EXPLORING DRIVING FORCES AND LIQUID PROPERTIES FOR ELECTROKINETIC ENERGY CONVERSION

TRIEU NGUYEN

Exploring Driving Forces and Liquid Properties for Electrokinetic Energy Conversion

Trieu Nguyen

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**EXPLORING DRIVING FORCES AND LIQUID
PROPERTIES FOR ELECTROKINETIC ENERGY
CONVERSION**

DISSERTATION

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Contents

1	Aim and Outline of Thesis	1
1.1	Introduction	2
1.2	Objectives and organisation of the thesis	2
1.2.1	Objectives	2
1.2.2	Organisation of the thesis	4
2	Fundamental and Theoretical Aspects	7
2.1	Electrostatics in solution	8
2.1.1	Surface charging	8
2.1.2	Electrical double layers	8
2.1.3	Zeta potential	9
2.1.4	Potential distribution	9
2.2	Flow in microchannels	15
2.2.1	Fluid	15
2.2.2	Mass conservation	16
2.2.3	Momentum conservation	16
2.2.4	Boundary conditions	17
2.2.5	Reynolds number	17
2.2.6	Flow profile	17
2.2.7	Ionic currents during pressure-driven flow	22
2.3	Electrokinetic energy conversion	23
2.3.1	Maximal energy conversion efficiency	24

2.3.2	Onsager's relations	25
2.3.3	Figure of merit	27
3	Polymer solution in microchannel	33
3.1	Introduction	34
3.2	Materials and methods	35
3.2.1	Chip fabrication	35
3.2.2	Chemicals	35
3.2.3	Capillaries	36
3.2.4	Experimental setup	37
3.2.5	Operation	37
3.3	Results and Discussions	38
3.3.1	Input power	38
3.3.2	Output power	41
3.3.3	Conversion efficiency	41
3.3.4	Streaming current and streaming potential behavior	43
3.3.5	Discussion on the practical significance	44
3.4	Conclusions	45
3.5	Appendix	46
3.5.1	Absolute conversion efficiency	46
4	Viscoelastic fluid	51
4.1	Introduction	52
4.2	Theoretical model	53
4.2.1	Potential distribution	53
4.2.2	Viscoelastic model	53
4.2.3	Momentum equation	53
4.2.4	Volume flow rate	56
4.2.5	Ionic current	57
4.2.6	Consideration of streaming potential and applied electric field	58
4.3	Results and discussions	59
4.3.1	Onsager's reciprocal relations	59

4.3.2	Maximal energy conversion efficiency with and without considering maximal output power	60
4.3.3	Oscillating pressure driven flow profile	64
4.3.4	Oscillating electro-osmotic flow profile	68
4.3.5	Effectiveness of electro-osmotic flow compared to pressure-driven flow	70
4.4	Conclusions	72
5	Rotary Atomizer Generator	77
5.1	Introduction	78
5.2	Methods	80
5.2.1	Glass rotary atomizer	80
5.2.2	Electrical measurement	80
5.3	Results	81
5.3.1	Micro-sized charged droplets	81
5.3.2	Streaming current and output power	84
5.4	Discussion	84
5.5	Conclusions	92
	Appendices	95
5.A	Energy conversion efficiency	95
5.B	Kinetic energy	96
5.C	Power losses	98
5.C.1	Frictional force at the solid-liquid interface	98
5.C.2	Power required to break the liquid into droplets	99
5.C.3	Power loss due to air friction	100
5.C.4	Comparison of the droplet kinetic power with other power contributions and losses	101
5.D	Motion equation for the flying droplets	101
5.E	Charge to mass ratio of individual droplet	103
5.F	Method of image charges	105

6	Conclusions and Recommendations	111
6.1	Conclusions	112
6.2	Recommendation	113
	Nederlandse samenvatting	117
	Acknowledgements	121
	List of Publications	125

Chapter 1

Aim and Outline of the thesis

1.1 Introduction

Each generation of mankind is faced with new confrontations and opportunities. We live in a closed planet earth, where the opportunity for one generation could unfortunately become a problem for the next ones. In last century, fossil fuels offered outstanding opportunities for industries in general and in particular for energy industries. The population of industrialized nations has increased and people have improved their standard of living, live healthier and longer lives. Figure 1.1 shows the role of fossil fuel in global energy sources in 2012 [1]. The increased extraction and usage of fossil fuels however has resulted in increased formation of carbon dioxide and other gases that are responsible for global warming. On the other hand, the current global energy consumption has continuously increased and we might be confronted with a lack of oil and gas by the 23rd century [2]. Energy therefore is one of the most important societal issues for the 21st century [3]. In order to prevent an energy crisis from traditional energy sources, people are eager to find new energy sources instead. However, as George Whitesides states *"because of climate changes, its not just a question of producing energy. Its a question of producing energy in a way that we can live with in the long term."* [4]. The developing "lab on a chip" technology provides new opportunities in the chain of energy management by offering new means of converting fluidic mechanical energy to electrical energy. The new energy conversion could open up new energy sources in future use.

1.2 Objectives and organisation of the thesis

1.2.1 Objectives

We aim to improve the conversion efficiency of the traditional microfluidic approach for energy conversion systems which is based on streaming potential effect. For this aim, we investigate theoretically and experimentally the utilization of different driving forces (including steady pressure, oscillation pressure, centrifugal force) and liquid properties (Newtonian, Non-Newtonian) to the streaming potential energy conversion

Figure 1.1: Global energy use by primary source in 2012 [1]

system.

1.2.2 Organisation of the thesis

The remainder of this thesis is constructed as follows: **Chapter 2** presents the fundamental and theoretical aspects of fluid flow in microchannels, introducing both electrostatics and electrokinetics, which concepts are encountered throughout the thesis. **Chapter 3** shows the results of experiments when polymers are added to the solution in microchannels for streaming potential energy conversion. In **chapter 4** we investigate the potential use of another kind of non-Newtonian fluid, namely a viscoelastic fluid for energy conversion using oscillation pressure. **Chapter 5** shows theory and experiments for ballistic energy conversion systems using the centrifugal force. **Chapter 6** offers conclusions based on this work and perspectives for future development.

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Chapter 2

Fundamental and Theoretical Aspects

In this chapter, the theory on electrostatics in solution, fluid dynamics, Onsager's relations, and electrokinetic energy conversion will be introduced with the intention to present relevant theoretical backgrounds for the work reported throughout the thesis.

2.1 Electrostatics in solution

2.1.1 Surface charging

When a solid surface (for example a glass surface) comes into contact with a polar solution (such as water), it will start bearing a surface charge due to chemical interactions (dissociation of covalently bonded groups or ion absorption) at the solid-liquid interface. This surface charge will influence the charge distribution in the bulk solution, since it will attract counter-ions and repel co-ions. Further away from the surface, ionic electroneutrality will be re-established. The distribution of ions at the solid-liquid interface is called the electrical double layer.

2.1.2 Electrical double layers

The redistribution of ions at the solid-liquid interface gives rise to the formation of the so called electrical double layer where one layer is the charge layer on the surface, and the other layer is the layer of counter-ions in the solution adjacent to it. This concept of the electrical double layer was first introduced by Helmholtz [1]. Thermal motion opposes the electrical attraction however, and causes the counter-ions in the second layer to become dispersed in a manner that leads to the formation of the diffuse double layer. The theory for the formation of such a diffuse double layer was introduced independently by Gouy [2] and Chapman [3]. In this model, the ions are considered as point charges immersed in a continuous dielectric medium. In real systems, ions possess finite size and can approach a surface to a distance not less than their radius. A modification to the Gouy–Chapman model was therefore introduced by Stern (1924) [4] in which the electric double layer inner boundary (Stern plane) is given by approximately one hydrated ion radius. In the Stern plane, at the surface potentials where the energy of electrical attraction of a single ion $ze\Psi$ (with z the ionic charge number, e the unit charge and Ψ the surface potential) is larger than its thermal energy $k_B T$, a number of ions will become less mobile. The space between the Stern plane and the surface is termed the Stern layer. Outside the Stern plane the diffuse layer commences with mobile ions.

Figure 2.1: Schematic of electrical double layer following Stern model

2.1.3 Zeta potential

One to two radii away from the surface, the solution is assumed to be able to slip past the surface. In physical chemistry this boundary is called the shear plane where the no-slip condition is applied [5]. The potential at the shear plane is called the zeta potential (ζ), which can be used to quantify electrokinetic phenomena such as the electroosmotic flow and the streaming potential.

2.1.4 Potential distribution

Boltzmann distribution

The work needed to transfer an ion from infinity into the interior of a solution is called the electrochemical potential, $\bar{\mu}_i$, and consists of a contribution of the chemical potential μ_i and electrical potential, $\bar{\mu}_i = \mu_i + z_i e \psi$. At equilibrium, $\bar{\mu}_i$ is the same for all locations, i.e. $\nabla \bar{\mu}_i = 0$ everywhere. Therefore, the electrical force is balanced to the chemical potential gradient force [6]:

$$\nabla \mu_i = -z_i e \nabla \psi \quad (2.1)$$

here, ψ is the electrical potential, e is the magnitude of the elementary charge. z_i and μ_i are the valency and the chemical potential for ion (i), respectively. μ_i can be expressed as:

$$\mu_i = \mu_i^\infty + k_B T \ln(n_i) \quad (2.2)$$

where n_i is the number of ions type i per unit volume, in the bulk solution $n_i = n_0$.

For a uni-dimensional charged flat surface with x the distance normal to the surface, eqn. (2.1) reduces to:

$$\frac{d\mu_i}{dx} = -z_i e \frac{d\psi}{dx} \quad (2.3)$$

substituting eqn. (2.2) into eqn. (2.3) and integrating from a point in bulk solution (where $\psi = 0$, $n_i = n_0$) to a point in the EDL, one obtains as result the Boltzmann equation for ion distribution near a flat charged surface:

$$n_i = n_0 \exp\left(-\frac{z_i e \psi}{k_B T}\right) \quad (2.4)$$

Poisson equation

The electrical potential ψ is related to the volume charge density ρ_e by the Poisson equation:

$$\nabla^2 \psi = -\frac{\rho_e}{\epsilon} \quad (2.5)$$

The volume charge density is given by:

$$\rho_e = e \sum_i n_i z_i \quad (2.6)$$

Poisson-Boltzmann equation

From eqns. 2.4, 2.5 and 2.6, one obtains the Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{e}{\epsilon} \sum_i n_0 z_i \exp\left(-\frac{z_i e \psi}{k_B T}\right) \quad (2.7)$$

Potential distribution in slit micro and nano-channels

We consider a fluid in a slit-like channel (with the height of the channel $2H$, $H \ll W \ll L$ with W and L resp. the width and length of the channel). The electrical potential $\psi(y)$ is obtained by solving the Poisson-Boltzmann equation at boundaries condition

Figure 2.2: Slit microchannel in Cartesian coordinate system.

$\psi = \zeta$, $y = 0$ and $y = H$, $\frac{d\psi}{dy} = 0$ for the symmetric electrolyte fluid $z_+ = -z_- = z$.

$$\frac{d^2}{dy^2}\psi(y) = \frac{2zen_0}{\epsilon} \sinh\left[\frac{ze\psi(y)}{k_B T}\right] \quad (2.8)$$

Eqn. 2.8 can be expressed using non-dimensional quantities as:

$$\frac{d^2}{d\bar{y}^2}\bar{\psi}(\bar{y}) = \frac{\sinh[\bar{\zeta}\bar{\psi}(\bar{y})]\bar{H}^2}{\bar{\zeta}} \quad (2.9)$$

in which the non-dimensional quantities are as follows: $\bar{y} = \frac{y}{H}$, $\bar{H} = \frac{H}{\lambda}$, λ is the electrical double layer thickness (Debye length), $\lambda = \sqrt{\frac{\epsilon k_B T}{2n_0 z^2 e^2}}$, $\bar{\zeta} = \frac{ze\zeta}{k_B T}$, $\bar{\psi}(\bar{y}) = \frac{\psi(y)}{\zeta}$.

Eqn. 2.9 can be solved by multiplying both sides with $2\frac{d}{d\bar{y}}\bar{\psi}(\bar{y})$ and integrating to obtain:

$$\left[\frac{d}{d\bar{y}}\bar{\psi}(\bar{y})\right]^2 = 2\frac{\cosh[\bar{\zeta}\bar{\psi}(\bar{y})]\bar{H}^2}{\bar{\zeta}^2} + C \quad (2.10)$$

The constant C of the integral is obtained by using the boundary condition $\bar{\psi}(\bar{y}) = 0$ at $\bar{y} = 1$. Then, by using the relation $\cosh[\bar{\zeta}\bar{\psi}(\bar{y})] = 2\sinh\left[\frac{\bar{\zeta}\bar{\psi}(\bar{y})}{2}\right]^2 + 1$, the eqn. 2.10 becomes:

$$\left[\frac{d}{d\bar{y}}\bar{\psi}(\bar{y})\right]^2 = 4\frac{\sinh\left[\frac{\bar{\zeta}\bar{\psi}(\bar{y})}{2}\right]^2 \bar{H}^2}{\bar{\zeta}^2} \quad (2.11)$$

Eqn. 2.11 is solved by squaring both sides and choosing the right root, which has negative sign since the potential vanishes away from the walls (i.e. the potential

Figure 2.3: Electrical potential distribution at various channel dimensions

gradient is negative);

$$\left[\frac{d}{d\bar{y}} \bar{\psi}(\bar{y}) \right] = -2 \frac{\sinh \left[\frac{\bar{\zeta} \bar{\psi}(\bar{y})}{2} \right] \bar{H}}{\bar{\zeta}} \quad (2.12)$$

By using the second boundary condition, $\bar{y} = 0$, $\bar{\psi}(\bar{y}) = 1$, eqn. 2.12 is solved to obtain:

$$\bar{\psi}(\bar{y}) = \frac{2}{\bar{\zeta}} \ln \left[\tanh \left(\frac{1}{2} \bar{y} \bar{H} + \operatorname{acrtanh} \left(e^{\frac{1}{2} \bar{\zeta}} \right) \right) \right] \quad \text{for} \quad 0 \leq \bar{y} \leq 1 \quad (2.13)$$

After isolating for the tanh function, we obtain:

$$\tanh \left[\frac{1}{4} \bar{\zeta} \bar{\psi}(\bar{y}) \right] = \tanh \left(\frac{1}{4} \bar{\zeta} \right) e^{(-\bar{y} \bar{H})} \quad (2.14)$$

The eqn. 2.14 is identical to eqn. (6.26) in ref. [7].

Fig. 2.3 shows the potential distribution (dimensionless quantities), plotted using eqn. 2.13 at various channel dimensions, for a given Debye length (and at $\bar{\zeta} = -1$). It is obvious that for high value of $\bar{H}$ ($= \frac{H}{\lambda} = 80$), the potential is zero at the center of

the channel. At small $\bar{H}$ ($= 2$ for example), the potential at the center is not zero due to the electrical double layer interaction.

Potential distribution in a cylindrical micro- and nano-channel

Figure 2.4: Cylindrical micro-channel in cylindrical coordinates

For the symmetric electrolyte fluid $z_+ = -z_- = z$, in cylindrical coordinate system, the combination of the eqns. 2.4, 2.6 and 2.7 give the unidimensional Poisson-Boltzmann equation:

$$\frac{d}{dr}\psi(r) + \frac{d^2}{dr^2}\psi(r) = 2 \frac{zen_0}{\epsilon} \sinh\left(\frac{ze\psi(r)}{k_B T}\right) \quad (2.15)$$

Eqn. 2.15 can be expressed using non-dimensional parameters as:

$$\frac{d^2}{d\bar{r}^2}\bar{\psi}(\bar{r}) + \frac{\frac{d}{d\bar{r}}\bar{\psi}(\bar{r})}{\bar{r}} = \frac{\bar{R}^2 \sinh(\bar{\zeta}\bar{\psi}(\bar{r}))}{\bar{\zeta}} \quad (2.16)$$

in which the non-dimensional quantities are as follows: $\bar{r} = \frac{r}{R}$, $\bar{\psi}(\bar{r}) = \frac{\psi(r)}{\zeta}$, $\bar{\zeta} = \frac{ze\zeta}{k_B T}$, $\bar{R} = \frac{R}{\lambda}$ and $\lambda = \sqrt{\frac{\epsilon k_B T}{2n_0 z^2 e^2}}$. In case the channel wall potential is small ($|\zeta| \leq 25$ mV) the Debye-Hückel linearization can be applied ($\sinh(\bar{\zeta}\bar{\psi}(\bar{r})) = \bar{\zeta}\bar{\psi}(\bar{r})$) and eqn. 2.16 reduces to

$$\frac{d^2}{d\bar{r}^2}\bar{\psi}(\bar{r}) + \frac{\frac{d}{d\bar{r}}\bar{\psi}(\bar{r})}{\bar{r}} = \bar{R}^2(\bar{\psi}(\bar{r})) \quad (2.17)$$

This linear second order differential equations has the modified Bessel's differential

equation form. The solution therefore is:

$$\bar{\psi}(\bar{r}) = C_1 I_0(\bar{R}\bar{r}) + C_2 K_0(\bar{R}\bar{r}) \quad (2.18)$$

C_1 and C_2 are arbitrary constants and can be found using the boundaries conditions as $\bar{\psi}(1) = 1$ and $\frac{d(\bar{\psi}(0))}{d\bar{r}} = 0$. We can therefore obtain the final solution for the non-dimensional surface potential:

$$\bar{\psi}(\bar{r}) = \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \quad (2.19)$$

or, converted back to dimensional quantities as

$$\psi(r) = \zeta \frac{I_0(\kappa r)}{I_0(\kappa R)} \quad (2.20)$$

in which $\kappa = 1/\lambda$. (Maple codes for solving equations in this section can be provided on request.)

