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RESEARCH PAPER

Molecular spin in nano-confined fluidic flows

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Abstract In this paper, we study the effect of molecular spin on the fluid dynamics of molecular nano-confined fluids using the extended Navier–Stokes equations. We show that the effect of spin is non-negligible for non-steady flows and we then discuss two examples, namely, a zero mean oscillatory flow and an oscillatory lid driven cavity flow. In the discussion of the former, we propose a dimensionless quantity that qualitatively predicts the effect of the spin. From this it is shown that only for sufficiently small system sizes and extremely high frequencies will molecular spin be relevant, depending on the molecular fluid's rotational inertia and the rotational viscosity. In the lid driven cavity flow we observe that the thermodynamic energy dissipation due to molecular spin undergoes period doubling when increasing the Reynolds number and, under some circumstances, it may be negative.

Keywords Nano-confined fluids · Effect of molecular spin · Angular velocity · Unsteady flows · Viscous energy dissipation

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1 Introduction

In recent years, there has been an increasing focus on the theory and applicability of nanofluidics and nanofluidic devices (Eijkel and van den Berg 2005; Tabeling 2005; Bruus 2008). In such devices very small volumes of fluid are transported around and mixed in nano sized channels and chambers, and the flow is often driven by using pumping and mixing mechanisms which generate non-zero mean oscillatory flows (Richter and Wioas 1998; Okkels and Tabeling 2004; Hansen and Ottesen 2006). Nanofluidic flows are characterised by many distinctive properties such as large surface to volume ratios and relatively low Reynolds number (Tabeling 2005; Bruus 2008). On these small length scales it is questionable whether the classical Navier–Stokes description is valid. Travis et al. (1997a) have shown via molecular dynamics simulations of a Poiseuille flow that the classical Navier–Stokes theory is a satisfactory fluid dynamical description for systems with a characteristic length scale as small as 7–8 atomic diameters. Data from molecular dynamics simulations have also been successfully compared with the solution to the Navier–Stokes equation of nano-confined fluids undergoing oscillatory flow with extremely high frequencies of up to 10^2 GHz (Hansen and Ottesen 2006; Hansen et al. 2007). In fact, molecular dynamics has proved to be a very potent method to study nanofluids, and it has been confirmed that the Navier–Stokes equation is valid for surprisingly small time and length scales, see for example Ashurst and Hoover (1975) and Travis et al. (1997a).

While successfully describing many systems on very small scales, the classical Navier–Stokes theory is rather coarse grained in that many microscopic degrees of freedom are ignored, and they are assumed to have no effect on the translational motion of the fluid. However, it is well known that for molecular fluids the translational momentum couples to the intrinsic angular momentum, due to the fact that there exists an exchange between the fluid vorticity and the molecular angular velocity (Born 1920; Snider and Lewchuk 1967; de Groot and Mazur 1984). This means that, in principle, the Navier–Stokes analysis should include the effects of these microscopic degrees of freedom. While this fact is well known no one has to our knowledge made a general study of the conditions under which the effects of microscopic degrees of freedom become important and should be included in the fluid dynamical description. It is the purpose of this paper to do just that. We shall limit ourselves to isotropic and relatively dense fluids composed of rigidly bonded uniaxial molecules for which the extended Navier–Stokes equations have already been formulated (de Groot and Mazur 1984; Evans and Streett 1978) and the relevant transport coefficients computed (Moore et al. 2008). It will become clear that the effect of the molecular spin cannot in general be ignored, but that any effect from the coupling is only observed under extreme situations of very highly confined fluids and extremely large frequencies. The spin may then be relevant, in for example acoustic mixing using surface acoustic waves (SAWs) pressure oscillations, where frequencies of around 0.1 GHz are used (Guttenberg et al. 2006; Sritharan et al. 2006). Also, since these high frequencies are the only obtainable frequencies in molecular dynamics, comparison between molecular dynamics simulation data and the Navier–Stokes equation must include the effect of spin.

The paper is organised as follows. In the next section, we write the extended Navier–Stokes equations and we justify a few approximations, which will lead to a set of tractable equations in some cases. In this section, we also show that if the flow is steady and is characterised by a low Reynolds number the effect from the fluid spin can be ignored. In Sect. 3 we discuss two different examples where the molecular spin has an effect on the flow, namely, a zero mean oscillatory flow in a cylinder and a two dimensional oscillatory lid driven cavity flow. The last section is devoted to summary and conclusions.

2 Extended Navier–Stokes equations

For a single component isotropic fluid consisting of rigidly bonded molecules and in the absence of external body forces and torques, the mass conservation equation and the extended Navier–Stokes equations, which include the coupling between the translational velocity field $\mathbf{u}$, and the spin angular momentum per unit mass $\mathbf{s}$, read (Snider and Lewchuk 1967; Evans and Streett 1978; de Groot and Mazur 1984):

$$\frac{D\rho}{Dt} = -\rho(\nabla\cdot\mathbf{u}) \tag{1}$$

$$\rho\frac{D\mathbf{u}}{Dt} = -\nabla p + (\eta_v + \eta_0/3 - \eta_r)\nabla(\nabla\cdot\mathbf{u}) + (\eta_0 + \eta_r)\nabla^2\mathbf{u} + 2\eta_r(\nabla\times\boldsymbol{\Omega}) \tag{2}$$

$$\rho\frac{D\mathbf{s}}{Dt} = 2\eta_r(\nabla\times\mathbf{u} - 2\boldsymbol{\Omega}) + (\zeta_v + \zeta_0/3 - \zeta_r)\nabla(\nabla\cdot\boldsymbol{\Omega}) + (\zeta + \zeta_r)\nabla^2\boldsymbol{\Omega} \tag{3}$$

Here ρ is the mass density, p the pressure, and $\boldsymbol{\Omega}$ the spin angular velocity. The transport coefficients η_v, η_0 and η_r are the bulk, shear and rotational viscosities respectively, and ζ_v, ζ_0 and ζ_r the equivalent vortex spin viscosities. It is important to note that the total angular momentum is a conserved quantity. However, since it is a sum of the orbital angular momentum and the spin angular momentum, these two contributions need not to be conserved, hence the production term in Eq. 3. The fluid is assumed to be perfectly viscous and the transport coefficients are true constants and independent of temperature and density. This assumption is not strictly true. It has been shown that the transport properties near the wall-fluid boundary are different from those in the bulk, see e.g. Hansen et al. (2007). However, as mentioned in the introduction the classical Navier–Stokes description is indeed valid for systems with channel widths of more than 7–8 molecular diameters, so we shall assume this is the situation throughout the paper. Using molecular dynamics simulations, Evans and Streett (1978) have calculated the transport coefficients for liquid nitrogen at $T = 78.2$ K and $\rho = 0.798$ g/cm^3. They found that the vortex spin viscosities, ζ_v, ζ_0 and ζ_r, are of the order of 10^{-24} kg m s^{-1}, which is many orders of magnitude smaller than the rotational viscosity which is $\eta_r = 4 \times 10^{-5}$ kg m^{-1} s^{-1} (Evans and Hanley 1982). It is here important to note that the rotational viscosity can be of the same order of magnitude as the shear and bulk viscosities (Moore et al. 2008). Thus, for a sufficiently dense incompressible fluid the Navier–Stokes equations can be approximated to:

$$\rho\frac{D\mathbf{u}}{Dt} = -\nabla p + (\eta_0 + \eta_r)\nabla^2\mathbf{u} + 2\eta_r(\nabla\times\boldsymbol{\Omega}) \tag{4}$$

$$\rho\frac{D\mathbf{s}}{Dt} = 2\eta_r(\nabla\times\mathbf{u} - 2\boldsymbol{\Omega}) \tag{5}$$

