(2R) = 10^1, 10^2, 10^3, 10^4$. The curves closely follow the prediction for the rotating sphere, except for small $L/(2R) \lesssim 10^2$ near the isotropic limit, which is not correctly recovered by the slender-rod approximation. Inset: The inverse translational versus the inverse rotational relaxation time of a spherical particle in an optical trap of varying strength; to be compared with figure 3(d) of [24]. The dotted line indicates the naive estimate obtained by identifying the effective viscosities for translational and rotational motion. Right: Variation of the first order coefficient of $T_{\text{HBM}}(\Delta T)$ with the eccentricity $\tau_0^{-1}$ of the spheroidal particle. No numerically stable integration was attained that covers the whole range 0, . . . , 1. Therefore, a 7th order series expansion of the dissipation function $\phi(\tau)$ in $\tau^{-1}$ was employed to generate the correct asymptotic behaviour as $\tau_0^{-1} \to 0$, while the full expression for $\phi(\tau)$ was evaluated numerically for the other branch. As a guide to the eye, a matching curve has been added by hand.

be higher and lower than their translational counterparts, respectively. This conclusion is supported by recently published experimental data for gold nanorods, where the effective temperature for their rotational Brownian motion in an optical trap is ‘found to be close to the particle’s temperature’ [24]. The plots of our predictions in figure 3 suggest that our results for a spherical particle should still provide a reasonably good approximation for these rods, which have an aspect ratio of about two. To make closer contact with the experiments, we have used equation (15) and the differential shell method [31] to calculate the rotational and translational friction coefficient for the viscosity field of equation (19). The inset of figure 3 depicts the ratio of the estimated rotational and translational relaxation times $\tau_{r,t} \propto \zeta_{\text{HBM}}^{\theta,x}/\Delta T$.
for the experimental particle in the optical trap, assuming a linear dependence between the trap stiffness and the heating $\Delta T$. The prediction is seen to be in good qualitative agreement with figure 3 of [24].

One may ask whether any more general statements can be made concerning the relative magnitude of the various effective temperatures of hot Brownian motion introduced so far, independent of the shape of the particle, and based on some generic material properties (e.g. that the solvent viscosity decreases upon heating). In particular, one expects that, under otherwise identical conditions, the effective temperature will usually be higher for rotational than for translational motion, because the solvent velocity field around the particle is more localized near the hot particle for rotation than for translation. This suggests that the temperature ordering

$$T_0 \leq T_{\text{HBM}}^T \leq T_{\text{HBM}}^\theta \leq T_s \leq T_p$$  

might be quite generic ($T_{\text{HBM}}^T$ is the effective temperature for the translational Brownian motion, $T_p$ and $T_s$ are the particle temperature and the solvent temperature at the particle surface, respectively, $T_0$ is the ambient temperature). The claim is corroborated by the results for a temperature-independent viscosity and for a viscosity step (see appendix), and also by experimental observations [17, 24].

3. Molecular dynamics simulations

Numerical simulations allow for a more accurate check of some of our theoretical prediction than the quoted experiments, since we can better control the ‘experimental’ conditions. Our simulations of rotational hot Brownian motion are based on the same setup as in the translational case [32]. In brief, the system is modelled as a Lennard-Jones fluid with a radial pair potential $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. While 107,233 particles are treated as solvent, a spherical cluster of 767 particles, additionally interconnected by a finite extensible nonlinear elastic (FENE) potential $V(r) = -0.5\kappa R_0^2\log[1 - (r/R_0)^2]$ with $\kappa = 30\epsilon/\sigma^2$, $R_0 = 1.5\sigma$, forms the nanoparticle.

Each simulation run consists of an initial isothermal equilibration phase at $T = 0.75\epsilon/k_B$, followed by a heating phase, where the nanoparticle is kept at a constant elevated temperature $T_p$, and a boundary layer at the periphery of the simulation volume is kept at $T = 0.75\epsilon/k_B$. All measurements were performed once a stationary state had been attained in the heating phase. The results were averaged over 30 independent trajectories of $2 \times 10^5$ steps (corresponding to a physical duration of 1 ns). For further details concerning the simulation method, we refer the reader to [32].