Figure 2.5: Electrical potential distribution at various cylindrical channel dimensions

2.2 Flow in microchannels

2.2.1 Fluid

From the view point of fluid mechanics, all matter can consist in only two states, fluid and solid [8]. Fluid is a substance which can be deformed continuously in response to an external shear force. In this context, there are two classes of fluids: gas (relatively low density and viscosity) and liquid (relatively high density and viscosity). The rate at which the fluid continuously deforms is dependent not only on the magnitude of the external shear force but also on the fluid viscosity [9]. Viscosity of a fluid is the quantity measuring its resistance to flow under an applied shear stress. For Newtonian fluid, the viscosity is constant. The relation between shear stress, velocity and viscosity for Newtonian fluid is expressed as Newton's law of viscosity:

$$\boldsymbol{\tau} = \eta \left(\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) \quad (2.21)$$

in which η is the fluid viscosity (kg/m/s), $\boldsymbol{\tau}$ is the stress tensor, $\mathbf{u}$ is the velocity vector.

Non-Newtonian fluids

Non-Newtonian fluids are fluids of which the viscosity does not obey Newton's law of viscosity, i.e. eqn. 2.21. Non-Newtonian fluids include: (i) Shear-thinning fluids of which the viscosities decrease with the increasing of strain rate; (ii) Shear-thickening fluids the viscosities increase with the increasing of strain rate; (iii) Bingham plastics, fluids for which a finite stress is required before they flow; (iv) Viscoelastic fluids, fluids that exhibit a combination of liquid-like (viscous) and solid-like (elastic) behavior.

Incompressible flow

The density of fluid (ρ) is measured by the ratio of mass over volume (kg/m³). When we consider the motion of a fluid in which the density remains constant, we call the flow incompressible.

2.2.2 Mass conservation

For fluid dynamics, the mass conservation law or the continuity law states that the rate of mass accumulation within the system is the difference between the mass entering and leaving the system. At the steady state condition where the system has the same spatial composition at all times, for incompressible fluids, the continuity equation is:

$$\nabla \mathbf{u} = 0 \quad (2.22)$$

Here $\mathbf{u}$ (m/s) is the fluid velocity vector (the bold-face represents for the vector quantity) relative to a stationary observer.

2.2.3 Momentum conservation

Cauchy momentum equation

For incompressible fluid, assuming that the fluid density is constant, the conservation of momentum equation is referred as Cauchy momentum equation.

$$\rho \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \nabla \boldsymbol{\tau} + \rho_e \mathbf{E} \quad (2.23)$$

in which ∇p is the pressure force and $\rho_e \mathbf{E}$ is the electrical body force due to an electrical field $\mathbf{E}$ (either applied or induced).

The Cauchy momentum equation can be used for non-Newtonian fluids. For the case of Newtonian fluids, Navier-Stokes equation is used.

Navier-Stokes momentum equation

The momentum conservation for incompressible Newtonian fluid in a circular pipe is governed by the Navier-Stokes equation (neglecting gravity force):

$$\rho \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \eta \nabla^2 \mathbf{u} + \rho_e \mathbf{E} \quad (2.24)$$

The Navier-Stokes equation can be solved after applying the boundary conditions corresponding to a given flow situation.

2.2.4 Boundary conditions

The no-slip condition specifies that the velocity of the fluid in contact with a solid surface equals to the surface velocity and is zero if the solid surface is stationary. The no-slip condition can be enforced in the Navier-Stokes momentum equation to obtain the velocity solution. In electrokinetics the no-slip condition is often applied at the plane of shear.

2.2.5 Reynolds number

Reynolds number is a dimensionless quantity representing the magnitude of the inertial force to the viscous force and is defined as:

$$Re = \frac{\rho U d}{\eta} \quad (2.25)$$

Here U (m/s) is the mean liquid velocity, d (m) is the diameter of the microchannels. When $Re < 2000$ in long straight channel, the flow is laminar.

2.2.6 Flow profile

At steady state, for laminar flow in micro-channel (where inertia is neglected), the momentum equation reduces to:

$$0 = -\nabla \mathbf{p} + \eta \nabla^2 \mathbf{u} + \rho_e \mathbf{E} \quad (2.26)$$

It should be stressed here that the electrical body force $\rho_e \mathbf{E}$ is induced by both applied and induced fields. Herewith we will illustrate the theory with some calculations applying it to a cylindrical channel (for a rectangular channel, the calculation steps are the same but in a Cartesian coordinate system). Considering the flow in the (axial) z direction of the cylindrical channel (unidimensional flow), see fig. 2.4, the

Figure 2.6: Pressure driven flow profile for Newtonian fluid in a cylindrical pipe in the absence of electrical forces.

scalar momentum equation can be expressed as:

$$-\frac{d}{dz}p(z) + \frac{\eta}{r} \frac{d}{dr}u(r) + \eta \frac{d^2}{dr^2}u(r) - 2ze n_0 \sinh\left(\frac{ze\psi(r)}{k_B T}\right) E(z) = 0 \quad (2.27)$$

Here $u(r)$ is the fluid velocity, $-\frac{d}{dz}p(z)$ is the applied pressure gradient and $E(z)$ is the total electric field. Eqn. 2.27 is expressed in dimensionless quantities as:

$$\frac{d^2}{d\bar{r}^2}u(\bar{r}) + \frac{1}{\bar{r}} \frac{d}{d\bar{r}}u(\bar{r}) = \frac{R^2 \frac{d}{dz}p(z)}{\eta} + \frac{R^2 \epsilon \zeta \bar{\psi}(\bar{r}) E(z)}{\lambda^2 \eta} \quad (2.28)$$

A further simplification of this equation is obtained by introducing the following quantities: $U_{refp} = -\frac{R^2 \frac{d}{dz}p(z)}{4\eta}$, $U_{refE} = \frac{\epsilon \zeta E(z)}{\eta}$ and $\bar{R} = \frac{R}{\lambda}$:

$$\frac{d^2}{d\bar{r}^2}u(\bar{r}) + \frac{1}{\bar{r}} \frac{d}{d\bar{r}}u(\bar{r}) = -4U_{refp} + \bar{R}^2 \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} U_{refE} \quad (2.29)$$

By using two boundary conditions: (i) at $\bar{r} = 1$, $u(\bar{r}) = 0$ and (ii) at $\bar{r} = 0$, $\frac{d}{d\bar{r}}u(\bar{r}) = 0$, the eqn. 2.29 is solved analytically to obtain:

$$u(\bar{r}) = (1 - \bar{r}^2)U_{refp} + \left[\frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} - 1 \right] U_{refE} \quad (2.30)$$

If we convert the variable $\bar{r}$ in the eqn. 2.30 back to dimensional variable r , the eqn. 2.30 will then be identical to eqn. (8.108) in ref. [5].

Pressure driven flow

In case of purely pressure-drive flow, neglecting the electroviscous effect, the flow velocity in the microchannel can be obtained from eqn. 2.30 by removing the electrical potential driven part:

$$u(\bar{r}) = (1 - \bar{r}^2)U_{refp} \quad (2.31)$$

For the sake of generality, a dimensionless velocity is used as following:

$$\bar{u}(\bar{r}) = \frac{u(\bar{r})}{U_{refp}} = (1 - \bar{r}^2) \quad (2.32)$$

Eqn. 2.32 is plotted in fig. 2.6, showing a parabolic flow profile. This is a classical and simple result for Newtonian fluid flow in a circular pipe or cylindrical micro- and nano-channels. As for the cases of non-Newtonian fluids, the flow profile will be different and will be shown in next chapter.

Electro-osmotic flow

The interaction of the mobile part of the diffuse electric double layer with an external electrical field gives rise to the electro-osmotic phenomenon. In more detail, as an electric field is applied tangentially along a charged surface, the electric field will exert a force on the ions in the diffuse double layer close to the charged surface resulting in their motion. In turn, the moving ions will drag the surrounding liquid along, thus resulting in the liquid flow. The flow profile of electro-osmosis in a cylindrical channel

Figure 2.7: Electro-osmotic flow profile for Newtonian fluid in a cylindrical pipe in the absence of pressure gradients.

can be obtained from eqn. 2.30 by eliminating the pressure driven part.

$$u(\bar{r}) = \left[\frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} - 1 \right] U_{refE} \quad (2.33)$$

Similarly to the case of pressure driven flow profile, here we also use dimensionless velocity units as:

$$\bar{u}(\bar{r}) = \frac{u(\bar{r})}{-U_{refE}} = \left[1 - \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \right] \quad (2.34)$$

Eqn. 2.34 is plotted and shown in fig. 2.7. It is obvious from fig. 2.7 that at small $\bar{R}$ (for example $= \frac{R}{\lambda} = 2$), there is a smaller electro-osmotic flow since the diffuse double layers overlap and the flow profile behaves as driven by a liquid body force similar to that of a pressure gradient (parabolic profile). At high values of $\bar{R}$, the electro-osmotic flow profile has a plug profile.

Volume flow rate

The volume flow rate can be calculated when the flow velocity is specified. As from eqn. 2.30, the velocity is known, the volume flow rate can be expressed as:

$$Q = 2\pi \int_0^R u(r) r dr \quad (2.35)$$

or using dimensionless radius $\bar{r}$, we have:

$$Q = 2\pi R^2 \int_0^1 u(\bar{r}) \bar{r} d\bar{r} \quad (2.36)$$

Substituting eqn.2.30 to eqn. 2.36 we obtain the volume flow rate as:

$$Q = 2\pi R^2 \left[\int_0^1 \left((1 - \bar{r}^2) U_{refp} + \left(\frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} - 1 \right) U_{refE} \right) \bar{r} d\bar{r} \right] \quad (2.37)$$

Integrating, we have:

$$Q = -\frac{\pi R^4 \frac{d}{dz} p(z)}{8\eta} + \left[-\pi R^2 + 2\pi R^2 \frac{I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right] \frac{\epsilon \zeta E(z)}{\eta} \quad (2.38)$$

in case of purely pressure driven flow, the second term on the right handside of eqn. 2.38 drops out, and the volume flow rate is then expressed as:

$$Q = -\frac{\pi R^4 \frac{d}{dz} p(z)}{8\eta} \quad (2.39)$$

In case $-\frac{d}{dz} p(z) = \frac{\Delta p}{L}$, eqn.2.39 can be re-written as:

$$Q = \frac{\pi R^4}{8\eta L} \Delta p \quad (2.40)$$

or the pressure drop Δp can be expressed as:

$$\Delta p = Q \frac{8\eta L}{\pi R^4} \quad (2.41)$$

or

$$\Delta p = QR_h \quad (2.42)$$

in which R_h is the hydrodynamic resistance for circular micro-channel and $R_h = \frac{8\eta L}{\pi R^4}$

2.2.7 Ionic currents during pressure-driven flow

The total ionic current (I) at pressure-driven flow is the summation of the streaming current (I_s) and conduction current (I_c). Streaming current is the current generated by advection of the charges in the diffuse part in the electrical double layer. The streaming current in a cylindrical micro-channel can thus be calculated from the flow velocity and the electrical potential distribution. Due to the downstream accumulation of the flowing charges, an electrical potential difference builds up between the channel ends, which is called streaming potential. This electrical potential causes the ionic charges to migrate back in the opposite direction of the streaming current, forming the conduction current. The total ionic current is:

$$I = 2\pi \int_0^R u(r) \rho_e r dr + 2\pi \int_0^R \frac{z^2 e^2 E(z)}{f} (n_+ + n_-) r dr + 2\pi R \sigma_s E(z) \quad (2.43)$$

in which f is the Stokes-Einstein friction factor, $f = \frac{k_B T}{D}$ and D is the diffusion coefficient [5], σ_s is the conductivity of the Stern layer [10, 11]. We can now use the non-dimensional quantities:

$$\begin{aligned} I = & -4\pi R^2 e z n_0 \int_0^1 u(\bar{r}) \sinh\left(\bar{\zeta} \bar{\psi}(\bar{r})\right) \bar{r} d\bar{r} + \\ & + \frac{4\pi R^2 z^2 e^2 n_0 E(z)}{f} \int_0^1 \cosh\left(\bar{\zeta} \bar{\psi}(\bar{r})\right) \bar{r} d\bar{r} + 2\pi R \sigma_s E(z) \end{aligned} \quad (2.44)$$

By applying the Debye-Hückel simplification and integrating, the total ionic current is obtained:

$$\begin{aligned}
 I = & \left(\frac{2I_1(\bar{R})}{\bar{R}I_0(\bar{R})} - 1 \right) \frac{\pi \bar{R}^2 \zeta \epsilon \left[-\frac{d}{dz} p(z) \right]}{\eta} + \\
 & + \left[\left(\left(\frac{I_1(\bar{R})}{I_0(\bar{R})} \right)^2 - 1 \right) \pi \bar{R}^2 \zeta \epsilon + 2\pi \bar{R} \zeta \epsilon \left(\frac{I_1(\bar{R})}{I_0(\bar{R})} \right) \right] \frac{\zeta \epsilon}{\eta} + \pi \bar{R}^2 \epsilon \frac{k_B T}{f} (2Du + 1) \Big] E(z)
 \end{aligned} \tag{2.45}$$

2.3 Electrokinetic energy conversion

Electrokinetics refers to the phenomena that involve the relative movement between two charged phases [5]. From the previous section, we know that when a liquid is forced to flow through a channel by applying a pressure difference between the channel ends, the moving liquid will also move the charge in the electrical double layer adjacent to the channel walls in the downstream direction. The movement of ionic charge represents an electrical current, which is called the streaming current. This current can perform work in an external electrical circuit, when it is picked up by external electrodes. Depending on the resistance of this load, a potential difference is built up between the channel ends. Via this mechanism the hydrodynamic input power which is defined by the product of the applied pressure difference and the volume flow rate is converted into the electrical output power which is defined by the product of output potential and output current. This system is then called an electrokinetic energy conversion system and was first introduced by J. Osterle in 1964 [12, 13]. The conversion efficiency (χ) of the converter is expressed by the ratio between the electrical output power ($P_{out} = I \times \Delta\Phi$) and input hydrodynamic power [$P_{in} = Q \times (-\Delta p)$]:

$$\chi = \frac{I \times \Delta\Phi}{Q \times (-\Delta p)} \tag{2.46}$$

Figure 2.8: Electric circuit for streaming potential energy conversion

2.3.1 Maximal energy conversion efficiency

We call the electrical current going the load resistor (R_l) I_l . According to Ohm's law:

$$I_l = \frac{\Delta\Phi}{R_l} \quad (2.47)$$

The voltage over the load resistor in the electrical circuit (shown in fig. 2.8) is:

$$\Delta\Phi = I_l \frac{R_c R_l}{R_c + R_l} \quad (2.48)$$

The output power is:

$$P = I_l \Delta\Phi \quad (2.49)$$

Substituting eqn. 2.47 and eqn. 2.48 into eqn. 2.49:

$$P = \frac{(\Delta\Phi)^2}{R_l} = I_l^2 \frac{R_c^2}{(R_c + R_l)^2} R_l \quad (2.50)$$

The function P of the variable R_l obtains its maximum at $R_l = R_0$ in which R_0 is the root of the equation $\frac{d}{d(R_l)}[P(R_l)] = 0$, in which:

$$\frac{d}{d(R_l)}[P(R_l)] = \frac{I_l^2 R_c^2 (R_c - R_l)}{(R_c + R_l)^3} \quad (2.51)$$

From eqn. 2.51 the root of the equation $\frac{d}{d(R_l)}[P(R_l)] = 0$ is $R_0 = R_l = R_c$ and substituting this root into eqn. 2.50, we obtain:

$$P_{max} = \frac{1}{4} I_l^2 R_l \quad (2.52)$$

Since $I_l = I_s$ (at maximum output power), the maximal output power from eqn. 2.52 can be re-written as:

$$P_{max} = \frac{1}{4} I_s \Delta \Phi \quad (2.53)$$

From eqn. 2.46 and 2.53, the maximal conversion efficiency when maximal output power is achieved is:

$$\chi_{P_{max}} = \frac{1}{4} \frac{I_s \Delta \Phi}{Q(-\Delta p)} \quad (2.54)$$

2.3.2 Onsager's relations

Classical thermodynamics deals with equilibrium processes meaning that the thermodynamic properties are constant in time and space. Irreversible thermodynamics is an extension of classical thermodynamics and it deals with the processes which are non-equilibrium, meaning that the thermodynamic properties are constant in time but not constant in space [14, 15]. The study of irreversible thermodynamics was carried out among others by Helmholtz, Boltzmann, Nernst, Einstein and Onsager.

Lars Onsager (1903-1976) was born in Oslo, Norway. He was awarded the Nobel Prize in Chemistry in 1968 [16] for his famous work on reciprocal relations in irreversible processes or Onsager's relations [17, 18]. Here, we focus on the application of Onsager's relations to the electrokinetic phenomena (especially the streaming potential for energy conversion) in micro-channels.