It should be noted that this approximation is not necessarily valid for dilute gases since η_r decreases as a function of density (Moore et al. 2008), leaving the diffusion term in Eq. 3 non-neglectable. For gasses the incompressibility criterion, $\nabla\cdot\mathbf{u} = 0$, is of course also compromised. The production term on the right hand side of Eq. 5 gives the effect the exchange between the fluid vorticity and the angular velocity has on the angular momentum. The case where:

$$\nabla \times \mathbf{u} = 2\boldsymbol{\Omega} \tag{6}$$

means that there exists no exchange, or equivalently no thermodynamical force, giving $\rho D\mathbf{s}/Dt = 0$. The force is denoted the sprain rate (Edberg et al. 1987) and is given directly by:

$$\mathbf{X}_s = \nabla \times \mathbf{u} - 2\boldsymbol{\Omega} \tag{7}$$

For fluids composed of rigidly bonded uniaxial molecules the angular momentum can be written as Travis et al. (1997a):

$$\mathbf{s} = \Theta\boldsymbol{\Omega} \tag{8}$$

where Θ is one third of the trace of the moment of inertia tensor per unit mass and is given as $\Theta = 2I_p/3$, where I_p is the principal moment of inertia (Goldstein et al. 2002). Here we have assumed that the molecules are sufficiently heavy and the temperature is sufficiently high such that the rotational energy levels are well approximated by a continuous spectrum, see also Hill (1986). For uniaxial molecules Eq. 5 can therefore be written as:

$$\rho\Theta\frac{D\boldsymbol{\Omega}}{Dt} = 2\eta_r(\nabla \times \mathbf{u} - 2\boldsymbol{\Omega}) \tag{9}$$

For small Reynolds numbers and for steady flows, $\partial\boldsymbol{\Omega}/\partial t = \mathbf{0}$, the substantial derivative vanishes, $D\boldsymbol{\Omega}/Dt = \mathbf{0}$ in Eq. 9, yielding the relation:

$$\boldsymbol{\Omega} = \frac{1}{2}(\nabla \times \mathbf{u}) \tag{10}$$

which is the relation given in Eq. 6. This means that:

$$\begin{aligned}\nabla \times \boldsymbol{\Omega} &= \frac{1}{2}\nabla \times (\nabla \times \mathbf{u}) = \frac{1}{2}\left(\nabla(\nabla \cdot \mathbf{u}) - \nabla^2\mathbf{u}\right)\\ &= -\frac{1}{2}\nabla^2\mathbf{u}\end{aligned} \tag{11}$$

due to the divergence free condition $\nabla \cdot \mathbf{u} = 0$. Substituting this into the right hand side of Eq.(4) we obtain the classical Navier–Stokes equation:

$$\rho\frac{D\mathbf{u}}{Dt} = -\nabla p + \eta_0\nabla^2\mathbf{u} \tag{12}$$

and the translational velocity field is independent of the molecular spin. This, however, is only true for flows where spin inertia effects are zero, i.e. the relation given in Eq. 6 cannot be applied in the general case, say in an oscillatory or turbulent flow. This means that the coupling between the angular and translational velocity fields should be included, and only careful analysis can reveal whether is it safe to ignore the coupling effect.

In a fluid where the divergence of the velocity and angular velocity fields are zero, it is straight forward to formulate the coupling between the angular velocity and the vorticity, $\boldsymbol{\omega} = \nabla \times \mathbf{u}$. Thus, taking the curl of both sides of Eq. 4 yields.

$$\rho\frac{D\boldsymbol{\omega}}{Dt} = (\eta_0 + \eta_r)\nabla^2\boldsymbol{\omega} + \boldsymbol{\omega} \cdot \nabla\mathbf{u} - 2\eta_r\nabla^2\boldsymbol{\Omega} \tag{13}$$

$$\rho\Theta\frac{D\boldsymbol{\Omega}}{Dt} = 2\eta_r(\boldsymbol{\omega} - 2\boldsymbol{\Omega}) \tag{14}$$

where the last term in Eq. 13 is due to $\nabla \cdot \boldsymbol{\Omega} = 0$:

$$\begin{aligned}\nabla \times (2\eta_r(\nabla \times \boldsymbol{\Omega})) &= 2\eta_r\left(\nabla(\nabla \cdot \boldsymbol{\Omega}) - \nabla^2\boldsymbol{\Omega}\right)\\ &= -2\eta_r\nabla^2\boldsymbol{\Omega}\end{aligned} \tag{15}$$

In this case the condition $D\boldsymbol{\Omega}/Dt = \mathbf{0}$ leads to:

$$\nabla^2\boldsymbol{\Omega} = \frac{1}{2}\nabla^2\boldsymbol{\omega} \tag{16}$$

and the vorticity decouples from the angular velocity, hence, the classical formalism is recaptured. The divergence free criteria, $\nabla\cdot\mathbf{u} = 0$ and $\nabla \cdot \boldsymbol{\Omega} = 0$, are of course assumptions. The former is just the ordinary incompressibility approximation, however, the latter condition may not be easily justified. For steady flows it is trivial to show since for sufficiently dense systems: $\nabla \cdot \boldsymbol{\Omega} \approx \frac{1}{2}\nabla \cdot \boldsymbol{\omega} = 0$. In, for example, two dimensional flows the angular velocity can be thought of as a vector quantity which is parallel to the homogeneous direction. In this direction, e.g. the z-direction, the angular velocity is constant, i.e. $\partial\Omega_z/\partial z = 0$. We will here only work in one or two dimensional systems, where the divergence free condition is valid, however, in general the condition may not apply and the second equation in Eq. 15 should be used.