The rotational diffusion coefficient $D_{\text{HBM}}^\theta$ was determined from the decay of the autocorrelation function of an orientation vector assigned to the freely diffusing hot nanoparticle of figure 1. The rotational friction coefficient $\zeta_{\text{HBM}}^\theta$ was determined by applying a constant external torque to the nanoparticle and measuring its angular velocity. To gain more insight into the microscopic details, we also recorded the radially varying angular velocity in concentric shells of thickness $\sigma/5$ around the nanoparticle, in this case. Figure 4 shows the excellent agreement of the measured angular velocity field $w(r)/r$ with the theoretical prediction in equation (11)—except in the close vicinity of the nanoparticle (inset of figure 4) where solvent density variations are prominent, which have been neglected in the analytical calculation. For a comparison with the predictions, we therefore treated the radius $R$ of the nanoparticle,
Figure 4. Radial variation of the measured angular velocity $w(r)/r$ normalized by the angular velocity of the hot nanoparticle for $T_p = 0.9\varepsilon/k_B$ (●) and 1.25\varepsilon/k_B (■). The solid lines are the corresponding plots of equation (11) evaluated using the measured viscosity and temperature profiles. Inset: The variation of the angular velocity near the nanoparticle surface. The vertical solid lines indicate the positions of the hydrodynamic boundary condition for the predicted hydrodynamic flow fields (11) fitted to the simulation data. The shaded region (its extension marked by an arrow) indicates the equivalent sphere radius for the nanoparticle (dot-dashed line) plus $\sigma/2$. The comparison reveals a weak apparent slip at high nanoparticle temperatures due to the radial solvent density variation induced by the heating.

which affects $w(r)$ via the boundary condition, as a free parameter. When the heating of the nanoparticle is small, $R$ agrees with the value $R_H + \sigma/2$, with the radius $R_H$ of an equivalent solid sphere given by $R_H^2 = \frac{\kappa}{6\pi \eta} \sum_{i,j=1}^{N} (r_i - r_j)^2$ [38, 39]. For strong heating, $R$ decreases slightly, due to the mentioned solvent density variation, which results in a weak surface slip of the hydrodynamic flow field (inset of figure 4).

Finally, we pursued three routes for determining the hot nanoparticle’s effective temperature: (i) by measuring the rotational diffusion and friction coefficients, $D_H^{\theta}$ and $\zeta_H^{\theta}$, and making use of the generalized Einstein relation in equation (3) (● in figure 2); (ii) by fitting the recorded angular distribution $p(\theta)$ in a harmonic angular confinement potential $V(\theta) = \frac{K}{2} (\theta - \pi/2)^2$ with a Boltzmann distribution $p(\theta) \propto \exp(-V(\theta)/k_B T_H^{\theta})$ (□ in figure 2); and (iii) by measuring the viscosity and temperature profiles, $\eta(r)$ and $T(r)$ and calculating $T_H^{\theta}$ via equation (18) (solid line in figure 2). All three methods agree within the error bars, thereby confirming our theoretical predictions for the effective friction $\zeta_H^{\theta}$, the effective temperature $T_H^{\theta}$, and the generalized Einstein relation of rotational hot Brownian motion, equation (3).
4. Conclusions

We have analysed the rotational Brownian motion of a heated (nano-)particle in an otherwise unheated solvent. Particles of spherical, spheroidal and slender cylindrical shape have been considered. While we have obtained exact results for the effective rotational friction and temperature in the case of spherical particles, we contented ourselves with approximate estimates for prolate shapes. Disregarding a potential temperature dependence of the ratio between the transverse and the longitudinal friction for a rod in equation (23) is justified for large particle aspect ratios, since the near-field solutions for the solvent flow are dominated by terms with the same radial dependence. Also, while Oseen’s treatment of the infinite cylinder in equation (21) adds a nonlinearity in $U$ to the Stokes problem, calling for a nonlinear (and non-Markovian) theory, the linear analysis of [32] remains valid for finite particles. It leaves only the (possibly difficult) technical problem of evaluating the flow velocity field from which the effective parameters are calculated.

We validated our theoretical predictions against large-scale MD simulations of a Lennard-Jones system with an immersed hot colloid, and by comparison with recent measurements of diffusing hot nanorods [24]. Thereby, we could quantitatively establish an effective equilibrium description for the nonequilibrium rotational motion of a heated Brownian particle. While the general procedures and results resemble those for translational motion [31], their analytical tractability and their detailed structure was found to be substantially different. From a comparison of the rotational and translational case, an ordering of the effective temperatures governing hot Brownian motion emerged. Our findings provide the basis for a quantitative investigation of the Brownian dynamics of particles of anisotropic shapes, interactions between hot particles [5] and self-thermophoretic Janus particles that move on persistent Brownian paths determined by mutual competition of rotational and translational hot Brownian motion [18].