For thermodynamic processes, the linear relation between forces (causes) and fluxes (effects) are described as transport equations [5, 19]:

$$J_\alpha = \sum_{\beta=1}^n L_{\alpha\beta} X_\beta \quad (2.55)$$

in which J_a represents flux, X represents driving force, and L_a is a phenomenological coefficient. Onsager's reciprocity relation states that for a linear flux-force relation, the matrix of the phenomenological coefficients L_a is symmetric.

$$L_{\alpha\beta} = L_{\beta\alpha} \quad (2.56)$$

In our pressure-driven flow and electro-osmotic flow as presented in the previous sections, the fluxes are ionic current and volume flow rate, the forces are pressure gradient and potential difference. The transport equation for this case is as follows:

$$Q = L_{11}(\Delta p) + L_{12}(\Delta\Phi) \quad (2.57a)$$

$$I = L_{21}(\Delta p) + L_{22}(\Delta\Phi) \quad (2.57b)$$

According to Onsager's reciprocal relation, we have $L_{12} = L_{21}$. Our assumptions satisfy his relation as we look at the eqn. 2.38 and eqn. 2.45 take into account that $-\frac{d}{dz}p(z) = \frac{\Delta p}{L}$ and $E(z) = \frac{\Delta\phi}{L}$, it follows that:

$$L_{12} = L_{21} = \left(\frac{2I_1(\bar{R})}{\bar{R}I_0(\bar{R})} - 1 \right) \frac{\pi R^2 \zeta \epsilon}{L\eta} \quad (2.58)$$

Now using Onsager's relation (eqn. 2.58) and transport equation (eqn. 2.57), we will derive the maximum energy conversion efficiency of the streaming potential energy converter. Substituting eqn. 2.57 into eqn. 2.46, we obtain for the efficiency:

$$\chi = \frac{\left[L_{21}(\Delta p) + L_{22}(\Delta\Phi) \right] \Delta\Phi}{\left[L_{11}(\Delta p) + L_{12}(\Delta\Phi) \right] (-\Delta p)} \quad (2.59)$$

For pressure driven flow, neglecting the electro-viscous effect ($L_{12}(\Delta\Phi) \ll L_{11}(\Delta p)$), eqn. 2.59 can be re-written as:

$$\chi = \frac{\left[L_{21}(\Delta p) + L_{22}(\Delta\Phi) \right] \Delta\Phi}{L_{11}(\Delta p)(-\Delta p)} \quad (2.60)$$

or

$$\chi = \frac{L_{21}}{L_{11}} \left(\frac{\Delta\Phi}{\Delta p} \right) - \frac{L_{22}}{L_{11}} \left(\frac{\Delta\Phi}{\Delta p} \right)^2 \quad (2.61)$$

We can now consider the variable $x = \frac{\Delta\Phi}{\Delta p}$ and χ as a function of the variable x . We have:

$$f(x) = -\frac{L_{22}}{L_{11}} x^2 + x \frac{L_{21}}{L_{11}} \quad (2.62)$$

The maximum of $f(x)$ is obtained at x_0 where x_0 is the root of the equation:

$$\frac{d}{dx} f(x) = 0 \quad (2.63)$$

Doing so, we obtain: $x_0 = \frac{L_{21}}{2L_{22}}$. Substitution of $x = x_0$ into eqn. 2.62, we obtain for the maximum of $f(x)$, i.e. the maximal energy conversion efficiency :

$$[f(x)]_{max} = \chi_{max} = \frac{1}{4} \left[\frac{(L_{21})^2}{L_{11}L_{22}} \right] \quad (2.64)$$

Eqn. 2.64 obtained above is the same as the eqn. (3) derived in the work of Berli [20]. This equation however is derived under the condition of neglecting the electro-viscous effect, which is the liquid flow that is generated by the induced streaming potential in the opposite direction of the pressure-driven flow. A more general equation will be derived in the next section.

2.3.3 Figure of merit

Maximal energy conversion efficiency

In the previous section, Onsager's relations are used to derive the formula for the energy conversion efficiency but in the case of neglecting the electro-viscous effect. We will now consider eqn. 2.59 without omitting the term $L_{12}(\Delta\Phi)$ but take into account that $L_{12} = L_{21}$ (eqn. 2.58). By introducing the variable $x = \frac{\Delta\Phi}{\Delta p}$ and considering χ as a function of the variable x . We have:

$$f(x) = -\frac{x(xL_{22} + L_{11})}{xL_{21} + L_{11}} \quad (2.65)$$

By differentiating $f(x)$, solving the equation $\frac{d}{dx}f(x) = 0$ and taking the positive root, we have

$$x_1 = \frac{-L_{11}L_{22} + \sqrt{L_{11}L_{22}(L_{11}L_{22} - L_{21}^2)}}{L_{21}L_{22}} \quad (2.66)$$

By substituting $x = x_1$ into eqn. 2.59, we obtain

$$[f(x)]_{max} = \chi_{max} = \frac{\sqrt{Z+1} - 1}{\sqrt{Z+1} + 1} \quad (2.67)$$

in which Z is called the figure-of-merit and is calculated by:

$$Z = \frac{L_{21}^2}{L_{11}L_{22} - L_{21}^2} \quad (2.68)$$

The conversion efficiency from eqn. 2.67 is the maximal conversion efficiency without considering a condition of maximal output power. Recently, some experimental works were reported that used this formula for calculation of the conversion [21–25].

Maximal conversion efficiency at maximum output power

We now consider the maximum conversion efficiency at maximum output power. Substitution of eqn. 2.57b into the output power $P = I(\Delta\Phi)$ gives:

$$P = \left[L_{21} \left(\Delta p \right) + L_{22} \left(\Delta\Phi \right) \right] (\Delta\Phi) \quad (2.69)$$

Doing the same operation as in the previous section by considering P as a function of $\Delta\Phi$ and P obtains its maximum when $\Delta\Phi$ is the root of the equation:

$$\frac{d}{d[(\Delta\Phi)]} P[(\Delta\Phi)] = 0 \quad (2.70)$$

Solving eqn. 2.70, we obtain:

$$\Delta\Phi = -\frac{1}{2} \frac{L_{21}}{L_{22}} (\Delta p) \quad (2.71)$$

This root is same as the one in eqn. (5) in the ref. [26]. Substituting eqn. 2.71 into eqn. 2.59, and taking into account the figure of merit in eqn. 2.68, we obtain:

$$\chi_{P_{max}} = \frac{1}{2} \left(\frac{Z}{Z+2} \right) \quad (2.72)$$

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Chapter 3

Energy Conversion from the Streaming Current by Polymer Addition¹

In this chapter, we present the experimental results of energy conversion from the streaming current when a polymer is added to the working solution. We added polyacrylic acid (PAA) in concentrations of 200 ppm to 4000 ppm to a KCl solution. By introducing PAA, the input power, which is the product of volumetric flow rate and the applied pressure, reduced rapidly as compared to the case of using only a normal viscous electrolyte KCl solution. The output power at the same time remained largely constant, whereby an increase of the streaming current and a decrease of the streaming potential simultaneously occurred. These combined factors led to the massive increase of the energy conversion efficiency.

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3.1 Introduction

As mentioned in section 2.3, streaming potential energy conversion was first introduced in 1964 by J. Osterle. Recently, thanks to the rapid development in micro-fabrication, energy harvesting from streaming potential in micro-nanofluidic systems has been investigated intensively. The main goal of researchers in the field is to increase the energy conversion efficiency (χ) of the systems (see eqn. 2.46). The route followed by most researchers thereby is to downscale the channel until its diameter is of the order of the electrical double layer (EDL) thickness with the aim of reducing the hydrodynamic input power while maintaining the same streaming current [1–10]. Opening a potentially new route for efficiency enhancement, Berli et al. [11] predicted theoretically that addition of polymer to the working fluid in the micro-fluidic channel can enhance the efficiency. However, this prediction has not yet been investigated experimentally. In this chapter, we present the results from experiments of energy conversion from streaming potential using polymer solutions as working fluids.

When non-adsorbing polymers are introduced into a microchannel, depletion layers near the channel walls are formed due to the repulsive force between polymer chains and the walls (Fig. 3.1a), which is largely of entropic origin [12] but can have an electrical contribution in the case of charged polymer. The thickness of these layers will be approximately equal to the radius of gyration of the polymers (R_g) at high polymer concentrations (0.1%) and increases with decreasing polymer concentration [11, 13, 14]. This results in two different viscosity zones in the channel, one of low viscosity within and the other of high viscosity outside the polymer depletion layers (the bulk) [15]. The decrease of the bulk velocity on polymer addition will decrease the hydrodynamic input power P_{in} (Fig. 3.1b). Because the thickness of the depletion layers (δ) can be varied from a few tens to a few hundreds of nanometers depending on the polymers of choice, it can be made larger than the thickness of the EDL (λ), so that the transport of charge and hence the output power P_{out} remains unaffected. Thus, one can gain χ by reducing the volumetric flow rate (Q) in the bulk liquid without affecting the electrokinetic phenomenon which happens only inside the EDL

[11].

Figure 3.1: (A) a scheme of depletion layers when polymer is added to the working fluid. (B) predicted velocity profile of the fluid flow for polymer solutions, (yellow curve) and for normal electrolyte solutions, (blue curve).

3.2 Materials and methods

3.2.1 Chip fabrication

Microfluidic devices were fabricated in the clean room of MESA⁺, using standard photolithography, wet etching and fusion bonding. The design of the device was drawn in a mask layout editor, Clewin 4.3.6 (WieWeb, Enschede, The Netherlands) and written onto a chromium mask by MESA⁺, NanoLab (Enschede, The Netherlands) for use in photolithography. The chip has 3 identical channels with dimensions of width (w) 40 μm , height (h) 10 μm and length (L) 3.8 mm (Fig. 3.2b). The chip-holder was home-made from aluminum (Fig. 3.2).

3.2.2 Chemicals

Polyacrylic acid (PAA, Mw 1250000 gmol^{-1}), polyethylene oxide (PEO, Mw 35000 gmol^{-1} ; 300000 gmol^{-1} ; 600000 gmol^{-1}) were obtained from SigmaAldrich (USA). KCl analytical grade was obtained from SigmaAldrich (USA). All solutions were prepared in Mili-Q (Millipore, Bedford, MA) 18 $\text{M}\Omega\cdot\text{cm}$ deionized water. Unless stated otherwise, all other chemicals were from Sigma – Aldrich.

In order to have a full insight into the effect, the experiments were conducted in two different batches. In the first batch, KCl 1 mM (approximate EDL thickness

Figure 3.2: (A) A schematic diagram of the experimental setup. (B) Microfluidic chip. (C) Home-made chip holder.

9.5 nm), pH 9.5 was used as the background electrolyte solution. This background solution was then employed as solvent for preparation of PAA solutions with varying concentrations of 200 ppm, 500 ppm, 1000 ppm, 2000 ppm, 4000 ppm. In the second batch of experiments, KCl 0.01 mM (approximate EDL thickness 100 nm) pH 9.5 was used to prepare PAA solutions with the same set of concentrations as the batch number one. All the PAA solutions were adjusted to the pH 9.5 following addition of the polymer.

3.2.3 Capillaries

Fused-silica tubes (internal diameter 100 μm) obtained from Polymicro Technologies Inc. (Phoenix, AZ) were used to connect microfluidic chip with the reservoirs.

3.2.4 Experimental setup

A schematic diagram of the experimental setup used for the streaming potential measurements is shown in figure 3.2. A 99% purity nitrogen gas source regulated at 1 bar overpressure was employed to drive the liquid flow from the reservoir via the capillary tube through the microfluidic chip to the downstream capillary and finally to the collector vessel by a high accuracy gas pressure pump (Fluigent MFCS). A flow meter (Fluigent Maesflo) was used to measure the liquid flow rate (Q). Two Ag/AgCl electrodes were placed in the reservoirs for electrical measurements. Voltages were applied by a Keithley 2410 voltage source.

In order to determine the streaming current, the Keithley model 6485 picoammeter controlled by Labview was used. We furthermore fabricated a home-built Faraday cage to shield the setup from electromagnetic radiation. The working solution in all experiments was allowed to flow through the system until equilibrium was reached which was manifested by the stability of the flow rate and the streaming current. Once equilibrium was established, the streaming current measurement was conducted. The experimental current background noise was ± 2.5 pA. All the measurements were repeated in triplicate and carried out at ambient temperature. For each curve a typical error bar is plotted, which gives the standard deviation of the data.

3.2.5 Operation

Prior to the introduction of the different solutions into the apparatus, the microchannel and the entire tubing system were bidirectionally rinsed with KOH 100 mM for 15 mins. Following that, a second 15-min rinsing cycle was initiated using MiliQ water and the third cycle was 15 mins of the desired solution before performing measurement. The transparent nature of the microchannel surfaces allowed visual inspection of the channel (via a microscope) to ensure that all bubbles had been removed.

(a)

(b)

Figure 3.3: Reduction of flow rate Q (a) and input power P_{in} (b) when PAA is added into the working fluid in different concentration. The applied pressure is kept constant at 1 bar.

3.3 Results and Discussions

3.3.1 Input power

Fig. 3.3 compares the reduction of the volumetric flow rate, and hence input power, following the increase of polymer concentration in both experimental batches. It is clear that the volumetric flow rate was reduced when the polymer concentration increased. This is reasonable since the polyelectrolyte viscosity is proportional to the square root of its concentration [16]. Moreover, it is seen that the reduction

of the flow rate in the case of 0.01 mM KCl with a small concentration added of PAA is larger than in 1 mM KCl. This can be explained by the changes of polymer conformation according to the ionic strength of the solvents (background electrolyte solution). In the case of a high ionic strength solution, counter ions, in our case K^+ ions, will strongly screen the negative charges on the polymer chains. This results in polymers having a more compact random coil conformation. If one now reduces the ionic strength of the solvent, the polymer coil will expand due to less screening and hence an increasing repulsive force of the negative charges along the polymer chains will be seen. The expanded random coils take up more space (Fig. 3.4 and Table 3.1), increasing the viscosity of the solution [17–19]. This explains why the volumetric flow rate, and hence input power, was reduced more rapidly in the case of PAA in a low ionic strength background solution.

Figure 3.4: Scheme of the changes on polymer conformation according to ionic strength in the solvent.

Table 3.1: : Gyration radius (R_g) of PAA in different ionic strength background solutions

KCl concentration	$R_g = 1.57 \times n^\nu$ (nm); n is the number of monomers per chain and ν is the Flory exponent [20–22]	
1 mM	$\nu = 0.5$	$R_g = 207$
0.01 mM	$\nu = 0.6$	$R_g = 549$

(a)

(b)

Figure 3.5: I-V characterizations of the system for (a) PAA in KCl 1 mM; (b) PAA in KCl 0.01 mM. The streaming current $I_s = I(V=0)$ and the streaming potential $\Delta V = V(I=0)$. The maximum output power is reached at the point where IV is maximal, which in every case is at $I(V=0)/2 = I_s/2$.

3.3.2 Output power

In order to find the maximum output power of the whole system (capillary-chip-capillary), an I-V characterization was employed by applying different voltages against the streaming potential between the electrodes, a procedure equivalent to introducing larger load resistances. Our previous work [23] can be referred to for further information on this procedure.

Figs. 3.5a and 3.5b show the I-V characterizations of the system. In both experimental batches, the streaming current (the measured current at $V = 0$ Volt) was increased and the streaming potential (the measured voltage for $I = 0$ Ampere) was decreased with increasing polymer concentration. Both phenomena will be discussed later in this paper. The combination of increased streaming current and decreased streaming potential left the electrical output practically unchanged on polymer addition.

Due to the benefit of the strong reduction of the hydrodynamic input power as reported in the previous section and the constancy of the electrical output power, the Eff of the entire system was strongly increased as shown in the next section.

3.3.3 Conversion efficiency

Relative efficiency improvement of the entire system

As mentioned earlier, the purpose of this study is to investigate the effect of adding polymers in working solution on the efficiency. The maximum efficiency of the entire system (connecting capillary-chip-connecting capillary) is obtained by estimating the maximum output power (P_{outmax}), which is reached at $\Delta V/2$ or, equivalently, $I_s/2$, where I_s is the streaming current and ΔV the streaming potential:

$$P_{outmax} = \frac{I_s \Delta V}{4} \quad (3.1)$$

and the maximum efficiency (χ_{max}) of the entire system can be expressed as: (see also chapter 2 section 2.3):

$$\chi_{max} = 0.25 \frac{I_s \Delta V}{PQ} \quad (3.2)$$

The applied pressure (P) is kept constant at 1 bar. Due to the benefit from the strong reduction of volumetric flow rate (Q) and the significant increase of streaming current, the efficiency of the entire system was strongly increased. In particular, as compared to the efficiency of normal viscosity electrolyte solution, the maximal enhancement of the efficiency for PAA added into KCl 0.01 mM solution was a factor of 447 ($\pm 2\%$) and it was a factor of 249 ($\pm 4\%$) for the case of PAA in KCl 1 mM (Fig. 3.6)

Figure 3.6: Normalized energy conversion efficiency of polymer solutions with respect to normal viscosity KCl 0.01 mM and 1 mM solutions.

Absolute conversion efficiency in the chip

At this stage, a further analysis of the results can be performed to separately obtain the absolute conversion efficiency in the chip part. Due to the high fluidic resistance per unit length of the chip channel, the pressure drop is by far the largest in the chip. Since the streaming current is linearly proportional to the pressure drop, the streaming current is by far the largest in the chip channel. The system can thus be simplified to a streaming current generator (the chip channel) with two electrical resistances in series (the two connecting capillaries). As shown in the appendix 3.5, the absolute conversion efficiency obtained in the chip can now be calculated as 0.34 %. Though this still seems low, it is worth stressing that the result from this work was obtained

in a 10 micrometer high microchannel where theoretically expected efficiencies would normally be much lower [2].