3 Discussion: two examples

3.1 Zero mean oscillatory flow

Consider a molecular fluid which is confined in a cylinder with coordinates (r, ϕ, z). We assume the fluid is symmetric around the main z-axis, i.e. the velocity is independent of the azimuthal angle ϕ, and that there exists a pressure gradient in the z-direction. Furthermore, if the pressure gradient is sufficiently small the extended Navier–Stokes equations in cylindrical coordinates read:

$$\begin{aligned}\frac{\partial u_z(r,t)}{\partial t} =& -\frac{1}{\rho}\frac{\partial p(z,t)}{\partial z} + (\nu_0 + \nu_r)\left[\frac{\partial^2 u_z(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial u_z(r,t)}{\partial r}\right]\\ &+ \frac{2\nu_r}{r}\frac{\partial\left[r\Omega_\phi(r,t)\right]}{\partial r}\end{aligned} \tag{17}$$

$$\Theta\frac{\partial\Omega_\phi(r,t)}{\partial t} = -2\nu_r\left[\frac{\partial u_z(r,t)}{\partial r} + 2\Omega_\phi(r,t)\right] \tag{18}$$

where ν_0 and ν_r are the kinematic viscosities. We will in this section show the r and t dependence of the translational and angular velocities explicitly. The simplest unsteady flow is probably a zero mean oscillatory flow, where the pressure gradient can be written as a trigonometric function in time, e.g. $-(1/\rho)\partial p(z, t)/\partial z = P_0 \cos(\omega_f t)$, where P_0 is the pressure gradient amplitude divided by the density and ω_f is the angular frequency of the pressure gradient. In accordance with the usual approach, the problem can be simplified by adopting complex notation (Engelund 1968), i.e:

$$-\frac{1}{\rho}\frac{\partial p(z,t)}{\partial z} = Re\{P_0 e^{i\omega_f t}\} \tag{19}$$

If we limit ourselves to only study the limiting behavior $t \to \infty$, where all transients have decayed to zero, the translational and angular velocities are decomposed into products of spatial and temporal parts:

$$u_z(r,t) = Re\{U(r)e^{i\omega_f t}\} \quad \text{and} \quad \Omega_\phi(r,t) = Re\{\Omega(r)e^{i\omega_f t}\} \tag{20}$$

Substituting Eqs. 19 and 20 into Eqs. 17 and 18 we obtain the following inhomogeneous second order ordinary differential equation system:

$$i\omega_f U(r) = P_0 + (\nu_0 + \nu_r)\left[\frac{d^2U(r)}{dr^2} + \frac{1}{r}\frac{dU(r)}{dr}\right] + \frac{2\nu_r}{r}\frac{d[r\Omega(r)]}{dr} \tag{21}$$

$$\Theta i\omega_f \Omega(r) = -2\nu_r\left[\frac{dU(r)}{dr} + 2\Omega(r)\right] \tag{22}$$

Equation 22 provides a useful relation between the angular and translational velocities, namely:

$$\Omega(r) = -\frac{2\nu_r}{i\Theta\omega_f + 4\nu_r}\frac{dU(r)}{dr} \tag{23}$$

Thus, Eq. 21 can be written as:

$$\frac{d^2U(r)}{dr^2} + \frac{1}{r}\frac{dU(r)}{dr} - \frac{i\omega_f}{\alpha}U = -\frac{P_0}{\alpha} \tag{24}$$

where

$$\alpha = \nu_0 + \nu_r - \frac{4\nu_r^2}{i\Theta\omega_f + 4\nu_r} \tag{25}$$

Equation 24 is the Bessel equation. Thus, applying no-slip boundary conditions $U(R) = 0$ where R is the cylinder radius, the solution for $u_z(r, t)$ is:

$$u_z(r,t) = Re\left\{\frac{P_0}{i\omega_f}\left[1 - \frac{J_0(\lambda r)}{J_0(\lambda R)}\right]e^{i\omega_f t}\right\} \tag{26}$$

where J_0 is the zero order Bessel function of the first kind and $\lambda = \sqrt{-i\omega_f/\alpha}$. This solution has the same functional form as the classical treatment where the molecular spin is ignored (White 2006), however, in this case Eq. 25 reads $\alpha = \nu_0$. The angular velocity is given by Eqs. 26 and 23:

$$\Omega_\phi(r,t) = Re\left\{\frac{2\nu_r P_0 \lambda}{\Theta\omega_f^2 + i4\omega_f\nu_r}\frac{J_1(\lambda r)}{J_0(\lambda R)}e^{i\omega_f t}\right\} \tag{27}$$

i.e. the angular velocity is related to the first order Bessel function of the first kind, J_1. Finally, the sprain rate follows directly from Eq. 7:

$$X_s(r,t) = Re\left\{\frac{\theta P_0 \lambda}{i\theta\omega_f + 4\nu_r}\frac{J_1(\lambda r)}{J_0(\lambda R)}e^{i\omega_f t}\right\} \tag{28}$$

A comment regarding Eq. 27 is in place. It is readily seen that at the wall boundary, $r = R$, $\Omega_\phi(R, t) \neq 0$. This is not strictly true. It has been shown in several molecular dynamics simulation studies of molecular fluids (Travis et al. 1997b; Travis and Evans 1997; Delhommelle and Evans 2002; Hansen et al. 2008), that the angular velocity is indeed zero for $r = R$, i.e. the correct boundary condition for the angular velocity is a non-slip condition. However, depending on the values of the vortex spin viscosities, ζ_0 and ζ_r, the effect from the boundary can be ignored even very close the wall. Here we only treat the limit $\zeta_r + \zeta_0 \to 0$, hence this boundary effect is ignored all together. The no-slip boundary condition, $U(R) = 0$, is not always true for nanofluidic flows (Bruus 2008). However, this condition is valid if the attraction between the wall and the fluid is sufficiently strong. We will here limit ourselves to study the effect of molecular spin and assume that the no-slip boundary condition is fullfilled. In Fig. 1 we have plotted two streaming velocity profiles given by Eq. 26, where $\nu_r \neq 0$ and $\nu_r = 0$ for liquid molecular chlorine. Table 1 lists the parameter values used in this section. First, it is important to notice that a difference between the two profiles is only observed for very high values of angular frequency ω_f, and small channel radii R. This is, as mentioned earlier, typical of the conditions under which molecular dynamics simulations operate. Also, it is

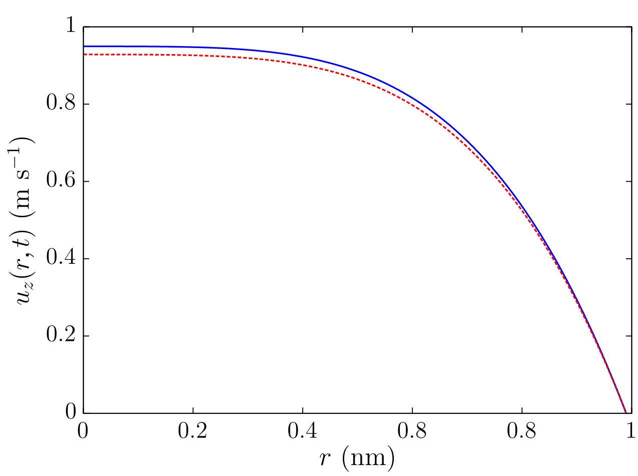

Fig. 1 Zero mean oscillatory flow: velocity profiles for $\nu_r = 0$ (*full line*) and for $\nu_r \neq 0$ (*broken line*). $\omega_f = 1 \times 10^2$ GHz and $t = 0$. See Table 1 for other parameter values