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Appendix. Stokes’ problem for a viscosity step

From equations (49) and (53) of [31], the viscous dissipation function $\phi(r) = \int \phi(r) \, d\theta \, d\phi$ for a translating sphere, driven by the constant force $F = Fe_z$, follows as

$$\phi(r) = \frac{4\pi \eta}{r^8} \left[ 15a^2 - 3Fa_3r^2/(2\pi \eta) + r^4 \left( F^2/(16\pi^2 \eta^2) + F/(\pi \eta)a_2r^3 + 10a_2^2r^6 \right) \right] , \quad (A.1)$$

which depends on $\eta(r)$ in an intricate way, namely via equations (44) of [31]. While this allows for an explicit computation of $T_{\text{HBM}}$ once $\eta(r)$ is specified, general statements about the relative magnitudes of $T_{\text{HBM}}$ and $T_{\text{HBM}}^\theta$ seem thus hard to attain, even for the highly symmetric case of a spherical bead. We therefore content ourselves with outlining the principles how such general considerations might proceed, namely by considering a spherical bead and the class of step profiles,

$$r \leq \beta R : \eta(r) = \eta_0/\kappa, \quad r > \beta R : \eta(r) = \eta_0, \quad (A.2)$$
for which both the translational and rotational effective temperatures can be calculated analytically. Note that the common case of a fluid viscosity that decreases upon heating corresponds to $\kappa > 1$, while $\kappa < 1$ holds for dilute gases.

The effective rotational temperature $T_{\text{HBM}}^\theta$ follows from equation (18) and takes the simple form

$$\frac{T_{\text{HBM}}^\theta - T_0}{\Delta TR} = \frac{3 (\beta^4 - 1) \kappa + 3}{4 (\beta^4 - \beta \kappa + \beta)},$$

where $T_0$ is the ambient temperature.

For the translational case, the general ansatz for the velocity and pressure fields, $u = u_r e_r + u_\theta e_\theta$ and $p$, reads [40]:

$$u_r (r, \theta) = \left( a_0 + \frac{a_1}{r} + a_2 r^2 + \frac{a_3}{r^3} \right) \cos \theta,$$

$$u_\theta (r, \theta) = - \left( a_0 + \frac{a_1}{2r} + 2a_2 r^2 - \frac{a_3}{2r^3} \right) \sin \theta,$$

$$p (r, \theta) = p_0 + \left( \frac{a_1}{r^2} + 10a_2 r \right) \eta \cos \theta,$$

where $u_r$ and $u_\theta$ denote the radial and polar velocity components, respectively. While the coefficients are [40]

$$a_0 = u_0, \quad a_1 = -3u_0 R/2, \quad a_2 = 0, \quad a_3 = u_0 R^3/2,$$

in an infinite homogeneous system, where $u_0$ denotes the particle velocity relative to the resting fluid at infinity, the coefficients $a_i$ each take two $r$-dependent values for the step profile of the viscosity. These coefficients are found by matching the boundary conditions for the velocity and the stress at $r = R, r = \beta R$ and $r \to \infty$. More precisely, the following linear system of equations needs to be solved:

$$Ma = v$$

with

$$M \equiv \begin{pmatrix}
0 & 0 & 0 & 0 & 1 & 0 & 0 \\
R^3 & R^2 & R^5 & 1 & 0 & 0 & 0 \\
-2R^3 & -R^2 & -4R^5 & 1 & 0 & 0 & 0 \\
R^3 \beta^3 & R^2 \beta^2 & R^5 \beta^5 & 1 & -R^3 \beta^3 & -R^2 \beta^2 & -1 \\
-2R^3 \beta^3 & -R^2 \beta^2 & -4R^5 \beta^5 & 1 & 2R^3 \beta^3 & R^2 \beta^2 & -1 \\
0 & \frac{R^2 \beta^2 \eta_0}{\kappa} & \frac{2R^3 \beta^5 \eta_0}{\kappa} & \frac{2\eta_0}{\kappa} & 0 & -R^2 \beta^2 \eta_0 & -2\eta_0 \\
0 & 0 & \frac{R^2 \beta^5 \eta_0}{\kappa} & \frac{\eta_0}{\kappa} & 0 & 0 & -\eta_0
\end{pmatrix},$$

$$a \equiv \begin{pmatrix}
a_0 (r < \beta R) \\
a_1 (r < \beta R) \\
a_2 (r < \beta R) \\
a_3 (r < \beta R) \\
a_0 (r > \beta R) \\
a_1 (r > \beta R) \\
a_2 (r > \beta R) \\
a_3 (r > \beta R)
\end{pmatrix}, \quad v \equiv \begin{pmatrix}
U \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0
\end{pmatrix}, \quad a_2 (r > \beta R) = 0.$$
Hence, for a viscosity profile that increases from
\[ \eta(\text{New Journal of Physics}) \]
Obviously, since \( \beta > 1 \) by definition, and thus \( \varepsilon > 0 \), each coefficient \( p_i \) in the numerator of equation (A.13) is strictly larger than the corresponding coefficient in the denominator, \( q_i \). Hence, for a viscosity profile that increases from \( \eta(R) \) to \( \eta_0 \) in a single step, we have shown that \( T_{\text{HBM}}^0 > T_{\text{HBM}}^1 \) holds.
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