3.3.4 Streaming current and streaming potential behavior

In an important aspect our work differs from the theoretical work of Berli [11], since we use a charged polymer while his work concerns non-charged polymers. Before we started experiments with polyacrylic acid (PAA), we indeed attempted experiments with polyethylene oxide (PEO) which is a non-ionic polymer. The flow rate reductions and efficiencies obtained with PEO are summarized in Fig. 3.7. It is obvious that even though the flow rate and hence hydrodynamic input power were reduced more than in the case of PAA, the use of PEO did not cause an efficiency enhancement of the system. This is due to the simultaneous reduction of both streaming current and streaming potential which we assume is due to the adsorption of PEO to the glass channel walls. We then decided to choose the negatively charged polymer PAA expecting less adsorption due to the opposite charged with the glass channel surface, which indeed proved to be the case.

In our experimental results with the negatively charged PAA we found an increase of streaming current and a decrease of streaming potential. We will now discuss the possible origins of these changes.

The decrease of the streaming potential can be explained as follows. The flow-induced streaming potential drives an ionic current in the opposite direction of the streaming current which is called conduction current and which increases with increasing bulk conduction. The reduction of streaming potential shown in figs. 3.5a and 3.5b can now be explained by the increase of bulk conduction when the acidic polyanion PAA was added to the working solution.

As to the increase of the streaming current, the streaming current for a rectangular microchannel (which has H as half of the channel height) in Cartesian coordinates for unit width is defined by

$$I_s = 2 \int_0^H u(y) \rho(y) dy \quad (3.3)$$

According to equation (3.3), the streaming current is a function of the velocity

Figure 3.7: Volumetric flow rate and normalized efficiencies of KCl 1 mM and different polymer additions: PEO (35 kDa) 2%, PEO (300 kDa) 2%, PEO (600 kDa) 2%, PAA (1125 kDa) 1000 ppm.

($u(y)$) and the charged density across the channel ($\rho(y)$). Hence, the increase of the streaming current must be caused by an increase of local net charge density and/or an increase of the local velocity of the unbalanced ions. This increased transport of counterionic charge could occur either in the depletion layer (when local velocity or charge density would increase) or within the anionic polymeric network if the polymer would somehow undergo friction. In this context it is interesting to note that Burns observed a decreasing thickness of both the electrical double layer and the depletion layer thickness with increasing PAA concentration. These observations show the complicated nature of this problem, since both effects could play a role here [13, 14]. At present this phenomenon therefore remains unexplained.

3.3.5 Discussion on the practical significance

We envisage that polymer addition can have practical significance in streaming-current based energy conversion in microchannel arrays. Recently Manouri et al. [24] demonstrated high-power electrokinetic conversion in a glass microchannel array. In their paper they address the problem of electrical losses in streaming-current

based power conversion in microchannels, successfully minimizing them. Using simple electrolyte solutions, the authors however do not address hydrodynamic losses. The authors show their highest efficiencies (1.3%) in demineralized water with a specific resistivity of 18.2 M Ω cm. Pure demineralized water however is not very practical to maintain and pollution by trace amounts of salt easily occurs. Manouri et al. show that the addition of KCl to a concentration of only 0.05 mM already leads to an efficiency collapse with a factor of almost 100. In a practical system the addition of polymer could maintain the efficiency at a reasonably high level as we showed here. In a nutshell, we here demonstrate that streaming-current based energy conversion can not only be optimized by reducing electrical losses, but also by reducing hydrodynamic losses.

3.4 Conclusions

Energy conversion efficiency from the streaming current in a single microchannel using a KCl solution with added polyacrylic acid (PAA) was investigated experimentally. The results showed that due to the presence of this charged polymer, there was a strong reduction of hydrodynamic input power while the electrical output power remained largely unchanged. These combined factors resulted in the enhancement of the energy conversion efficiency of the system with a factor of 447 ($\pm 2\%$) in case of PAA in KCl 0.01 mM and a factor of 249 ($\pm 4\%$) for PAA in KCl 1 mM. The maximal energy conversion efficiency we obtained was 0.34% for the chip. Furthermore, we discovered that PAA in the small ionic strength solution (KCl 0.01 mM) reduced the input power and increased the streaming current more rapidly than at higher ionic strength (KCl 1 mM). Finally, we observed a decrease of the streaming potential when polymer was added, and an increase of the streaming current, where the latter remains unexplained. Further investigation on optimizing polymer molecular size and channel size would need to be done in order to achieve higher efficiency. Limits will for example be posed when channel size will become of the order of the polymer gyration radius.

3.5 Appendix

3.5.1 Absolute conversion efficiency

Our experimental setup can be divided into three sections including inlet tubing; chip; outlet tubing. An equivalent circuit of this energy conversion system is depicted in Fig. 3.8. Each section can be considered as a constant current source (numbered i) with an internal electrical resistance R_i determined by the cross section (A_i), length (L_i) and solution conductivity ($\gamma_i = C_i \lambda_i$), (eqn. 3.4). The system is finally connected in series with the external resistance R_{ext} which in our case was represented by the voltage source. The resistance of the Ag/AgCl electrodes to charge transport is neglected.

Figure 3.8: An equivalent circuit of the energy conversion system

Table 3.2: Length and cross sectional area of each section

	L_i mm	A_i (μm) ²
Inlet tubing	440	2500π
Outlet tubing	150	2500π
Microfluidic chip	3.8	400

$$R_i = \frac{L_i}{\gamma A_i} \quad (3.4)$$

Here C_i is the solution concentration in i section, λ_i is the molar conductivity of i th section [25]. The maximum output power of the entire system (connecting capillary/chip/connecting capillary) is (P_{outmax}), (see also chapter 2, section 2.3)

$$P_{outmax} = \frac{I_s \Delta V}{4} \quad (3.5)$$

According to Kirchhoffs laws, the streaming current of the whole system can be expressed as

$$I_s = \frac{I_1 R_1 + I_2 R_2 + I_3 R_3}{R_1 + R_2 + R_3} \quad (3.6)$$

At equilibrium, the streaming potential of the entire system is equal to

$$\Delta V = I_1 R_1 + I_2 R_2 + I_3 R_3 \quad (3.7)$$

Substituting equations (3.6) and (3.7) into equation (3.5),

$$P_{outmax} = \frac{(I_1 R_1 + I_2 R_2 + I_3 R_3)^2}{4(R_1 + R_2 + R_3)} \quad (3.8)$$

Substituting values of L_i and A_i from table (3.2) into the equation (3.4), we obtained $R_1 \approx 6R_2$ and $R_3 \approx 2R_2$. On the other hand, we have $I_3 \approx 3I_1$ (streaming current in the same diameter tubing with 1/3 length). Therefore, equation (3.8) becomes

$$\begin{aligned} P_{outmax} &= \frac{(I_1 6R_2 + I_2 R_2 + I_3 2R_2)^2}{4(6R_2 + R_2 + 2R_2)} \\ &= \frac{R_2(4I_3 + I_2)^2}{36} \end{aligned} \quad (3.9)$$

At this stage, it is interesting to make a comparison between I_2 and I_3 . Theoretically, the streaming current for a normal electrolyte solution in both a capillary tube and a rectangular channel depends on the channel dimensions and is proportional to the pressure gradient. The pressure gradient, in turn, depends on the hydraulic resistance (R_{hyd}) of the capillary or the channel in which it is applied. Therefore, the streaming current eventually is proportional to the channel dimensions and the hydraulic resistance. Eqns. (3.10) and (3.11) show the hydraulic resistance of the capillary (R_{hyd3}) and the rectangular channel (R_{hyd2}) respectively [26].

$$R_{hyd3} = \frac{8\eta L_3}{\pi r^4} \quad (3.10)$$

$$R_{hyd2} = \frac{12\eta L_2}{(1 - 0.63(h/w))} \frac{1}{h^3 w} \quad (3.11)$$

in which, r is the radius of the capillary tubing (μm), L_i is the length of the channel or capillary tubing (mm), h is the channel height (μm), w is the channel width (μm) and η (Pa.s) is the viscosity of the electrolyte solution (KCl 1mM or 0.01 mM).

On substituting values of channel and tubing dimensions from table (3.2) into eqn. (3.10) and eqn. (3.11), we obtain that the ratio $R_{hyd2}/R_{hyd3} = 22.14$. Hence, the pressure gradient in the chip channel is much larger than in the capillary. Substituting this result in the equation for streaming current (e.g. equation (1) in ref [23]), we find that the ratio $I_2/I_3 = 44.5$. Thereby, the factor $(4.I_3)$ can be neglected in eqn. (3.9) and the maximal output power P_{outmax} of the entire system from eqn. (3.9) becomes

$$\begin{aligned} P_{outmax} &\approx \frac{(R_2(I_2))^2}{36} \\ &= \frac{1}{9} P_{outmax}^{chip} \end{aligned} \quad (3.12)$$

In which P_{outmax}^{chip} is the maximal output power obtained from the microchannel. The maximal absolute energy conversion efficiency we obtained for the entire system is 0.038%. From eqn. (3.12), the maximal energy conversion efficiency of our chip can be derived as 0.34%. Though this still seems low, it is worth stressing that the result from this work was obtained in a 10 micrometer high microchannel where theoretically expected efficiencies would normally be much lower [2].

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Chapter 4

Viscoelastic Fluid Flow in Circular Narrow Confinements Driven by Periodic Pressure and Potential Gradients¹

In this chapter we present an in-depth analysis and analytical solution for AC hydrodynamic flow (driven by a time-dependent pressure gradient and electric field) of viscoelastic fluid through cylindrical micro-, nano-channels. Particularly, we solve the linearized Poisson-Boltzmann equation, together with the incompressible Cauchy momentum equation under no-slip boundary conditions for viscoelastic fluid in the case of a combination of time-periodic pressure-driven and electro-osmotic flow. The resulting solutions allow us to predict the electrical current and solution flow rate. The results satisfy the Onsager reciprocal relation. The validity of these Onsager relations is important since it results in the analogy between fluidic networks in this flow configuration and electric circuits. They especially are of interest for micro, nano-fluidic energy conversion applications.

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4.1 Introduction

Micro and nanofluidic applications (e.g. on-chip bio-analysis, on-chip diagnostic devices, DNA molecules separation, energy harvesting, and so on) require the transportation of fluids to be driven by an external driving force, which can be either using a pressure gradient (pressure driven flow (PDF)) or an external electric field (electro-osmotic flow (EOF)) or the combination of these two driving forces, which results in the coupled flow of matter and ionic current, called electro-kinetic flow. Based on each physical problem of interest, these driving forces can be steady or time-dependent. The application of steady driving forces for Newtonian fluids, like aqueous electrolyte solutions, whose viscosity is constant, was extensively investigated in the past [1, 2]. Recently, the necessity of manipulation of biofluids (for example blood, DNA solutions) and polymeric liquids in small confinements has triggered the renewable interest in dynamics of non-Newtonian fluid. Berli theoretically studied the utilization of steady PDF [3], EOF [4, 5], and steady mixed PDF-EOF [6] for inelastic non-Newtonian fluids using a power law constitutive equation in both micro rectangular and cylindrical channels. Experiments carried out for steady pressure-driven non-Newtonian flow in a rectangular microchannel inspired by Berli's theory were reported by us in chapter 3. Suman Chakraborty and colleagues have theoretically studied transport of non-Newtonian fluids (inelastic power law fluids and very recently extended to viscoelastic constitutions) using separately steady PDF [7], EOF [8] and time dependent PDF [9, 10], EOF [11] in rectangular narrow confinements. Liu, Q. S et al. also studied AC EOF of viscoelastic fluid rectangular [12], cylindrical [13] and semicircular microchannels [14]. However, so far no one seems to have discussed on the transient mixed PDF-EOF of viscoelastic flow through a narrow confinement (micro-nanochannel). In this context, our work in this chapter aim to fill this gap by attempting to investigate the theoretical relations between fluxes and forces for AC electrokinetic (mixed PDF-EOF) flow of viscoelastic fluid. It is important to note that knowing the relationships between driving forces and conjugate fluxes, (which for simple Newtonian fluid and steady mixed PDF-EOF can be described by the Onsager relations of nonequilibrium thermodynamics [1]), is a

crucial aspect for miniaturization and integration, hence the design and operation of micro-, and nanochannels in fluidic networks (lab-on-chip platforms) as well as for understanding the underlying fundamental physics of fluid. The validity of the Onsager's relations is also important for practical electric implementation as it results in the analogy between fluidic networks and electric circuits. Therefore, the results are also of interest for energy conversion in micro-nanofluidic systems.

4.2 Theoretical model

We consider the flow of a linearized Maxwell fluid (see section 4.2.2) in an infinitely long cylindrical micro-channel (with channel radius R) under application of both an oscillating pressure and electric field in a cylindrical coordinate system (see Fig. 2.4 in chapter 3 for the sketch of the coordinate system).

4.2.1 Potential distribution

The electrical potential was derived in section 2.1 chapter 2.

$$\bar{\psi}(\bar{r}) = \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \quad (4.1)$$

4.2.2 Viscoelastic model

Viscoelastic behavior is presented using linear Maxwell model.

$$\tau(r, t) = \eta \frac{\partial}{\partial r} u(r, t) - t_n \frac{\partial}{\partial t} \tau(r, t) \quad (4.2)$$

t_n is the liquid relaxation time (defined as time required for applied stress to decay), η is the liquid viscosity and τ is the stress tensor.

4.2.3 Momentum equation

The flow is governed by the incompressible Cauchy momentum equation. Considering the flow in z direction (unidimensional flow), the scalar momentum equation can be

expressed as:

$$\rho \frac{\partial}{\partial t} u(r, t) = -\frac{\partial}{\partial z} p(z, t) + \frac{\tau(r, t) + r \frac{\partial}{\partial r} \tau(r, t)}{r} - 2 z e n_0 \sinh\left(\frac{z e \psi(r)}{kT}\right) E(z, t) \quad (4.3)$$

ρ the fluid density, $u(r, t)$ is the fluid velocity, $-\frac{\partial}{\partial z} p(z, t)$ is the applied pressure gradient, and $E(z, t)$ is the total electric field.

$$p(z, t) = \Re(P e^{-it\omega}), \quad (4.4a)$$

$$E(z, t) = \Re\left[\left(E_s + E_A e^{-i\varphi}\right) e^{-it\omega}\right], \quad (4.4b)$$

$$u(r, t) = \Re(U e^{-it\omega}), \quad (4.4c)$$

It is important to note that $E(z, t)$ in eqn. 4.4b is included 2 components: (i) the induced electric field by the applied pressure gradient $E_s e^{-it\omega}$ and (ii) the applied electric field $E_A e^{-i(t\omega+\varphi)}$, φ is the phase different between the applied pressure gradient and the applied electric field. We now call E_0 as:

$$E_0(z) = E_s + E_A e^{-i\varphi} \quad (4.5)$$

Therefore, $E(z, t) = \Re\left(E_0(z) e^{-i\omega t}\right)$. By substituting eqns. 4.4 and 4.2 into eqn. 4.3 one can obtain the analytical solution for the eqn. 4.3 in case of considering the channel wall potential is small ($|\zeta| \leq 25$ mV) so that the Debye-Hückel linearization can be applied. The eqn. 4.3 after removing real-operator from both sides, as well as the common multiplier $e^{(-i\omega t)}$ reduces to:

$$\begin{aligned} \left(\frac{d^2}{dr^2} U(r) + \frac{\frac{d}{dr} U(r)}{r}\right) R^2 + \chi^2 U(r) &= \frac{(-I\omega^* + 1) R^2 \frac{dP}{dz}}{\eta} + \\ &+ \frac{(-I\omega^* + 1) R^2 \psi(r) \epsilon \zeta E_0}{\lambda^2 \eta} \end{aligned} \quad (4.6)$$

in which the simplification factor χ has the form $\chi^2 = (I\omega^* + \omega^{*2})\vartheta$ and $\vartheta = \frac{R^2 \rho}{t_n \eta}$; $\omega^* = \omega t_n$. By using non-dimensional variables and taking into account eqn. 4.1, eqn. 4.6

has hence the form:

$$\begin{aligned} \frac{d^2}{d\bar{r}^2} U(\bar{r}) + \frac{\frac{d}{d\bar{r}} U(\bar{r})}{\bar{r}} + \chi^2 U(\bar{r}) &= (4i\omega^* - 4) U_{refP} + \\ &+ \frac{(-i\omega^* + 1) \bar{R}^2 I_0(\bar{R}\bar{r}) U_{refE}}{I_0(\bar{R})} \end{aligned} \quad (4.7)$$

in which $\bar{R} = \frac{R}{\lambda}$; $\bar{r} = \frac{r}{R}$; $U_{refP} = -\frac{R^2 \frac{d}{dz} P(z)}{4\eta}$ and $U_{refE} = \frac{\epsilon\zeta E_0}{\eta}$. This is a second-order linear non-homogeneous differential equation. When we call U the solution for eqn. 4.7, then U has the following form:

$$U = U_0 + U_1 + U_2 \quad (4.8)$$

in which U_0 is the complementary solution of the eqn. 4.9a, U_1 is the particular solution of the eqn. 4.9b and U_2 is the particular solution for the eqn. 4.9c).