Table 1 Parameter values for liquid molecular chlorine and the pressure gradient amplitude divided with the density P_0

Coefficient	Value	Units
ρ	1354.6	kg m^{-3}
T	178	K
ν_0	9.88×10^{-8}	m^2 s^{-1}
ν_r	9.18×10^{-9}	m^2 s^{-1}
Θ	1.44×10^{-20}	m^2
$P_0\rho$	0.62	mPa

The inertia is calculated as $\Theta = 2\ I_p/3$, where I_p is the principal inertia of the chlorine molecule. The viscosities are taken from Moore et al. (2008)

important to realize that the Navier–Stokes equations are valid even under these conditions, as it has been shown in several studies, see for example (Travis and Evans 1997; Hansen and Ottesen 2006; Hansen et al. 2008).

Equation 25 is quite informative in that the limits:

$$\lim_{\Theta\omega_f \to 0} \alpha = \nu_0 \quad \text{and} \quad \lim_{\Theta\omega_f \to \infty} \alpha = \nu_0 + \nu_r \tag{29}$$

indicate the minimum and maximum effect we can expect the molecular spin to have on the fluid's translational motion. The first limit is of course the classical situation where the spin is ignored, $\Theta = 0$. The second limit states that the effect from the spin is limited to the relative value between the rotational and the shear viscosities. This could indicate that the relative effect from the molecular spin can be estimated from the dimensionless fraction $\Theta\omega_f\nu_r/\nu_0^2$. However, for very large values of ω_f the flow is characterised by an Euler fluid (Engelund 1968), i.e. the inertia forces dominate and the velocity profile is flat except from near the wall. According to Eq. 23 this means that the angular velocity is zero almost everywhere having an effect only in the vicinity of the wall. Thus, the near-wall effects are relatively small compared with the total fluid flow. This can be quantified by the Stokes parameter, $\Lambda = \sqrt{\omega_f/\nu_0}R$, such that for sufficiently large values of Λ the inertia forces dominate, and the viscous terms are negligible. We therefore propose the following number to qualitatively describe the relative effect of the spin:

$$\varepsilon = \frac{\omega_f\Theta\nu_r}{\nu_0^2}\frac{1}{\Lambda} = \frac{\Theta\nu_r}{R}\left[\frac{\omega_f}{\nu_0^3}\right]^{\frac{1}{2}} \tag{30}$$

such that:

$$\alpha \to \nu_0 \quad \text{for} \quad \varepsilon \to 0 \quad \text{and} \quad \alpha \to \nu_0 + \nu_r \quad \text{for} \quad \varepsilon \to \infty \tag{31}$$

It is interesting to notice that Eq. 30 states that the effect of molecular rotation is independent of the pressure amplitude and therefore the Reynolds number. The reason for this is that it is the exchange between vorticity and spin angular velocity that affects the translational motion of the fluid. Now, this exchange does not depend on the absolute value of the flow velocity, but on the difference between the vorticity (which is related to the gradients of the velocity) and the spin angular velocity. It does not matter how fast the fluid flows, i.e. how high the Reynolds number is; if the vorticity is two times the angular velocity no exchange between the vorticity and the angular velocity takes place and no effect will be observed. One can also define a characteristic frequency based on the relaxation time (de Groot and Mazur 1984):

$$\omega_s = \frac{4\nu_r}{\Theta} \tag{32}$$

such that if $\omega_f \approx \omega_s$ spin inertia effect will be present. This, however, does not describe the relative effect of spin nor the effect from the confinement.

One way to quantitatively study the effect is by defining the absolute flow difference during a pressure cycle as:

$$\Delta Q = 2\int_0^{\frac{2\pi}{\omega_f}}\int_0^R |\Delta u_z(r,t)|\,\mathrm{d}r\,\mathrm{d}t \tag{33}$$

where:

$$\Delta u_z(r,t) = |u_z(r,t;\varepsilon = 0)| - |u_z(r,t;\varepsilon \neq 0)| \tag{34}$$

The absolute flow difference can be normalized with the absolute flow in the case where the spin is ignored:

$$Q_{\varepsilon=0} = 2\int_0^{\frac{2\pi}{\omega_f}}\int_0^R |u_z(r,t;\varepsilon = 0)|\,\mathrm{d}r\,\mathrm{d}t \tag{35}$$

in order to extract the relative effect.

Using the parameter values listed in Table 1, the fraction $\Delta Q/Q_{\varepsilon=0}$ is calculated for different values of the angular frequency, ω_f, and cylinder radius, R. The results are depicted in Fig. 2. It is particularly interesting to note that ε roughly captures the qualitative effect of varying ω_f and R, i.e. the effect is inversely proportional to R and square root dependent on ω_f. For even larger frequencies, $\omega_f > 1 \times 10^4$ GHz, the effect shows a dramatic drop since the system moves into the Euler regime which is not captured by ε. Using the fraction $\Delta Q/Q_{\varepsilon=0}$ as a direct measure of the effect of including the molecular spin, it can be observed that for $\varepsilon \approx 3 \times 10^{-3}$ the effect is around 1%.

For the chlorine molecule:

$$\varepsilon \approx 4.6 \times 10^{-18}\,\mathrm{m}\sqrt{\mathrm{s}}\,\frac{\sqrt{\omega_f}}{R} \tag{36}$$

over a very large range of temperatures and densities (Moore et al. 2008), which means that we can only expect any effect from the molecular spin for extremely large values of ω_f and low values of R. The reason for the small

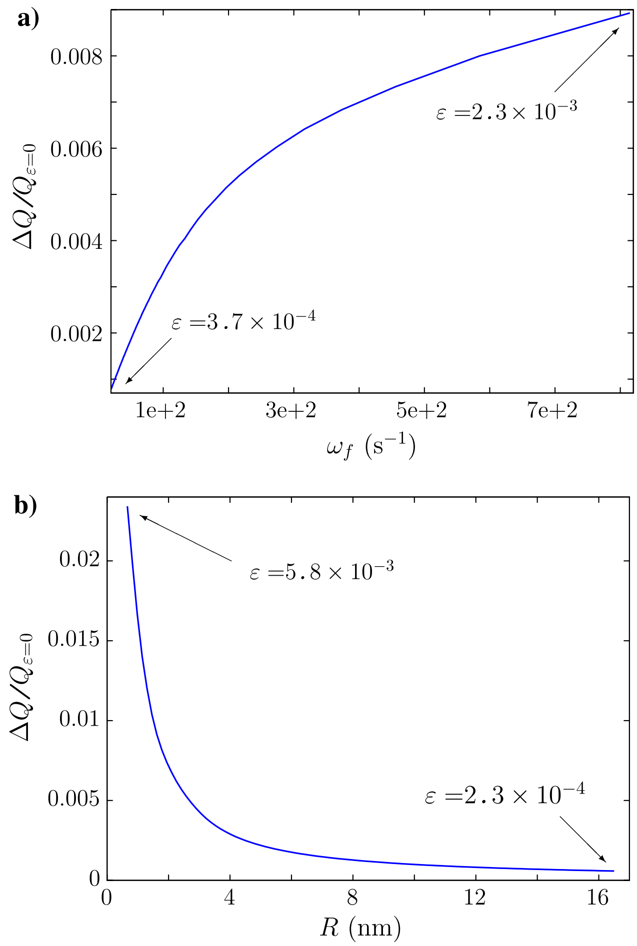

Fig. 2 Zero mean oscillatory flow: **a** $\Delta Q/Q_{\varepsilon=0}$ as a function of ω_f. $R = 0.53$ nm. **b** $\Delta Q/Q_{\varepsilon=0}$ as a function of R. $\omega_f = 8.1 \times 10^2$ GHz. The other parameter values are listed in Table 1

numerical factor with units of $\mathrm{m}\sqrt{\mathrm{s}}$ in Eq. 36 is due to the very small value of the principal moment of inertia, I_p, for the chlorine molecule. It is important to note here that I_p can be orders of magnitude larger for alkenes, large rod-like and liquid crystal molecules. Furthermore, from Eq. 30 it can be seen that increasing the fraction ν_r/ν_0 will also increase the effect of the molecular spin. For a molecular chlorine fluid this fraction is around 0.1, but it has been shown that it can be as large as 0.5 (Moore et al. 2008). Figure 3 shows the effect of increasing ν_r/ν_0 using larger value of the principal inertia. It is seen that the flow is dramatically effected (more than an 11% deviation), which is also expected from the fact that $\varepsilon = 0.36$ for $\nu_r/\nu_0 = 1$. It must be stressed, however, that for large molecules the frequency dependence of the viscosities must be considered. For a confined fluid where $\Theta = 1 \times 10^{-19}$ m^2, $\nu_r = \nu_0/2$, $\nu_0 = 1 \times 10^{-6}$ m^{2}s^{-1} and $R = 5$ nm, $\varepsilon \approx 1 \times 10^{-3}$ for $\omega_f = 0.1$ GHz. This means that for such a system the SAWs technique could be used to study the effect of molecular spin. As mentioned above, ε predicts that the effect of the spin is independent of the Reynolds number. We have varied $P_0\,\rho$ from 0.62 to 62 mPa without seeing any notable change in $\Delta Q/Q_{\varepsilon=0}$.

3.2 Two dimensional divergence free lid-driven cavity flow

From Eqs. (13) and (14) the vorticity-stream function formulation is written in two spatial dimensions $\mathbf{r} = (x, y)$ as:

$$\frac{\partial \omega}{\partial t} = -(\mathbf{u}\cdot\nabla)\omega + (\nu_0 + \nu_r)\nabla^2\omega - \nu_r\nabla^2\Omega_z \tag{37}$$

$$\frac{\partial \Omega_z}{\partial t} = \frac{2\nu_r}{\Theta}(\omega - 2\Omega_z) \tag{38}$$

$$\nabla^2\psi = -\omega, \quad u = \frac{\partial \psi}{\partial y}, \quad v = -\frac{\partial \psi}{\partial x} \tag{39}$$

where $\mathbf{u} = (u, v)$ is the two dimensional velocity field and ψ the streaming function. The boundary conditions are formulated as:

$$\psi = 0, \quad \frac{\partial \psi}{\partial \mathbf{n}} = \mathbf{0} \quad \text{on} \quad \partial\Gamma \tag{40}$$

where $\partial\Gamma$ denotes the boundary of the square domain $\Gamma = [0, L] \times [0, L]$, where $L = 100$ is the box length (x-direction) and height (y-direction). Equation 40 is the no-flux no-slip boundary condition (Meth 1994). In the stationary case, the cavity flow is often driven by moving the upper boundary (the lid) by letting u be given by some functional form, e.g. $u_b = 1$ or $u_b = 16(x/L)^2(1-(x/L)^2)$ (EW and Liu 1996a). Since there is no justification for the choice of upper boundary condition, we have here chosen for convenience to let the flow be driven by the vorticity rather than the velocity by letting:

$$\omega_b = \frac{4Ax}{L}\left(1 - \frac{x}{L}\right)\cos(\omega_f t) \tag{41}$$

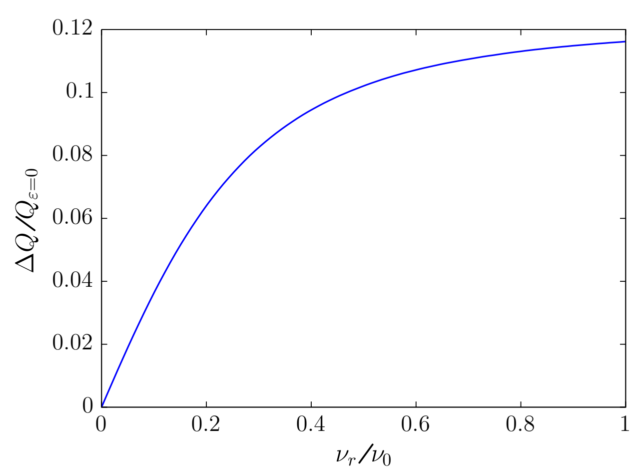

Fig. 3 Zero mean oscillatory flow: $\Delta Q/Q_{\varepsilon=0}$ as a function of ν_r/ν_0 for $\Theta = 2.5 \times 10^{-19}$ m^2, $R = 1.8$ nm and $\omega_f = 8.1 \times 10^2$ GHz

at the upper y-boundary. In Eq.(41) A is a parameter that controls the amplitude and therefore the Reynolds number. As it is seen in Fig. 4 the chosen boundary condition results in very reasonable profiles for u at the upper boundary. Especially, is it worth noting that at the upper corners of the domain, $(0,L)$ and (L, L), the velocity is zero as one would expect and not a constant value. In fact, this driving boundary condition closely resembles the polynomial expression used in E and Liu (1996a). Equations (37)–(39) with boundary conditions given by Eq.(40) can then be solved numerically using a finite difference scheme. We have applied a scheme which is of second order accuracy in space and fourth order accuracy in time which is needed for arbitrary values of the Reynolds number (E and Liu 1996a). In Appendix A we describe the numerical implementation in detail.