$$\frac{d^2}{d\bar{r}^2} U(\bar{r}) + \frac{\frac{d}{d\bar{r}} U(\bar{r})}{\bar{r}} + \chi^2 U(\bar{r}) = 0, \quad (4.9a)$$

$$\frac{d^2}{d\bar{r}^2} U(\bar{r}) + \frac{\frac{d}{d\bar{r}} U(\bar{r})}{\bar{r}} + \chi^2 U(\bar{r}) = (4i\omega^* - 4) U_{refP}, \quad (4.9b)$$

$$\frac{d^2}{d\bar{r}^2} U(\bar{r}) + \frac{\frac{d}{d\bar{r}} U(\bar{r})}{\bar{r}} + \chi^2 U(\bar{r}) = \frac{(-i\omega^* + 1) \bar{R}^2 I_0(\bar{R}\bar{r}) U_{refE}}{I_0(\bar{R})}, \quad (4.9c)$$

Eqn. 4.9a has as solution the Bessel's function of the first kind and zero order:

$$U_0 = C_3 J_0(\chi\bar{r}) + C_4 Y_0(\chi\bar{r}) \quad (4.10)$$

C_3 and C_4 are arbitrary constants. Eqn. 4.9b has the particular solution as:

$$U_1 = \frac{4(I\omega^* - 1)U_{refP}}{\chi^2} \quad (4.11)$$

Inspecting the right hand side of eqn. 4.9c, the particular solution of this equation should have the form:

$$U_2 = \alpha I_0(\bar{R}\bar{r}) \quad (4.12)$$

By substituting eqn. 4.12 into eqn. 4.9c, we obtain:

$$\alpha = \frac{-I(I + \omega^*)U_{refE}\bar{R}^2}{I_0(\bar{R})(\chi^2 + \bar{R}^2)} \quad (4.13)$$

The solution of eqn. 4.7 therefore is:

$$U = C_3 J_0(\chi\bar{r}) + C_4 Y_0(\chi\bar{r}) + \frac{4(I\omega^* - 1)U_{refP}}{\chi^2} + \frac{-I(I + \omega^*)U_{refE}\bar{R}^2 I_0(\bar{R}\bar{r})}{I_0(\bar{R})(\chi^2 + \bar{R}^2)} \quad (4.14)$$

Using the no-slip boundary conditions ($U(\bar{r}) = 0$ at $\bar{r} = 1$, and $\frac{dU(\bar{r})}{d\bar{r}} = 0$ at $\bar{r} = 0$), C_3 and C_4 can be obtained as:

$$C_3 = \frac{-4I(I + \omega^*)U_{refP}}{\chi^2 J_0(\chi)} + \frac{I(I + \omega^*)U_{refE}\bar{R}^2}{(\bar{R}^2 + \chi^2)J_0(\chi)} \quad (4.15a)$$

$$C_4 = 0 \quad (4.15b)$$

Back-substituting eqn. 4.15 into the eqn. 4.14, we obtain the complex velocity amplitude:

$$U(\bar{r}) = \frac{4I(I + \omega^*)}{\chi^2} \left(1 - \frac{J_0(\chi\bar{r})}{J_0(\chi)} \right) U_{refP} + \frac{I(I + \omega^*)\bar{R}^2}{\chi^2 + \bar{R}^2} \left(\frac{J_0(\chi\bar{r})}{J_0(\chi)} - \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \right) U_{refE} \quad (4.16)$$

4.2.4 Volume flow rate

The flow rate $q = \Re(Qe^{-I\omega t})$, in which the flow rate amplitude has the form: $Q = 2\pi \int_0^R U(r)rdr$, changing to non-dimensional variable $\bar{r}$,

$$Q = 2\pi R^2 \int_0^1 U(\bar{r})\bar{r}d\bar{r} \quad (4.17)$$

integrating to obtain $Q = \left[\frac{I(I+\omega^*)R^4}{\eta\chi^2} \left(\pi - \frac{2\pi J_1(\chi)}{J_0(\chi)\chi} \right) \right] \left(-\frac{d}{dz} P(z) \right) + \left[\frac{I(I+\omega^*)R^2}{\eta(\chi^2+\bar{R}^2)} \left(\frac{2\pi J_1(\chi)}{J_0(\chi)\chi} - \frac{2\pi I_1(\bar{R})}{J_0(\bar{R})\bar{R}} \right) \right] \epsilon\zeta\bar{R}^2 E_0(z)$. Note that, $-\frac{d}{dz} P = \frac{\Delta P}{L}$ and $E_0(z) = \frac{d}{dz} \Phi = \frac{\Delta\Phi}{L}$, then the complex flow rate Q amplitude has the form:

$$Q = \left[\frac{I(I+\omega^*)R^4}{\eta\chi^2} \left(\pi - \frac{2\pi J_1(\chi)}{J_0(\chi)\chi} \right) \right] \left(\frac{\Delta P}{L} \right) + \left[\frac{I(I+\omega^*)R^2\epsilon\zeta\bar{R}^2}{\eta(\chi^2+\bar{R}^2)} \left(\frac{2\pi J_1(\chi)}{J_0(\chi)\chi} - \frac{2\pi I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right) \right] \left(\frac{\Delta\Phi}{L} \right) \quad (4.18)$$

4.2.5 Ionic current

The ionic current $i = \Re(Ie^{(-I\omega t)})$, in which the current amplitude has the form: $I = 2\pi \int_0^R \rho_e U(r) r dr + 2\pi \int_0^R \frac{z^2 e^2 E_0(z)}{f} (n_+ + n_-) r dr + 2\pi R \sigma_s E_0(z)$ in which f is the Stokes-Einstein friction factor, $f = \frac{k_B T}{D}$ and D is the diffusion coefficient, σ_s is the conductivity of the Stern layer [1, 15, 16]. Changing to non-dimensional variable $\bar{r}$,

$$I = -2\pi \bar{R}^2 \epsilon \zeta \left(\int_0^1 \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} U(\bar{r}) \bar{r} d\bar{r} \right) + \pi \epsilon E_0 \bar{R}^2 D + 2\pi \bar{R} \lambda E_0(z) \sigma_s \quad (4.19)$$

By substituting the velocity in eqn. 4.16 to the eqn. 4.19 and integrating, we obtain the complex amplitude current:

$$I = \left[\frac{I(I+\omega^*)R^2\epsilon\zeta\bar{R}^2}{\eta(\chi^2+\bar{R}^2)} \left(\frac{2\pi J_1(\chi)}{J_0(\chi)\chi} - \frac{2\pi I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right) \right] \left(\frac{\Delta P}{L} \right) + \left[\frac{I(I+\omega^*)\pi\epsilon\zeta^2\bar{R}^4}{\eta} \left(-\frac{I_1^2(\bar{R})}{(\chi^2+\bar{R}^2)I_0^2(\bar{R})} + \frac{1}{(\chi^2-\bar{R}^2)} - \frac{2I_1(\bar{R})\bar{R}}{(\chi^2+\bar{R}^2)^2 I_0(\bar{R})} + \frac{2J_1(\chi)\chi}{(\chi^2+\bar{R}^2)^2 J_0(\chi)} \right) + \pi\epsilon\bar{R}^2 D + 2\pi\bar{R}^2 Du\epsilon D \right] \left(\frac{\Delta\Phi}{L} \right) \quad (4.20)$$

Du is the Dukhin number and $Du = \frac{\sigma_s}{R\sigma_b}$, σ_b is the conductivity of the bulk solution.

4.2.6 Consideration of streaming potential and applied electric field

By substituting eqn. 4.5 into the eqn. 4.16, the complex velocity amplitude can be written as:

$$\begin{aligned}
 U(\bar{r}) = & \frac{4I(I + \omega^*)}{\chi^2} \left(1 - \frac{J_0(\chi\bar{r})}{J_0(\chi)} \right) U_{refP} + \frac{I(I + \omega^*)\bar{R}^2}{\chi^2 + \bar{R}^2} \left(\frac{J_0(\chi\bar{r})}{J_0(\chi)} - \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \right) U_{refE_S} + \\
 & + \frac{I(I + \omega^*)\bar{R}^2}{\chi^2 + \bar{R}^2} \left(\frac{J_0(\chi\bar{r})}{J_0(\chi)} - \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \right) e^{-i\varphi} U_{refE_A}
 \end{aligned} \tag{4.21}$$

in which $U_{refE_A} = \frac{\epsilon\zeta E_A}{\eta}$ and $U_{refE_S} = \frac{\epsilon\zeta E_S}{\eta}$. The velocity field therefore can be viewed as the superposition of the velocity fields caused by (i) pressure gradient coupling with its streaming potential field (the first and the second terms on the right hand side of eqn. 4.21) and (ii) the applied electric field (the third term on the right hand side eqn. 4.21). In this context, if one considers solely pressure driven system, where no electric field is applied $E_A e^{-i\varphi} = 0$, hence the streaming potential $E_S = E_0$. The total ionic current at streaming potential is zero, this gives us the opportunity to extract the relation between U_{refP} and U_{refE_S} from eqn. 4.20 as following:

$$\begin{aligned}
 I = & \left[\frac{4I(I + \omega^*)\epsilon\zeta\bar{R}^2}{(\chi^2 + \bar{R}^2)} \left(\frac{2\pi J_1(\chi)}{J_0(\chi)\chi} - \frac{2\pi I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right) \right] \left(U_{refP} \right) + \\
 & + \left[\frac{I(I + \omega^*)\pi\epsilon^2\zeta^2\bar{R}^4}{\eta} \left(\frac{I_1^2(\bar{R})}{(\chi^2 + \bar{R}^2)I_0^2(\bar{R})} - \frac{1}{(\chi^2 + \bar{R}^2)} + \right. \right. \\
 & \left. \left. + \frac{2I_1(\bar{R})\bar{R}}{(\chi^2 + \bar{R}^2)^2 I_0(\bar{R})} + \frac{2J_1(\chi)\chi}{(\chi^2 + \bar{R}^2)^2 J_0(\chi)} \right) + \pi\epsilon\bar{R}^2 D + 2\pi\bar{R}^2 Du\epsilon D \right] \left(\frac{\eta}{\epsilon\zeta} U_{refE_S} \right) = 0
 \end{aligned} \tag{4.22}$$

Therefore, with an attempt to express the velocity amplitude from eqn. 4.21 as formula of only U_{refP} and U_{refE_A} , it is seen that the eqn. 4.22 gives us the relation

between U_{refP} and U_{refE_S} :

$$U_{refE_S} = \frac{- \left[\frac{8I(I+\omega^*)\bar{\zeta}}{(\chi^2+\bar{R}^2)} \left(\frac{J_1(\chi)}{J_0(\chi)\chi} - \frac{I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right) \right] \left(U_{refP} \right)}{\left[(I\omega^* - 1)\bar{\zeta}\bar{R}^2 \left(\frac{-I_1^2(\bar{R})}{(\chi^2+\bar{R}^2)I_0^2(\bar{R})} + \frac{1}{(\chi^2+\bar{R}^2)} - \frac{2J_1(\chi)\chi}{(\chi^2+\bar{R}^2)^2J_0(\chi)} - \frac{2I_1(\bar{R})\bar{R}}{(\chi^2+\bar{R}^2)^2I_0(\bar{R})} \right) + (2Du + 1)\Omega \right]} \quad (4.23)$$

in which Ω is a dimensionless quantity and $\Omega = \frac{ze\eta}{f\epsilon\zeta}$. The velocity amplitude $U(\bar{r})$ is therefore expressed as:

$$U(\bar{r}) = 4U_{refP} \left[- \frac{I(I+\omega^*)}{\chi^2} \left(\frac{J_0(\chi\bar{r})}{J_0(\chi)} - 1 \right) + \frac{(I+\omega^*)^2 2\bar{\zeta}\bar{R}^2}{(\chi^2+\bar{R}^2)^2} \left(\frac{-J_1(\chi)}{J_0(\chi)\chi} + \frac{I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right) \left(\frac{J_0(\chi\bar{r})}{J_0(\chi)} - \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \right) + \frac{(I\omega^* - 1)\bar{\zeta}\bar{R}^2 \left(\frac{-I_1^2(\bar{R})}{(\chi^2+\bar{R}^2)I_0^2(\bar{R})} + \frac{1}{(\chi^2+\bar{R}^2)} - \frac{2J_1(\chi)\chi}{(\chi^2+\bar{R}^2)^2J_0(\chi)} - \frac{2I_1(\bar{R})\bar{R}}{(\chi^2+\bar{R}^2)^2I_0(\bar{R})} \right) + (2Du + 1)\Omega}{\left[(I\omega^* - 1)\bar{\zeta}\bar{R}^2 \left(\frac{-I_1^2(\bar{R})}{(\chi^2+\bar{R}^2)I_0^2(\bar{R})} + \frac{1}{(\chi^2+\bar{R}^2)} - \frac{2J_1(\chi)\chi}{(\chi^2+\bar{R}^2)^2J_0(\chi)} - \frac{2I_1(\bar{R})\bar{R}}{(\chi^2+\bar{R}^2)^2I_0(\bar{R})} \right) + (2Du + 1)\Omega \right]} \right] + \frac{I(I+\omega^*)\bar{R}^2}{\chi^2+\bar{R}^2} \left(\frac{J_0(\chi\bar{r})}{J_0(\chi)} - \frac{I_0(\bar{R}\bar{r})}{I_0(\bar{R})} \right) e^{-i\varphi} U_{refE_A} \quad (4.24)$$

4.3 Results and discussions

4.3.1 Onsager's reciprocal relations

The complex flow rate amplitude and complex ionic current amplitude in the eqns. 4.18 and 4.20 can be re-written as follows:

$$Q = L_{11}(\Delta P) + L_{12}(\Delta\Phi) \quad (4.25a)$$

$$I = L_{21}(\Delta P) + L_{22}(\Delta\Phi) \quad (4.25b)$$

The transport eqn. 4.25 shows that flow rate amplitude Q and ionic current amplitude I are linear with applied pressure and electric potential amplitudes. L_{ij}

are phenomenological coefficients. In particular, L_{11} characterizes the hydraulic conductance and L_{22} the electric conductance. L_{12} characterizes the electro-osmosis and L_{21} characterizes streaming potential effect. Onsager's reciprocal relation is complied with if $L_{12} = L_{21}$. We see that this relation is indeed satisfied because from eqns. 4.18 and 4.20 we have:

$$L_{12} = L_{21} = \left[\frac{I(I + \omega^*)R^2\epsilon\zeta\bar{R}^2}{\eta L(\chi^2 + \bar{R}^2)} \left(\frac{2\pi J_1(\chi)}{J_0(\chi)\chi} - \frac{2\pi I_1(\bar{R})}{I_0(\bar{R})\bar{R}} \right) \right] \quad (4.26)$$

Therefore, our AC electrokinetic flow for viscoelastic fluid complies with the Onsager's reciprocal relations and it is first time this is reported in literature. This is an important result for AC electrokinetics using Maxwell viscoelastic fluid. It is important since eqn. 4.25 can be used to construct an analogy between micro-, nanofluidic-channel networks and electric circuits since it describes the electrokinetic phenomenon as a generalization of Ohm's law where linear relations between currents (of mass or charges) and applied gradients (voltage or pressure) occur [17, 18]. In this context, it is interesting to apply our calculation results to examine the energy conversion efficiency of the streaming potential energy harvesting system in a manner comparable to the work of Bandopadhyay and Chakraborty [10] .

4.3.2 Maximal energy conversion efficiency with and without considering maximal output power

The electrokinetic energy conversion efficiency (χ) in a microchannel for a Newtonian fluid under steady pressure-driven flow was theoretically predicted to be less than 1 % [19] and for an inelastic polymer, it was predicted to be about 1 % [20]. Recently, the theoretical paper of Aditya Bandopadhyay and Suman Chakraborty, "Giant augmentations in electro-hydro-dynamic energy conversion efficiencies of nanofluidic devices using viscoelastic fluids" [10] reported interesting and valuable contributions on the thermodynamic conversion efficiency by taking into account the utilization of Maxwell viscoelastic fluid and oscillating pressure-driven flow in slit rectangular micro- and nanochannels. The remarkable results of Suman and colleagues showed

that for slit-rectangular micro-channel ($\frac{H}{\lambda} = 500$, H is the half of channel height and λ is the Debye length) the conversion efficiency can be in the order of 10 %, and for the case of a nano-channel without taking into account surface conductance, the conversion efficiency can be larger than 95 % [see figs. 1 and S3 in [10]]. When we apply our calculation results for investigating the conversion efficiency in cylindrical micro-nanochannels, we indeed find in fig. 4.1 that an efficiency can be obtained in the order of 30 % for the case of a cylindrical micro-channel and that the maximum efficiency is larger than 95 % for a nano-channel. For the purpose of comparison, plots are constructed using the same input data as provided by the work of Aditya Bandopadhyay and Suman Chakraborty [10], (ie. $\vartheta = 10^{-4}$, $\bar{\zeta} = -1$, $\Omega = -10$). For the case of a cylindrical micro-channel, the efficiency is higher than for the case of a rectangular micro-channel due to the lower hydraulic resistance of the former. It must

Figure 4.1: Maximal thermodynamic energy conversion efficiency (not at maximal output power in cylindrical micro- and nanochannels)

be remarked that the maximal efficiencies shown in Fig. 4.1) and those predicted by Aditya Bandopadhyay and Suman Chakraborty are thermodynamic efficiencies [$\chi = \frac{I_s \Delta \phi}{Q(\Delta p)}$]. For practical purposes, the maximal conversion efficiency needs also to be considered under the condition of maximal output power at a load resistor, [see chapter 2 section 2.3 for the derivation], $\chi_{max} = \frac{1}{4} \frac{I_s \Delta \phi}{Q \Delta p}$. The efficiencies at maximal output power are now shown in fig. 4.2. In this figure, the maximum efficiencies

at maximal output power are 24.3 % and 7.7 % for a cylindrical nanochannel and microchannel respectively. These values though much lower than the thermodynamic efficiencies, are still very much higher than the conventional predictions cited above, especially for the micro-channel.