An example of the instantaneous velocity field is given in Fig. 5 where $\varepsilon = 0.014$. Two counter rotating vortices are seen. For other times only one main vorticity is observed, due to the oscillatory lid. In Fig. 6a and b u and v are shown as a function of the y coordinate at $x = L/2$. For this system $\varepsilon = \Theta v_r/L\sqrt{\omega_{\rm f}/v_0^3} = 0.014$ which is realistic for molecular fluids with sufficiently high moment of inertia and rotational viscosity as discussed above. The resulting value for the fraction $\Delta Q/Q_{\varepsilon=0}$ is as large as 0.30, that is, including the molecular spin into the fluid dynamical description will lead to a 30 % deviation in the absolute flow compared to the classical formulation. In the classical fluid dynamical description the angular momentum due to the molecular spin is ignored all together, however, using the extended theory valuable fluid dynamical information is readily available. As an example, the angular velocity and the sprain rate are plotted in

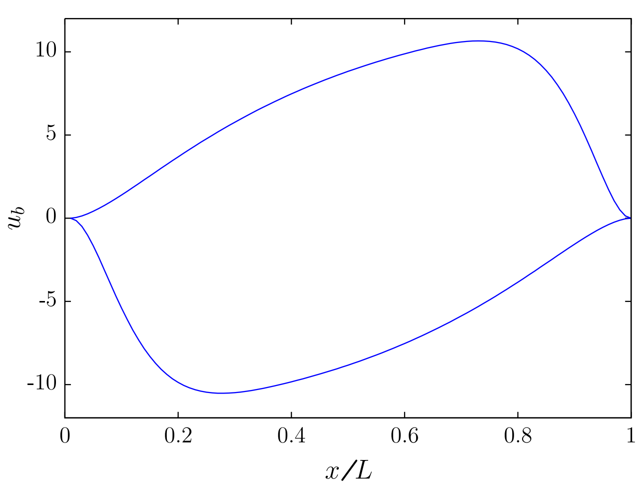

Fig. 4 Lid-driven cavity flow: examples of two velocity profiles for the velocity component u at the upper boundary, $y = L$. The profiles are $\pi/\omega_{\rm f}$ out of phase. The velocity is given in arbitrary units

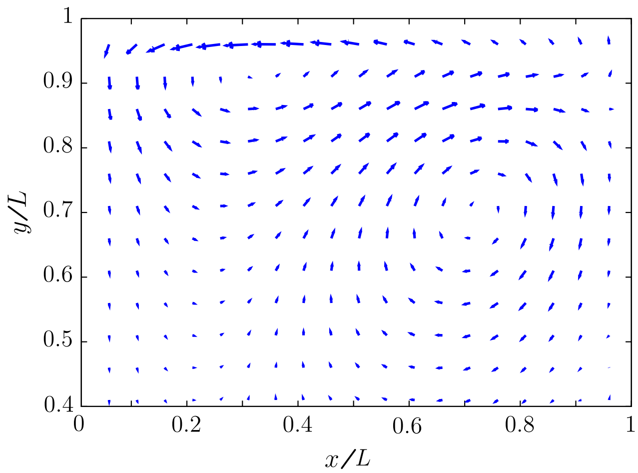

Fig. 5 Lid-driven cavity flow: snap shot of the velocity field. Notice that not all the y points are shown in order to highlight the system near the lid

Fig. 6c. It can be seen that the sprain rate is largest in the region next to the moving lid, which will result in large deviations in this region, as also depicted in Fig. 6a and b.

Another interesting quantity to study is the thermodynamic energy dissipation. To this end we write the balance equation for the internal energy field ϕ, as Evans and Streett (1978):

$$\rho\frac{D\phi}{Dt} = -\nabla\cdot\mathbf{J}_q - \nabla\mathbf{u} : \mathbf{P}^T - 2\overset{d}{\mathbf{P}}\cdot\mathbf{\Omega} \tag{42}$$

where $\mathbf{J}_q$ is the heat flux vector, $\mathbf{P}$ is the pressure tensor, and $\overset{d}{\mathbf{P}}$ is the pseudo dual vector of the anti symmetric part of the pressure tensor. Note that the term involving the couple tensor (Evans and Streett 1978) has been ignored as discussed in Sect. 2. For a purely viscous two dimensional incompressible fluid the dissipation function, Φ, can then be written as:

$$\Phi = \rho v_0\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right) : \nabla\mathbf{u} - \rho v_r(\omega - 2\Omega_z)\Omega_z \tag{43}$$

by applying the constitutive relations given in Evans and Streett (1978). From this we can see that Φ is a sum of the viscous dissipation due to the translational motion, Φ_t, and the molecular spin, Φ_r, such that:

$$\begin{aligned}\Phi_t &= \rho v_0\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right) : \nabla\mathbf{u} \quad \text{and}\\ \Phi_r &= -\rho v_r(\omega - 2\Omega_z)\Omega_z\end{aligned} \tag{44}$$

while the thermodynamic dissipation due to the translational motion is always positive (for nonzero velocity gradients), the contribution from the spin may be zero, negative or positive. If the angular velocity is less than one half the vorticity the effect of the molecular spin on the dissipation is negative. On the other hand, if the angular velocity is larger than one half the vorticity, the molecular spin will lead to a positive contribution to

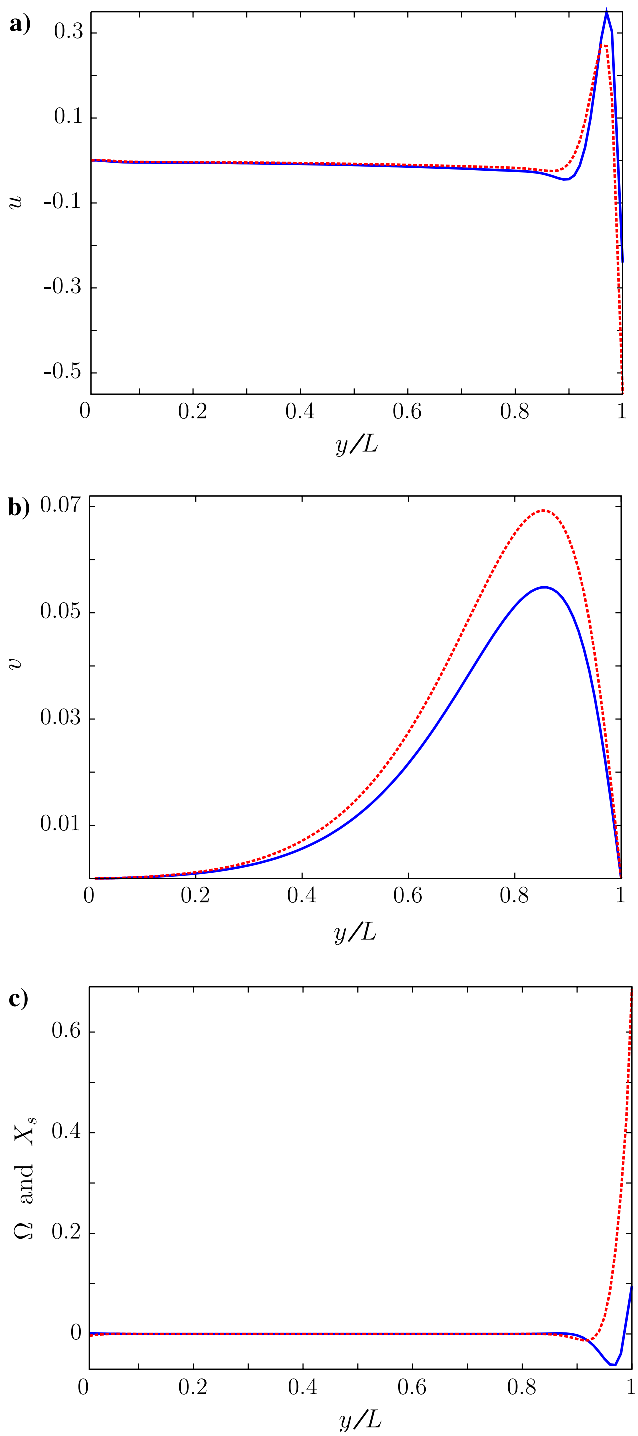

Fig. 6 Lid-driven cavity flow: **a** u as a function of y at $x = L/2$ for a given time. Full line is the situation where $\varepsilon = 0$, punctured line where $\varepsilon = 0.014$. **b** v as a function of y at $x = L/2$ for a given time. Full line is the situation where $\varepsilon = 0$, punctured line where $\varepsilon = 0.014$. **c** Example of the angular velocity (*full line*) and sprain rate (*punctured line*) as a function of y for $\varepsilon = 0.014$ at $x = L/2$. The quantities are given in arbitrary units

the dissipation. This is the same inertia effect as discussed in Sect. 2. The system's translational dissipation and spin dissipation are found by integrating over space:

$$\phi_t(t) = \int_\Gamma \Phi_t \mathrm{d}\mathbf{r} \quad \text{and} \quad \phi_r(t) = \int_\Gamma \Phi_r \mathrm{d}\mathbf{r} \tag{45}$$

where we have shown the time dependence explicitly. Figure 7a and b depict the dissipation due to molecular spin for relatively low and high Reynolds numbers which we define as:

$$Re = \sup_{0<t<2\pi/\omega_f} \left\{ \frac{\sup_{0<x<L}\{u_b(x,t)\}L}{v_0} \right\} \tag{46}$$

There are two interesting points to make. (1) It can be seen from Fig. 7a that for low Reynolds numbers $\phi_r(t)$ shows regular oscillations with constant amplitude. As the Reynolds number increases it is indicated in Fig. 7b that $\phi_r(t)$ undergoes a period doubling due to the nonlinear nature of the system at high Reynolds numbers. (2) The dissipation due to the molecular spin will contribute both negatively and positively to the overall dissipation over time, however, in this context it must be noted that:

$$\phi_t(t) \gg |\phi_r(t)| \tag{47}$$

and therefore the total dissipation is not greatly affected by the molecular spin and is always positive. The fact that the dissipation contribution from the molecular rotation can be negative is due to inertia effects. Consider some point in the oscillatory cycle, where the spin angular velocity is smaller than half the fluid vorticity. In this case there is an exchange between the system's vorticity and spin angular momentum, leading to an acceleration in molecular spin. Due to inertia effects this process is associated with an energy accumulation. This argument can also explain that when the angular velocity decelerates, $\Omega_z > \omega/2$, then due to inertia effects energy is released. Also, it should be mentioned that $\phi_t(t)$ features regular oscillations over the range of Reynolds numbers studied here.

4 Conclusion

In this paper, we have analysed the effect of including molecular spin into the fluid dynamical description. We argue that the extended Navier–Stokes equations can be simplified considerably due to the very low values of the vortex spin viscosities. This leads to a set of tractable equations in certain simple cases. We show that for low Reynolds number steady state flows, where the substantial

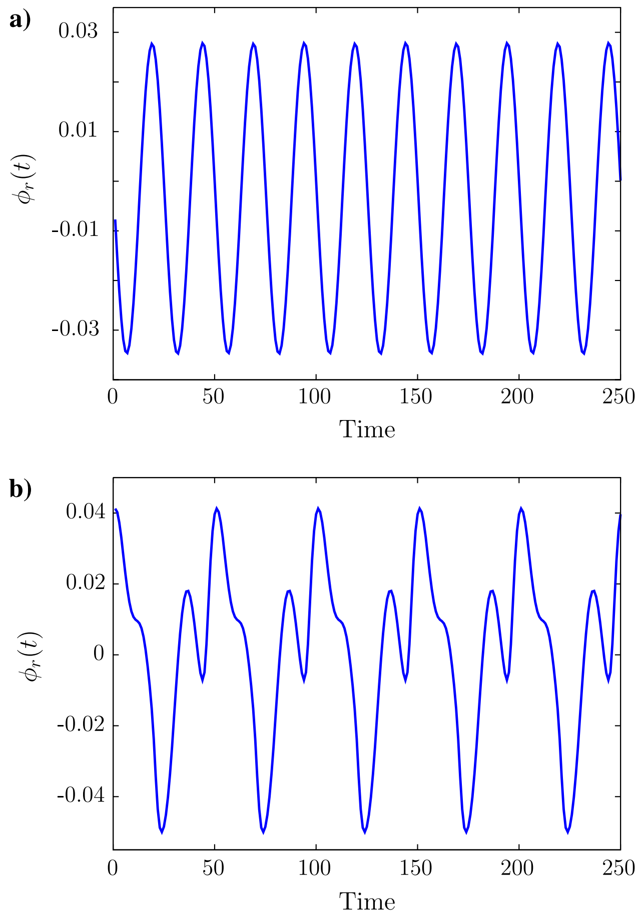

Fig. 7 Lid-driven cavity flow: **a** ϕ_r as a function of time for low Reynolds number of $Re = 64$, **b** ϕ_r as a function of time for high Reynolds number of $Re = 412$. The quantities are given in arbitrary units

derivative can be safely ignored, the translational motion decouples from the angular motion. However, this is not true in the general case and the dynamics of the fluid angular velocity should be included, and the effect analysed.