Figure 4.2: Maximal energy conversion efficiency at maximal output power in cylindrical micro- and nanochannels

Understanding the mechanism

In the work of Aditya Bandopadhyay and Suman Chakraborty [10], the mechanism behind the massive enhancement of the energy conversion efficiency was not in detail described. Herewith, we will provide a description of the mechanism that enhances the efficiency. Fig. 4.3 shows the maximal energy conversion efficiency following ω^* and the inverse Deborah number ϑ for a nano-channel at $\bar{R} = 5$. Here,

$$\vartheta = \frac{\rho R^2}{t_n \eta} \quad (4.27)$$

Deborah number gives the ratio between relaxation time t_n to viscous diffusion time t_v [21].

$$De = \frac{t_n}{t_v} = \frac{t_n \eta}{\rho R^2} \quad (4.28)$$

Figure 4.3: 3D plot of maximal energy conversion efficiency following ω^* and the inverse Deborah number ϑ

ω^* is Weissenberg number [22].

$$\omega^* = \omega t_n \quad (4.29)$$

It is obvious from fig. 4.3 that in the limit $\vartheta \rightarrow 0$ (high relaxation time, elastic dominant zone), the efficiencies are high. On the other hand, at high ϑ , (low relaxation time, viscous dominant zone), no efficiency peaks appear. This behaviour can be explained from the linear Maxwell viscoelastic model that presents fluid as a the serial connection between a spring (elastic behaviour) and a dashpot (viscous behaviour). The closer to the dominantly elastic zone (lower ϑ), the more the fluid behaves as a Hookean solid in responding, resulting in a shift of the resonance peak towards the higher ω^* values, see also fig. 4.4. When $\vartheta \rightarrow 0$, at resonance frequencies, the fluid inside the channel exhibits an entirely elastic character and hence moves frictionlessly, as a result providing high conversion efficiencies.

The peak locations at which maximal efficiencies are observed depend on the oscillation frequencies that are also determined by the channel dimension. This can be seen when for ϑ constant, meaning at constant polymer properties, the maximal efficiency peaks shift to smaller frequencies at an increase of channel dimensionless

radius, $\bar{R}$ (shown in fig. 4.4). Furthermore, the peaks also split into two separate peaks so that they can be shifted to smaller frequencies when increasing the channel radii (for example the peak at ω^* approximate 550 and $\bar{R} = 100$ in fig. 4.4). This is because the larger the channel radii are, the smaller the De number is as expressed in eqn. 4.28, and hence the stronger viscous behavior dominates. As a result of viscous behavior, the resonances occur at smaller frequencies [shown in fig. 4.3 when $\vartheta \rightarrow \infty$], whereby more dissipation occurs, and lower efficiencies. As a result, the larger the channels are, the smaller the resonance frequencies and the smaller the efficiencies obtained.

Figure 4.4: Dependence of maximal energy conversion efficiency on ω^* and channel dimension $\bar{R}$

4.3.3 Oscillating pressure driven flow profile

For the sake of generality all the plots are presented using the non-dimensional quantity: $\bar{u}_{pdf} = Re[(\frac{U}{U_{refP}})exp(-i\omega t)]$, in which $U_{refP} = -\frac{R^2 \frac{d}{dz} P(z)}{4\eta}$ has the form of the maximal velocity of the Poiseuille flow, see the eqn. 4.24 for $U(\bar{r})$. Fig. 4.5 show the oscillating pressure driven flow profile of viscoelastic fluid following ω^* and channel

radius $\bar{r}$ at $\bar{R} = 20$. In order to compare with the case of oscillating electro-osmotic flow, the velocity amplitude is also plotted and shown in fig. 4.6.

It is important to stress that while the pressure gradient $-\frac{\partial p}{\partial z}$ and the velocity $u(r, t)$ appear to have the same oscillatory form in the time variable t (see eqns. 4.4), this does not mean that they actually are in phase with each other. The reason for this is that the other part of the velocity, namely, the $U(r)$ or $U(\bar{r})$ is a complex quantity. The product of this complex quantity with $e^{-it\omega}$ as shown in eqn. 4.4c causes changes in the phases of the real and imaginary parts of the $U(r)$ or $U(\bar{r})$ and hence of the velocity $u(r, t)$ so that a phase shift will occur with respect to the pressure gradient $-\frac{\partial p}{\partial z}$.

Complex and Real velocity amplitude

The velocity u has the form

$$u = \Re(Ue^{(-i\omega t)}) \quad (4.30)$$

Since U is a complex number, we can express it as:

$$U = U_a + iU_b \quad (4.31)$$

Substituting eqn. 4.31 into eqn. 4.30 and isolating the Real part, we have:

$$u = U_a \cos(\omega t) + U_b \sin(\omega t) = U_c \cos(\omega t - \theta) \quad (4.32)$$

in which $U_c = \sqrt{(U_a^2) + (U_b^2)}$, $\theta = \tan^{-1}(U_b/U_a)$ is the phase shift, and hence $U_c = |U|$ is the (real) velocity amplitude [23], see fig. 4.6.

Figure 4.5: Oscillating pressure driven flow profile of viscoelastic fluid following ω^* and dimensionless channel radius $\bar{r}$ at $\bar{R}=20$.

Figure 4.6: The velocity amplitude in case of oscillating PDF at (a) $\bar{R} = 20$ and (b) $\bar{R} = 500$

4.3.4 Oscillating electro-osmotic flow profile

$\bar{u}_{eof} = Re[(\frac{U}{U_{refE}})exp(-i\omega t)]$, in which $U_{refE} = \frac{\epsilon\zeta E_0}{\eta}$ is the Helmholtz-Smoluchowski velocity. The phase difference is $\varphi = \pi$, see eqn. 4.24. Fig. 4.7 show the oscillating

Figure 4.7: Oscillating electro-osmotic flow profile of viscoelastic fluid following ω^* and channel radius $\bar{r}$

electro-osmotic flow profile of viscoelastic fluid following ω^* and channel radius $\bar{r}$ at $\bar{R} = 20$. The velocity amplitude is also plotted and shown in fig. 4.8.

Figure 4.8: The velocity amplitude in case of oscillating EOF at (a) $\bar{R} = 20$ and (b) $\bar{R} = 500$

4.3.5 Effectiveness of electro-osmotic flow compared to pressure-driven flow

It can be seen from figs. 4.5, 4.6 and figs. 4.7, 4.8 that at resonance frequencies, the maximal velocity in the case of oscillating EOF is much higher than in the case of oscillating PDF even though at low frequencies these flows have the same maximal velocities as shown in fig. 4.9.

In the textbook, for DC electrokinetic flow, the concept of effectiveness (B) of electro-osmotic flow as compared to pressure-driven flow is given by the ratio of volume flow rate, see page 244 of ref. [1].

$$B = \frac{Q_{eof}}{Q_{pdf}} \quad (4.33)$$

In our case, for AC electrokinetics with a Maxwell fluid, the volume flow is expressed by the eqn. 4.18. The effectiveness B therefore has the form:

$$B = \frac{|Q_{eof}|}{|Q_{pdf}|} \quad (4.34)$$

(a)

(b)

Figure 4.9: (a) Oscillating PDF and (b) Oscillating EOF, both are at $\omega^* = 1$

Figure 4.10: Effectiveness of oscillating electro-osmotic flow compared to oscillating pressure-driven flow of viscoelastic fluid following ω^* and dimensionless $\bar{R}$

It can be clearly seen from fig. 4.10 that at the resonance frequencies, the oscillating EOF flow rate amplitude has increased much more than in the case of oscillating PDF even though at small frequencies maximal velocities are the same as shown in fig 4.9. Furthermore, at nanochannels, the effectiveness is much more increased than in microchannels due to higher hydraulic resistance for pressure-driven flow.

4.4 Conclusions

We report for the first time an analytical solution for time dependent electrokinetic flow (mixed oscillating pressure gradient and electrical field) when using a linear Maxwell viscoelastic fluid model in cylindrical micro-nanochannels. The analytical solution is derived by solving the linearized Poisson-Boltzmann equation, together with the incompressible Cauchy's momentum equation in no-slip boundary conditions for the case of a combination of time periodic pressure driven flow and electro-osmotic flow (PDF/EOF). The results show that the Onsager's reciprocal relations are complied for our case. The validity of these Onsager's relations is important

for practical implementation since it results in the analogy between fluidic networks in this flow configuration and electric circuits. We applied our calculation results for energy conversion systems in cylindrical micro-nanochannels. and compare the results with the work of Bandopadhyay and Chakraborty [10] which was performed in rectangular micro-nanochannels. It is shown that in the case of a cylindrical microchannel the efficiency enhancement is higher than in the rectangular channel due to the lower hydraulic resistance of the former case. We furthermore provided a mechanism to understand the massive efficiency enhancement. We also found that AC electro-osmotic flow in many cases is much stronger enhanced than AC pressure-driven flow when comparing the flow profiles of oscillating PDF and EOF in micro-, and nanochannels. The findings advance our understanding of AC electrokinetic phenomena of viscoelastic fluids and provide insight in flow characteristic as well as assist the design of devices for lab-on-chip applications.

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Chapter 5

Rotary Atomizer Generator¹

In this chapter, we report experimental and theoretical results on a ballistic energy conversion method based on a rotary atomizer working with a droplet acceleration-deceleration cycle. In a rotary atomizer, liquid is fed onto the center of a rotating flat surface, where it spreads out under the action of the centrifugal force and creates "atomized" droplets at its edge. The advantage of using a rotary atomizer is that the centrifugal force exerted on the fluid on a smooth and large surface is not only a robust form of acceleration as it avoids clogging but also easily allows high throughput and producing a high electrical power. We successfully demonstrate an output power of 4.9 mW, and a high voltage up to 3120 Volts. To our knowledge, this is the first time electrical power is generated using a rotary atomizer. At present, the efficiency of the system is still low (0.14 %). However, the conversion mechanism of the system is fully interpreted in this paper, permitting a conceptual understanding of system operation and providing a roadmap for system optimization. This observation will open up a new road for building power generation systems in the near future.

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5.1 Introduction

Since the first introduction in 1964 by J.F. Osterle [1], energy conversion from streaming current has been extensively explored in the last 20 years thanks to the rapid development of micro-nano fabrication methods [2]. For a detail description of streaming current in a micro-nanochannel, please refer to chapter 2, section 2.3. Here, only a brief introduction is provided. When a glass surface is in contact with aqueous solutions, it bears a negative charge due to ionization of surface silanol groups. Counterions will be attracted from the adjacent solution, forming an electrical double layer (EDL) with a net positive charge. The mobile counter-ionic charges in the diffuse part of the EDL are transferred if the solution is driven by an external force. Fig. 5.1a shows such a conventional single-phase pressure driven flow (PDF) system. The resulting electrical current is called the streaming current (I_s). The downstream accumulation of ionic charges creates an electrokinetic (streaming) potential which acts to drive a current in the opposite direction to the streaming current, called the conduction current (I_c). The net current is the difference between streaming current and conduction current and can be directed to an external load to generate electrical power. Both the conduction current reducing the net current and the high hydrodynamic friction limit the efficiency of this pressure driven single phase (liquid) system (Fig. 5.1a) [3–7]. Classically experimental efficiencies were limited to 5 %, [8] but recently efficiencies up to 46 % were mentioned in highly charged membranes [9]. Also recently, ballistic microfluidic energy conversion was introduced by Xie and colleagues [10], converting mechanical to electrical energy by an acceleration-deceleration cycle of high-speed charged droplets launched through a membrane micropore, largely avoiding conduction current generation and much increase efficiency (up to 50 %). All these methods use porous membranes, however, which are subject to the risk of clogging and require high quality filtering. Here instead of using a membrane pore, we report ballistic energy conversion using a rotary atomizer. Fig. 5.1b shows the configuration of our new two-phase (liquid and air) power generation system based on a glass rotary atomizer and demineralized water. Ballistic energy conversion (BEC) systems such as presented by Xie et al. [10],

Figure 5.1: (a) Single-phase conventional pressure driven flow; I_s : streaming current, I_c : conduction current; (b) Schematic view of our new approach using centrifugal force in a two-phase system. We denote the electrical current through the load resistor (Z) as I_2 . Current is supplied from the grounded central electrode at the fluid supplier and denoted as I_1 . A small amount of charged droplets will also land on the shielding ring. This electrical current is denoted as I_3 .

and in the paper here use a two-phase configuration in which a two-step conversion mechanism occurs. First, we convert mechanical energy to kinetic energy of the air-isolated droplets and then the droplets kinetic energy to electrical energy. This mechanism gives an elegant simultaneous demonstration of two fundamental laws of physics: the law of energy conservation and Newton's second law of motion as we will show. To our knowledge, this is the first time energy generation using a rotary atomizer generator has been studied, either experimentally or theoretically.

5.2 Methods

5.2.1 Glass rotary atomizer

Fig. 5.2 shows the schematic of the device structure. The motor model YM-261A-9 was supplied from Germany <http://www.rakuten.de/>. The motor rotational speed was controlled by a voltage regulator. The rotational speed of the atomizer was measured by two different methods: (i) using Fastscan SA-X (Photron, Japan) and (ii) using ACT-3X tachometer by Monarch Instruments coupled to a remote optical sensor [11] (Monarch Instruments, model ROS-5W, USA). Droplet velocity and droplet size were analysed using ImageJ [12] version 1.46r. A glass Petri dish (Fisher Scientific) connected to the top of the motor functioned as the rotating plate.

5.2.2 Electrical measurement

The currents I_1 , I_2 and I_3 are measured using Keithley instruments, namely Keithley models 6487, 6485, 2410, respectively. Resistors with a voltage rating of 20 kV were used with varying values from 0.1 GOhm to 5 GOhm. The electrical potential of the charge collector was calculated following Ohms law $V = I_2 Z$. The resistors were immersed in insulating oil (Shell Diala S2-ZU-I) to prevent electrical losses by discharge. All experiments were performed in air at atmospheric pressure and ambient temperature.

5.3 Results

5.3.1 Micro-sized charged droplets

The exploded view and the top view of the glass rotary atomizer are shown in Fig. 5.2a and 5.2b respectively. Demineralized water (DI water) is gravitationally supplied from a supplier bottle where the water level is kept constant by using an over-flow valve. Upon contacting the center of the rotating glass Petri dish, the water is outwardly accelerated. The manner in which droplets are produced is dependent on 6 quantities: the dish diameter, rotary speed, liquid flow rate, surface tension, viscosity and liquid density [13]. Disintegration of the continuous water layer on the Petri dish occurs when surface tension and viscous forces are overcome by the centrifugal forces. It has been established in literature that droplets are produced by one of three operational modes, namely: direct droplet mode, ligament mode and sheet mode [13, 14]. In ligament mode, stable liquid ligaments are formed at the dish circumference and disintegrate into droplets. In this investigation, the spinning dish was maintained at ligament operation mode to ensure the highest uniformity of droplets and minimal droplet size [13, 15]. Once formed, driven by inertia, these droplets travel toward and land on the aluminum collector. Electrically, the ionic charges from the mobile part of the EDL on the Petri dish surface are transferred into the flying droplets and then electrochemically converted to an electron current at the aluminum collector. This electrical current (I_2) then passes through a load resistor (Z) connected to ground finally generating electrical power. To complete the circuit, the charges in the EDL are replenished by a current flowing through the grounded central electrode immersed in the solution supplied to the center of the disk (Figure. 5.1b). A metal shielding ring having an opening of 4 mm and being electrically grounded is placed 1.5 mm from the rotating disk to shield the solution from electrostatic induction from the high potential of the charge collector, which is generated when resistors are used (as depicted in Fig. 5.2c). The ring can also be used to induce extra charge on the droplets by applying a negative potential to it. The typical droplet sizes and velocities of the captured droplets are shown in Fig. 5.3a obtained at a rotational speed of 720 rad/s

Figure 5.2: (a) Exploded view of the atomizer set-up; (b) Top view of the atomizer set-up. (c) Schematic of the shielding ring. (d) Example of high speed camera images obtaining from our experimental measurement (captured using Fastscan SA-X (Photron, Japan)) at rotational speed 152 rad/s, volume flow rate 5 ml/s. The droplets formed are spherical.

(a)

(b)

Figure 5.3: (a) Droplet size versus droplet velocity. (b) Droplet size distribution (bars) fitted with a log-normal distribution (line). Experiments were performed at angular velocity $\omega = 720$ rad/s and flow rate $Q = 2.7$ ml/s.

and a volume flow rate of 2.7 mL/s. The droplet size distribution can be fitted well with the log-normal function (see Fig. 5.3b). This is in agreement with the literature for rotary atomizer systems [16].

5.3.2 Streaming current and output power

Power is harvested by the load resistor. We denote the electrical current through the load resistor as I_2 . Current supplied from the grounded electrode at the fluid supplier is denoted as I_1 . A small amount of charged droplets will also land on the shielding ring and generate an electrical current denoted as I_3 (See Fig. 5.1b). Figs. 5.4a and 5.4b shows the electrical currents I_1 , I_2 , I_3 with ((a), $I_3 > 0$) and without ((b), $I_3 = 0$) the use of the grounded shielding ring. The current I_1 represents the sum of streaming current and conduction current ($I_1 = I_s + I_c$). The current I_2 equals I_1 minus losses of charged droplets. The generated target voltage ($V = I_2 Z$) and output power ($P_{out} = V I_2$) in both cases, with and without use of the grounded shielding ring are depicted in Figs. 5.5a and 5.5b.