We qualitatively and quantitatively estimate the effect of the coupling using two different examples of unsteady flows, namely, a zero mean oscillatory flow in a cylindrical channel and a two dimensional lid driven cavity flow. In the first case, the extended Navier–Stokes equations can be solved analytically giving a solution. From this solution we are able to propose a dimensionless quantity, ε, in order to predict the qualitative effect of the spin as well as of the system size and frequency. By comparing the absolute flow difference between the extended and classical Navier–Stokes treatments for a molecular chlorine fluid, we find that this effect is roughly inversely proportional to the cylinder radius which is also predicted by ε. Moreover, the frequency dependence is found to follow an approximately square root law as predicted. For liquid molecular chlorine we find the absolute flow is reduced by around 1% when $\varepsilon \approx 3 \times 10^{-3}$.

For other fluids. e.g. alkene fluids, ε may be orders of magnitude larger due to higher value of the moment of inertia and relatively large rotational viscosity compared with the shear viscosity. For $\varepsilon = 0.14$ we find that the absolute flow difference in a two dimensional lid driven cavity flow can exceed more that 30%. For this system we also evaluated the dissipation due to the molecular spin. We find that for low Reynolds numbers the dissipation features temporal oscillatory behavior and can be negative. Moreover, as the Reynolds number increases these oscillations undergo a period doubling. The contribution to the total dissipation from the translational motion is always positive and orders of magnitude larger than the contribution from the spin, hence, the total dissipation is only slightly affected by the molecular spin.

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Numerical method

It is known that for incompressible advection diffusion equations a straight forward spatial central difference and forward Euler method is unconditionally unstable (E and Liu 1996a). However, by applying a third or higher order Runge–Kutta method this problem can be overcome (E and Liu 1996a, b, c). We will here use the fourth order Runge–Kutta method, which is extended straight forwardly to include the angular velocity:

$$\omega^{n+1} = \omega^n + \frac{\Delta t}{6}(f_1 + 2f_2 + 2f_3 + f_4) \tag{48}$$

$$\Omega_z^{n+1} = \Omega_z^n + \frac{\Delta t}{6}(g_1 + 2g_2 + 2g_3 + g_4) \tag{49}$$

$$\nabla^2\psi^{n+1} = -\omega^{n+1}, \quad u^{n+1} = \frac{\partial\psi^{n+1}}{\partial y}, \quad v^{n+1} = -\frac{\partial\psi^{n+1}}{\partial x} \tag{50}$$

where f_1 and g_1 are given by:

$$\frac{\omega_1 - \omega^n}{\frac{1}{2}\Delta t} = -(\mathbf{u}^n \cdot \nabla)\omega^n + (v_0 + v_r)\nabla^2\omega^n - v_r\nabla^2\Omega_z^n = f_1$$

$$\frac{\Omega_{z,1} - \Omega_z^n}{\frac{1}{2}\Delta t} = \frac{2v_r}{\Theta}(\omega^n - 2\Omega_z) = g_1$$

$$\nabla^2\psi_1 = -\omega_1, \quad u_1 = \frac{\partial\psi_1}{\partial y}, \quad v_1 = -\frac{\partial\psi_1}{\partial x} \tag{51}$$

f_2 and g_2:

$$\frac{\omega_2-\omega^n}{\frac{1}{2}\Delta t} = -(\mathbf{u}_1\cdot\nabla)\omega_1 + (\nu_0+\nu_r)\nabla^2\omega_1 - \nu_r\nabla^2\Omega_{z,1} = f_2$$
$$\frac{\Omega_{z,2}-\Omega_z^n}{\frac{1}{2}\Delta t} = \frac{2\nu_r}{\Theta}(\omega_1 - 2\Omega_{z,1}) = g_2 \tag{52}$$
$$\nabla^2\psi_2 = -\omega_2,\quad u_2 = \frac{\partial\psi_2}{\partial y},\quad v_2 = -\frac{\partial\psi_2}{\partial x}$$

f_3 and g_3:

$$\frac{\omega_3-\omega^n}{\Delta t} = -(\mathbf{u}_2\cdot\nabla)\omega_2 + (\nu_0+\nu_r)\nabla^2\omega_2 - \nu_r\nabla^2\Omega_{z,2} = f_3$$
$$\frac{\Omega_{z,3}-\Omega_z^n}{\Delta t} = \frac{2\nu_r}{\Theta}(\omega_2 - 2\Omega_{z,2}) = g_3$$
$$\nabla^2\psi_3 = -\omega_3,\quad u_3 = \frac{\partial\psi_3}{\partial y},\quad v_3 = -\frac{\partial\psi_3}{\partial x} \tag{53}$$

and, finally, f_4 and g_4:

$$f_4 = -(\mathbf{u}_3\cdot\nabla)\omega_3 + (\nu_0+\nu_r)\nabla^2\omega_3 - \nu_r\nabla^2\Omega_{z,3}$$
$$g_4 = \frac{2\nu_r}{\Theta}(\omega_3 - 2\Omega_{z,3}) \tag{54}$$

ω^n and Ω^n are the values of the vorticity and the angular velocity at any given point at time t, and ω^{n+1} and Ω^{n+1} are the new values at time $t+\Delta t$, where Δt is the time step. The spatial derivatives are evaluated by using the second order central difference scheme (Ferziger and Perić 2002) and the Poisson equation is solved using a relaxation method (Anderson 1995). The domain $\Gamma = [0,L]\times[0,L]$, where $L = 100$, was discretized into a uniform grid of size 100×100 given grid size of $\Delta x = \Delta y = 1$.

The non-flux no-slip boundary conditions were imposed on the stream function as stated in Sect. 2. For these boundary conditions, we applied Thom's formula (E and Liu 1996b):

$$\omega_{(i,1)} = -\frac{2}{\Delta x^2}\psi_{(i,2)}\quad \omega_{(i,100)} = -\frac{2}{\Delta x^2}\psi_{(i,99)}$$
$$\omega_{(1,j)} = -\frac{2}{\Delta y^2}\psi_{(2,j)} \tag{55}$$

where $(i, 1)$ runs over the boundary grids in the y-direction with $x = 0$ and so forth. For the angular velocity we used a simple linear extrapolation of the interior points to the boundary, e.g. for the boundary where $x = 0$:

$$\Omega_{z,(i,1)} = 2\Omega_{z,(i,2)} - \Omega_{z,(i,3)} \tag{56}$$

The time step was set to $\Delta t = 1\times10^{-3}$ or 5×10^{-4} (in arbitrary units) in order to satisfy the standard diffusive contraint:

$$\frac{\nu_0\Delta t}{\Delta x^2} \approx 0.002 < \frac{1}{2} \tag{57}$$

The initial conditions were set to $\omega_{(i,j)} = 0$ and $\Omega_{(i,j)} = 0$ in all interior grid points and the system ran for 10 periods which was enough to give steady amplitude oscillations. After this initialisation data were collected over a single period.

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