5.4 Discussion

From Fig. 5.4a and 5.4b, it is clearly seen that without the shielding ring, the currents I_1 and I_2 both decrease with an increase of load resistor value and that I_2 is approximately equal to I_1 . In this case, the increase of load resistor value leads to an increase of the target potential and thereby increases the conduction current via an inductive mechanism, reducing I_1 and thereby I_2 . This induction occurs at the water-air interface through a continuously distributed resistance and capacitance as formed by the aqueous solution and its interface with the air [17, 18]. It is obvious from Figs. 5.4a and 5.4b that the use of the grounded shielding ring prevents induction and hence the reduction of I_1 which now remains constant for load resistors up to $R = 1900$ Mohm (target potential up to 2 kV), though at the cost of an increasing current loss I_3 . With load resistor values higher than 1900 Mohm, $I_1 \geq I_2 + I_3$ and we assume current is lost to other processes such as to electrical breakdown at high target voltage ($V > 2.5$ kV).

(a)

(b)

Figure 5.4: Measured current versus resistor values with (a) and without (b) using the grounded shielding ring.

(a)

(b)

Figure 5.5: Output power and output voltage with (a) and without (b) using the grounded shielding ring. Experiments were performed using demineralized water at pH 6.

When no load resistor is used, an increase of both I_1 and I_2 is seen in case the grounded shielding ring is used when compared to the case without shielding ring (from 600 nA to 1400 nA, Fig. 5.4). We hypothesize that this is caused by the change of the electrical potential at the location of the grounded ring from strongly positive in its absence (due to the generated streaming potential) to ground potential when present. In the former case a strong conduction current will be generated, decreasing I_1 , while in the latter case the conduction current will be much smaller. This hypothesis can be demonstrated by using the method of image charges (please refer to **appendix 5.F** [19]).

The maximum output power we can generate with the grounded shielding ring is 1.7 mW (as shown in Fig. 5.5a). In order to further increase the charge on the droplets and the output power, we applied a negative potential to the shielding ring making it an induction electrode, attracting positive charges to the water/air interface. This induction charging occurs at the water/air interface through a continuously distributed resistance and capacitance as formed by the aqueous solution and its interface with the air. As the jets break up, the droplets retain the induced charge. We applied a voltage of -1 kV in the experiments reported here. It is clearly seen from Fig. 5.6a that for $Z = 0$ Mohm, the current I_1 now is 3074 nA, which is 2 times larger than in case of the grounded shielding ring (1400 nA, Fig. 5.4a), and can be contributed to the charge induction mechanism. The maximal output power we obtained for the case of applied negative potential to the shielding ring is 4.9 mW (Fig. 5.6b) at an output voltage of 3120 V. The energy conversion efficiency of the system (χ) is defined by the ratio between the electrical output power (P_{out}) and the mechanical input power (P_{in}).

$$\chi = \frac{P_{out}}{P_{in}} = \frac{I_2 V}{\tau \omega} = \frac{I_2 V}{\dot{M} v_0^2} \quad (5.1)$$

In this equation, $\tau = \dot{M} v_0 R_e$ is the torque [20] required to rotate the glass dish excluding all loss sources except water acceleration. $\dot{M}$ is the mass flow rate. The tangential velocity is $v_0 = \omega R_e$. R_e is the radius of the rotating dish and ω is the angular velocity. For details on the derivation of the equation for the input power

(a)

(b)

Figure 5.6: (a) Measured current and (b) calculated output power and output voltage versus resistor values when -1 kV was applied to the shielding ring.

Figure 5.7: Components of the rotary atomizer generator.

and its components, please refer to the *appendix 5.A* [21–23]. For the current experiments with rotational speed $\omega = 720$ rad/s, $v_0 = 36$ m/s, the energy conversion efficiency of the system calculated from eqn. (5.1) is 0.14 %.

In the following, we will discuss the conversion mechanism, the energy conversion efficiency of the system and the way to optimize the system to maximize conversion efficiency. In order to achieve clarity in the analysis, we divided our atomizer generator process into 4 component steps: (1) water feeding, (2) charging & accelerating, (3) droplet formation & transport, (4) droplet landing & charge transfer (Fig. 5.7). Charging of the droplets occurs at step 2 by double layer advection and induction. In step 2 we also accelerate the liquid by frictional coupling between the solid surface and the liquid mass. This is a high-loss coupling, with the loss determined by the internal friction in the liquid during the acceleration. The entire invested energy (P_{in}) will thus be the sum of the final (liquid) kinetic energy (P_k) and the frictional losses ($P_{f,liq}$). As mentioned in the *appendix 5.C* the frictional losses $P_{f,liq}$ cost 50 % of the input power. The other 50 % of the input power goes to the kinetic energy of the water (P_k) leaving from the dish edge. In step 3, droplets are formed and transported towards the target through the air. As shown in the *appendix 5.C.2* the energy needed for surface creation can be neglected. The theoretical maximum conversion efficiency will be less than 50 % by taking account of the energy loss in step 3 due to the air friction. In the *appendix 5.C.4*, we show that under the present

operating conditions the air friction consumes 33 % of the droplet kinetic energy. At step number 4, the charged droplets land on the collector, charging it up to a steady state potential $V = I_2 Z$. The potential V gives rise to an electrical field $\vec{E}$ and droplet (i) with charge q_i by its kinetic energy has to overcome the electrical force $\vec{E}q_i$ to land on the collector. From Newton's second law for droplet mass (m_i) and acceleration $\vec{a}$, $\vec{F} = m_i \vec{a}$, we obtain the force balance on an individual droplet i

$$m_i \vec{a} = -\vec{E}q_i \quad (5.2)$$

Now we assume that the surface charge density is equal for all droplets and independent of their size. The charge to mass ratio of individual droplets $(q/m)_i$ then is [24] (for derivation and nomenclature see in **appendix 5.E** [25–28])

$$\left(\frac{q}{m}\right)_i = \frac{I_1}{r_i \dot{M}} \frac{\sum_i^n n_i r_i^3}{\sum_i^n n_i r_i^2} \quad (5.3)$$

The maximal energy conversion efficiency of the system for droplet i now is obtained when the droplet kinetic energy ($\frac{m_i v_i^2}{2}$) equals the generated electrical potential energy ($q_i V$).

$$\chi_{max_i} = 0.5 \left(\frac{q_i V}{\frac{1}{2} m_i v_i^2} \right) \quad (5.4)$$

where the factor 0.5 stems from the energy loss in step 2. Droplet velocity at landing then equals zero, and no energy is lost to collision.

By substituting $(q/m)_i$ from eqn. (5.3) into eqn. (5.4)

$$\chi_{max_i} = \left(\frac{I_1}{\dot{M}}\right) \left(\frac{V}{v_i^2}\right) \left(\frac{\sum_i^n n_i r_i^3}{r_i \sum_i^n n_i r_i^2}\right) \quad (5.5)$$

Eqn. (5.5) is identical to eqn. (5.1) if the following conditions are satisfied:

- (a) the droplet size distribution is monodisperse $\left(\frac{\sum_i^n n_i r_i^3}{r_i \sum_i^n n_i r_i^2} = 1\right)$
- (b) the droplet velocity is equal to the rotating tangential velocity ($v_i = v_0$), meaning no loss due to air friction.
- (c) $I_2 = I_1$, meaning no current loss by leakage to the shielding ring.

Figure 5.8: Theoretical maximum energy conversion efficiency from experimentally determined droplet sizes and velocities at a target potential of 3.12 kV and no droplet loss (i.e. maximum efficiency at $I_2 = I_1$).

Fig. 5.8 shows the theoretical maximum energy conversion efficiency for individual droplets plotted from eqn. (5.5), in which v_i and r_i are the measured droplet velocity and droplet radius (when droplets pass through the shielding ring, 3 mm from the dish edge) implying that no droplets loss occurs and V is 3.12 kV. It is obvious that from the smaller droplet sizes with a higher charge to mass ratio (please refer to the **appendix 5.E** for $(q/m)_i = C(1/r_i)$) larger energy conversion efficiencies can be obtained. Even for the smallest droplets of 20 μm radius, however, only a small fraction of the kinetic energy (3.2 % at an overall efficiency of 1.6 %) can be harvested at the target potential of 3.12 kV. Theoretically, one can obtain overall maximum conversion efficiency of the system at $(100\% - 50\%) \times (100\% - 33\%) = 33.5\%$ when all droplet kinetic energy is converted to electrical energy (with 33 % loss of kinetic energy to the air friction). To obtain this optimal conversion, droplets need to be maximally decelerated, which occurs when $\vec{a} = -\vec{E} \frac{q_i}{m_i}$ (from eqn. 5.2) is maximized. Further increasing the charge to mass ratio ($\frac{q_i}{m_i}$) therefore is crucial as this will allow harvesting a larger proportion of the kinetic energy, which is now lost on droplet impact. Our present droplet mean charge-to-mass ratio is still less than

13 times compared to the Rayleigh limit [29] ($q_{max} = (8\pi^2\epsilon^0\sigma d^3)^{0.5}$), implying the electrical force at the same target potential can still be increased by at least one order of magnitude if the charge to mass ratio can be efficiently increased. It is obvious that in the future work, decreasing the droplet size as well as increasing the monodispersity have to be the aim, coupled to an efficient charge induction, so that higher conversion efficiencies can be obtained. One of the ways to obtain a smaller and more uniform droplet size is to reduce the volume flow rate of the system (in case we decide to maintain the other liquid properties) since it was shown [14] that the mean droplet size d_{mean} is proportional to Q , $d_{mean} = Q^\alpha f(\omega, R_e, \sigma, \rho, \mu)$. Here α is a positive constant (always > 0.1) which is dependent on the atomization modes. Consider the future use of other liquids than water, the liquid of choice should allow a maximal charge over mass ratio. The density should therefore be low while the Rayleigh limit indicates the surface tension should be high. Furthermore the effect of liquid properties such as viscosity and density on droplet size as mentioned in the formula above should be considered. A fundamentally different centrifugal ballistic system could also be envisaged, based on using non-conducting liquids coupled to charge injection from a conducting plate. Finally, as can be seen in eqn. 5.4, increasing the target voltage is another aim, as this will increase the electrical field $\vec{E}$ (in eqn. 5.2), and hence deceleration. At present, we found target voltage was limited to 3.12 kV due to spontaneous discharge.

5.5 Conclusions

To conclude, we show an approach to generate electrical energy from a rotary atomizer system. The principle demonstrated is extremely simple, as it only needs water, a rotating disk and a metal droplet collector. The rotary atomizer generator presented in this work interestingly is the opposite process of electrospraying which is used e.g. in rotary atomizers for electrostatic painting and crop dusting applications, and where a high voltage is needed to generate charged droplets. Apart from being an energy generation method, our approach opens up a way for charging droplets from which applications, requiring either charged droplets, a rotary atomizer or both such

as electrostatic painting and crop dusting, can benefit.

Appendix

This appendix provides the theoretical calculation for the work presented in chapter 5

5.A Energy conversion efficiency

We consider a Petri Glass disk of radius R_e rotating about its vertical axis with angular velocity ω . Liquid falls onto the centre of the disk from a nozzle located h_0 above the disk with volumetric flow rate Q . Upon impacting the surface of the disk, the liquid is driven radially outward due to the centrifugal force. The resulting velocity of the liquid therefore has two component: the radial one $u(z, r)$ and the tangential one $v(r) = \omega r$ (Figure 5.B.1). In order to estimate the energy conversion efficiency of the system, we will need to estimate the power required (P_{in}) to stream the liquid from the center of the disk to the charge collector.

The input power is converted to the droplet kinetic energy per unit time added to the sum of power losses. In the case of no slippage, only the viscous resistance needs to be taken into account and the input power follows the following relationship:

$$P_{in} = P_{f,liq} + P_k + P_\sigma \quad (5.6)$$

in which $P_{f,liq}$ is the power loss due to the friction at the solid-liquid interface. P_σ is the power loss to form individual droplets and P_k is the kinetic energy of the droplets formed per unit time, consisting of a radial component (P_k^r) and tangential

component (P_k^t).

$$P_k = P_{f,air} + P_{k,final} + P_{out} \quad (5.7)$$

here P_{out} is the electrical output power (the part of the droplet kinetic energy which is lost to deceleration by electrical field). $P_{(k,final)}$ is the kinetic energy that the droplets still have on landing on the target and $P_{(f,air)}$ is the power loss due to air friction. Now we can insert the (Eqn. 5.7) into (Eqn. 5.6) which describes the power balance prior to and including the droplet generation. This results the following

$$P_{in} = P_{f,liq} + P_{\sigma} + P_{k,final} + P_{f,air} + P_{out} \quad (5.8)$$

The energy conversion efficiency (χ) of the system is defined by the ratio between output electrical power (P_{out}) and input power (P_{in})

$$\chi = \frac{P_{out}}{P_{in}} = \frac{I_2 V}{\tau \omega} \quad (5.9)$$

τ is the torque required to rotate the glass dish and ω is the angular velocity. At the steady state the angular momentum balance on the rotating dish gives $\tau = \dot{M} R_e v_0$ [20]. Here, $\dot{M}$ is the mass flow rate, R_e is the radius of the rotating dish and the tangential velocity $v_0 = R_e \omega$. Therefore, the input power needed to drive the rotating dish is equals to

$$P_{in} = \dot{M} v_0 R_e \omega = Q \rho v_0^2 \quad (5.10)$$

in which ρ is the liquid density. Now we focus on estimating each of the aforementioned powers in the right-hand side of the equation (5.8).

5.B Kinetic energy

In order to estimate the kinetic energy of the liquid at the edge of the disk, we first estimate the energy used to accelerate the liquid from the center of the disk to velocity at the edge $\mathbf{u}_e$ (the boldface denotes a vector quantity). Here, the liquid velocity is a two-component vector with the radial and tangential components: $\mathbf{u}_e = (u, v)$. We assume that the air drag applied on the liquid as it flows on the disk is negligible, and

Figure 5.B.1: Schematic (not to scale) of the rotary atomizer. (a) top view, (b) side view.

the liquid film is sufficiently thin so that the flow is laminar. The radial flow in the film is then driven by centrifugal forces and resisted by the shear at the wall [21]. As a result, the radial velocity $u(z, r)$ of the liquid in the film at radial location r and distance z is governed by the equation

$$\nu \frac{d^2 u}{dz^2} = -\omega^2 r \quad (5.11)$$

where ν is the liquid kinematic viscosity. This equation, together with no-slip boundary condition ($u(z = 0) = 0$ and $u'(z = \delta) = 0$), can be solved to give the radial velocity distribution across the film

$$u(r, z) = \frac{r\omega^2\delta^2}{\nu} \left(\frac{z}{\delta} - \frac{z^2}{2\delta^2} \right) \quad (5.12)$$

Herein, δ is the thickness of the liquid film and can be calculated using the mass conservation

$$Q = \int_0^\delta 2\pi r u(r, z) dz \quad (5.13)$$

Thus we obtain the expression for the film thickness

$$\delta(r) = \left(\frac{3}{2\pi} \frac{\nu Q}{\omega^2 r^2} \right)^{1/3} \quad (5.14)$$

At the edge of the disk, the liquid has the tangential velocity $v_0 = \omega R$, radial velocity $u(z) = u(r = R_e, z)$ and the liquid film thickness is δ . The kinetic power of the liquid at the edge of the disk is then

$$P_k = P_k^t + P_k^r \quad (5.15)$$

where the tangential component of the kinetic energy is

$$P_k^t = \int_0^\delta \frac{1}{2} v^2 dm \quad (5.16)$$

in which $dm = \rho 2\pi R_e u dz$ is the liquid mass that is ejected out from the edge of the disk per unit time.

$$P_k^t = \int_0^\delta \frac{1}{2} v^2 \rho 2\pi R_e u dz = \frac{1}{2} \rho Q R_e^2 \omega^2 \quad (5.17)$$

The radial component of the kinetic energy is

$$P_k^r = \int_0^\delta \frac{1}{2} u^2 \rho 2\pi R_e u dz = 0.147 \frac{\omega^{4/3} Q^{7/3} \rho}{\pi^{4/3} (\nu R)^{2/3}} \quad (5.18)$$

5.C Power losses

5.C.1 Frictional force at the solid-liquid interface

From equation 5.12, one has the shear stress (S) at the solid-liquid interface ($z = 0$)

$$S(r) = \mu \frac{\partial u}{\partial z} \quad (5.19)$$

Therefore, the power caused by this shear stress for entire liquid on the disk is

$$P_f = \int_{R_0}^{R_e} 2\pi r S \bar{u} dr \quad (5.20)$$

where $\bar{u}$ is the averaged velocity of the liquid across the film, $R_0 > 0$ is the radius of the liquid column that falls on the disk. Note that $\delta(r)$ diverges at $r = 0$, but the finite size of the falling liquid column ensures that $\delta(r)$ can only be calculated for $r > R_0$. The vertically-averaged radial velocity $\bar{u}(r)$ can be calculated as follows

$$\bar{u}(r) = \frac{1}{\delta(r)} \int_0^{\delta(r)} u(r, z) dz = \frac{1}{3} \frac{r \delta^2 \omega^2}{\nu} \quad (5.21)$$

From eqns. (5.19), (5.20) and (5.21), we have

$$P_f = \frac{1}{2} Q \rho \omega^2 (R_e^2 - R_0^2) \quad (5.22)$$

This is exactly the same as the kinetic power of the tangential velocity (in the limit $R_0 \rightarrow 0$), which makes sense (see eqn. (5.17)) because the centrifugal force acts on the liquid to overcome the frictional force and drives the liquid radially outward.

5.C.2 Power required to break the liquid into droplets

Consider droplet with radius r_d (sufficiently small so that gravity is negligible), the surface energy of the droplet in flight is $4\pi r_d^2 \sigma$, in which σ is the liquid/air surface tension [22]. The volume of the free droplet is $(4/3)\pi r_d^3$. Therefore the power required to break up the flowing liquid into droplet is

$$P_\sigma = \left(\frac{Q}{\frac{4}{3}\pi r_d^3} \right) (4\pi r_d^2 \sigma) = \frac{6Q\sigma}{d} \quad (5.23)$$

Figure 5.C.1: Illustration of droplet trajectory l .

here, $\left(\frac{Q}{\frac{4}{3}\pi r_d^3}\right)$ is the number of droplet ejected per unit time, assuming that they all have the same diameter d .

5.C.3 Power loss due to air friction

The power lost due to air drag that is applied on the flying droplets can be estimated by assuming that their trajectories and velocities are not affected by the electrical field induced by the charged collector and the air drag. This assumption is consistent with the experimental visualization obtained by high-speed recording of flying droplets and can be explained by the fact that the kinetic energy of the droplets is very high due to high angular velocity of the disk. Therefore, the trajectory of an ejected droplet is a straight line (blue line in figure (5.C.1)) that is tangential to the disk circumference, with length $l = \sqrt{(R_c^2 - R_e^2)}$. According to Stokes law, the drag force that works on each droplet of diameter d is $F_d = C_d \left(\frac{\pi d^2}{4}\right) \frac{1}{2} v^2 \rho_a$, and the power lost to air drag that exerted on flying droplets therefore is

$$P_{air} = \left(\frac{Q}{\frac{4}{3}\pi r_d^3}\right) F_d l = \left(\frac{Q}{\frac{4}{3}\pi r_d^3}\right) F_d \sqrt{(R_c^2 - R_e^2)} \quad (5.24)$$

Table 5.C.1: Comparison between droplet kinetic power and other power contributions

P_k^t/P_k^r	$P_k^t/P_{f,liq}$	P_k^t/P_σ	$P_k^t/P_{f,air}$
1133	1	112	3

where $C_d = 0.4$ is the drag coefficient [23] and ρ_a is the air density ($= 1.2 \text{ kg/m}^3$)

5.C.4 Comparison of the droplet kinetic power with other power contributions and losses

By substituting the experimental value of all the parameters as follows: $R_e = 5 \text{ cm}$; $R_c = 6 \text{ cm}$; $Q = 2.7 \text{ mL/s}$; $r_d = 37.5 \text{ }\mu\text{m}$; $\omega = 720 \text{ rad/s}$; $\rho = 1000 \text{ kg/m}^3$; $\rho_a = 1.2 \text{ kg/m}^3$; $\nu = 10^{-6} \text{ m}^2/\text{s}$; $\sigma = 0.072 \text{ N/m}$; $C_d = 0.4$ into the equations for each of the power contributions (derivation is shown in previous sections), we obtained the power ratios as shown in Table 5.C.1.

According to table 5.C.1, the radial kinetic energy (P_k^r) is much lower than the tangential kinetic energy (P_k^t) and hence the radial kinetic energy is negligible. From now on, we therefore refer to droplet kinetic energy as the tangential kinetic energy. Also the power loss by break-up of the water layer into droplets is negligible compared to the droplet kinetic energy. Importantly, we learn from table 5.C.1 that the droplet kinetic energy is equal to the frictional loss at the solid-liquid interface. Therefore, the input power is equal to twice the droplet kinetic energy. Furthermore, the energy loss due to air friction at present costs 33% of the droplet kinetic energy. Therefore, the theoretical maximum energy conversion efficiency for the present system is $1/2(100\%)(100 - 33)\% = 33.5\%$.

5.D Motion equation for the flying droplets

To discuss the influence of air friction and electrical forces on droplet motion, we start with Newton's second law in a force balance for the droplet motion with air drag and electrical force.

$$v(x)\frac{dv}{dx} = -\frac{F_e}{m} - \frac{F_d}{m} \quad (5.25)$$

F_e is the electrical force and F_d is the air drag force acting on the moving charge droplet, respectively. Thus:

$$v(x) \frac{dv}{dx} = -\frac{F_e}{m} - \frac{0.5C_d\pi r_i^2 \rho_a v^2(x)}{m} \quad (5.26)$$

We now simplify Eqn. (5.26) by denoting α as the influence of electrical field and β as the influence of air resistance on droplet velocity, respectively.

$$\alpha = \frac{F_e}{m}; \quad \beta = \frac{0.5C_d\pi r_i^2 \rho_a}{m} \quad (5.27)$$

Equation (5.26), therefore becomes,

$$v(x) \frac{dv}{dx} = -\alpha - \beta v^2(x) \quad (5.28)$$

Solving this non-linear differential equation, taking into account of 2 boundary conditions $v(x) \geq 0$ and $v(0) = v_0$, we obtain

$$v^2(x) = \frac{-\alpha + e^{-2\beta x}(\alpha + \beta v_0^2)}{\beta} \quad (5.29)$$

In order to separately investigate the influence of the electrical field and the air friction on the droplet velocity we take the limit of the function $v^2(x)$ in two cases.

Case 1: The influence of air drag, when $\alpha \rightarrow 0$

$$v^2(x) = v_0^2 e^{-2\beta x} \quad (5.30)$$

From eqs. (5.25), (5.26), (5.27) and (5.30) we obtained

$$\frac{F_d}{m} = \beta v_0^2 e^{-2\beta x} \quad (5.31)$$

Eqn. (5.31) indicates that air friction force is reduced with the increase of droplet travel distance x . This can be explained by the fact that droplet velocity is also decreased with trajectory distance (can be seen in eqn. (5.30)).

Case 2: The influence of electrical field, when $\beta \rightarrow 0$

$$v^2(x) = v_0^2 - 2\alpha x \quad (5.32)$$

It can be seen from eqn. (5.32) that by increasing of the travel distance (x), the droplet velocity is reduced due to influence of electrical field.

5.E Charge to mass ratio of individual droplet

A method was developed and reported by Toljic Nikola [24] to estimate the charge-to-mass ratio (q/m) distribution based on the droplet size.

It is considered that the droplet population has N droplets in which each one has its own mass m_i and charge q_i . The total mass (M) and charge (G) therefore equal to

$$M = \sum_i^n n_i \rho K_i \quad (5.33)$$

$$G = \sum_i^n n_i \left(\frac{q}{m} \right)_i \rho K_i \quad (5.34)$$

Here n_i is the number of droplets with diameter d_i and K_i is the volume of the droplets, equal to $(4/3)\pi r_i^3$ with r_i the radius of the individual droplet i . q_i and m_i are the charge and mass of the individual droplet number i . The average charge G to mass M ratio therefore can be expressed as following

$$\frac{G}{M} = \frac{\sum_i^n n_i \left(\frac{q}{m} \right)_i \rho K_i}{\sum_i^n n_i \rho K_i} = \frac{\sum_i^n n_i \left(\frac{q}{m} \right)_i r_i^3}{\sum_i^n n_i r_i^3} \quad (5.35)$$

If the liquid has the mass flow rate, we also have for the average charge to mass ratio [25, 26]:

$$\frac{G}{M} = \frac{I_1}{\dot{M}} \quad (5.36)$$

Therefore, we obtain

$$\frac{I_1}{\dot{M}} = \frac{\sum_i^n n_i \left(\frac{q}{m} \right)_i r_i^3}{\sum_i^n n_i r_i^3} \quad (5.37)$$

Some reports used the terms 'liquid flow rate' [27] or 'particle flow rate' [24] for in the equation (5.37), here we specifically named $\dot{M}$ [kg/s] as mass flow rate to distinguish it from the volume flow rate Q [m³/s]. For the individual droplets, the charge to mass ratio is a function of droplet radius, for which we have the following general relation [28]:

$$\left(\frac{q}{m}\right)_i = C r_i^\varphi \quad (5.38)$$

in which C is a coefficient, and φ is a constant dependent on the charge distribution assumption. Here, we consider two cases.

(b) $\varphi = 0$, meaning that the droplet volume charge is constant and q/m is independent of droplet radius r_i

$$\frac{q}{m} \sim \frac{K}{\rho K} \text{ or } \left[\left(\frac{q}{m}\right)_i\right] \text{ is not a function of } r_i \quad (5.39)$$

(a) $\varphi = -1$, meaning the droplet surface charge density is constant and q/m is inversely proportional to the droplet radius r_i

$$\frac{q}{m} \sim \frac{A}{\rho K} \text{ or } \left[\left(\frac{q}{m}\right)_i\right] \sim \frac{1}{r_i} \quad (5.40)$$

(in which A represents the surface area of the droplet).

By substituting eqn. (5.38) to eqn. (5.37), we obtain

$$\frac{I_1}{\dot{M}} = \frac{\sum_i^n n_i (C r_i^\varphi)_i r_i^3}{\sum_i^n n_i r_i^3} \quad (5.41)$$

Eqn. (5.41), then gives us an expression for the coefficient C :

$$C = \frac{I_1}{\dot{M}} \frac{\sum_i^n n_i r_i^3}{\sum_i^n n_i r_i^{3+\varphi}} \quad (5.42)$$

Hence, from eqns. (5.38) and (5.42) we can obtain the equation for the charge to mass ration of the individual droplet

$$\left(\frac{q}{m}\right)_i = \frac{I_1}{\dot{M}} \frac{\sum_i^n n_i r_i^3}{\sum_i^n n_i r_i^{3+\varphi}} r_i^\varphi \quad (5.43)$$

Figure 5.F.1: Schematic of a point charge A below the grounded conducting shielding ring.

Now if we assume the surface charge density is equal for all droplet, which means $\varphi = -1$, eqn. (5.43) becomes

$$\left(\frac{q}{m}\right)_i = \frac{I_1}{r_i M} \frac{\sum_i^n n_i r_i^3}{\sum_i^n n_i r_i^2} \quad (5.44)$$

By using eqn. (5.44) and measuring the current I_1 , the mass flow rate and the droplet radii, we can obtain the charge to mass ration of the individual droplet.

5.F Method of image charges

The increase of streaming current I_1 and I_2 when the grounded shielding ring is used can be explained due to the reduction of the positive electric potential at the zone in-between the rotational disk and the grounded shielding ring. To demonstrate this, in a general case we randomly consider a point charge Q at location $A (0, d, 0)$ on the surface of the rotating glass disk (Fig. 5.F.1) and the grounded conducting shielding ring is considered as of large extent (so that the electrical field is uniform).

In the case without shielding, the electrical potential at point $P(x_p, y_p, z_p)$ close

to the point charge A is defined by

$$V_0 = \frac{Q}{4\pi\epsilon_0 r_1} \quad (5.45)$$

in which

$$r_1 = \sqrt{(x_P - x_A)^2 + (y_P - y_A)^2 + (z_P - z_A)^2} = \sqrt{x^2 + (y - d)^2 + z^2} \quad (5.46)$$

Therefore,

$$V_0 = \frac{Q}{4\pi\epsilon_0 \sqrt{x^2 + (y - d)^2 + z^2}} \quad (5.47)$$

When the grounded shielding ring is in place, the classical method of images [19] can be applied by removing the conducting shielding ring and creating an image charge point B located at $(x, y, z) = (0, -d, 0)$. Using principle of superposition to determine electric potential V at point P now gives

$$V_{12} = \frac{Q}{4\pi\epsilon_0 r_1} + \frac{-Q}{4\pi\epsilon_0 r_2} = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (5.48)$$

here,

$$r_2 = \sqrt{(x_P - x_B)^2 + (y_P - y_B)^2 + (z_P - z_B)^2} = \sqrt{x^2 + (y + d)^2 + z^2} \quad (5.49)$$

Therefore,

$$V_{12} = \frac{Q}{4\pi\epsilon_0 \sqrt{x^2 + (y - d)^2 + z^2}} - \frac{Q}{4\pi\epsilon_0 \sqrt{x^2 + (y + d)^2 + z^2}} \quad (5.50)$$

This solution for V_{12} is satisfied the boundary condition $V_{12} = 0$ at all points in the plane $y=0$ (meaning the case of presenting the grounded conducting shielding ring at $y=0$). Therefore, according to uniqueness theorem in electrostatic solution, this is the only possible solution.

By substituting eqn. (5.47) into eqn. (5.50), we obtain

$$V_{12} = V_0 - \frac{Q}{4\pi\epsilon_0 \sqrt{x^2 + (y + d)^2 + z^2}} \quad (5.51)$$

Because $\frac{Q}{4\pi\epsilon_0\sqrt{x^2 + (y+d)^2 + z^2}} > 0$, eqn. (5.51) results in $V_{12} < V_0$. In other words, the positive electric potential in locations in-between the point charges and the grounded shielding ring has been reduced. Because the superposition principle holds for the electric potential, the grounded conducting plane above multiple point charges can be replaced by the mirror images of each of the charges individually and no other modifications are necessary.

On the other hand, we can also consider that the positive point charge Q induces negative charges on the surface of the grounded conducting plane. This results in a surface charge density $(-|\gamma|)$ on the conducting plane. Therefore the electric potential in the zone between the positive point charge Q and the conducting plane (at $y > 0$) is

$$V_1 = \frac{Q}{4\pi\epsilon_0\sqrt{x^2 + (y-d)^2 + z^2}} + \frac{Q}{4\pi\epsilon_0} \int_{\Omega} \frac{(-|\gamma|)}{r} d\Omega \quad (5.52)$$

Here r is the distance from $d\Omega$ to the point P of consideration and Ω is the surface of the conducting plane. Now in the case of applying a fixed negative potential to the conducting shielding ring we can even further increase current I_1 and I_2 . The situation of applying a fixed negative potential to the shielding ring is equivalent to the situation where we start with the grounded conducting plane and then we disconnect the ground wire and add to the conducting plane an amount of negative charge with surface charge density $(-|\sigma|)$ and $|\sigma| > |\gamma|$. The electric potential in the zone between the rotational disk and the conducting plane is now

$$V_2 = \frac{Q}{4\pi\epsilon_0\sqrt{x^2 + (y-d)^2 + z^2}} + \frac{Q}{4\pi\epsilon_0} \int_{\Omega} \frac{(-|\sigma|)}{r} d\Omega \quad (5.53)$$

From eqns. (5.47), (5.52), (5.53), we obtain $V_2 < V_1 < V_0$. In other words, the positively electric potential at the zone in-between the rotational disk and the shielding ring with applied negative potential is reduced more strongly compared to the case of grounded shielding ring.

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Chapter 6

Conclusions and Recommendations

6.1 Conclusions

This thesis presents an effort to understand electrokinetic energy conversion systems which are based on motion of ionic charges in micro- and nano-confinements. In particular, both experimentally and theoretically the utilization of different kind of liquids was investigated to convert mechanical to electrical energy in both on-chip and off-chip platforms by applying different forces to drive the fluids: a steady pressure, a periodic pressure and a centrifugal force. The fluids included Newtonian and non-Newtonian fluids.

In the effort to explore the utilization of various liquids, we carried out an experimental study on the effect of adding high concentrations of polymers to the working solution in a micro-channel. It is shown for the first time that the addition of charged polymers to the electrolyte solution greatly enhances the energy conversion efficiency from the pressure induced streaming current as compared to Newtonian fluids, opening up a potential route for efficient mechanical to electrical energy conversion.

In a second effort related to using polymers, we investigated theoretically the effect of using a Maxwell viscoelastic fluid in cylindrical micro-, and nanochannels under the actuation of both oscillating pressure gradients and electrical fields. We found that the Onsager's reciprocal relation is complied with this case. When implementing the calculations, it was found that the energy conversion efficiency from the streaming potential is massive, the same conclusion as reached in earlier work [1] performed for rectangular micro- and nanochannels. For the case of cylindrical microchannels the enhanced efficiency is even still higher than for the rectangular channels due to the lower hydraulic resistance of the former. Our theoretical work improved our understanding of the mechanism of the massive efficiency enhancement which we now see as the result of the fact that at the resonance frequencies the fluid inside the channel exhibits an almost entirely elastic behavior, leading to almost frictionless flow. We also found that oscillating EOF in Maxwell fluids has a much higher increase of its maximal velocity than oscillating PDF with respect to the low frequency behaviour where the maximal velocities for two flows are the same. All these findings advance

our understanding of AC electrokinetic phenomena for viscoelastic fluids and provide insight for describing flow characteristic as well as assist the design of devices for lab-on-chip applications.

The traditional approaches in streaming potential energy conversion systems deal with a single phase process in which the conversion of mechanical energy to electrical energy occurs only in the liquid phase. This leads to the drawback of a conduction current in the opposite direction of the streaming current, reducing the conversion efficiency. A newly developed process which is called ballistic energy conversion deals with a two-phase system, first converting mechanical energy to kinetic energy in the liquid phase and then converting kinetic energy to electrical energy for droplets dispersed in the gas phase (air). This acceleration-deceleration mechanism is new, and was first reported in a pressure-driven system using a micropore membrane [2]. One of the potential drawbacks of this system was the possibility that membrane pore would become clogged. Hence a high quality filter is needed and the system will be vulnerable. The output power of this version at least for a single pore membrane is also significantly small. We therefore developed a new platform for ballistic energy conversion based on the use of the centrifugal force and a high surface area of a glass dish. A streaming current energy converter without membranes or small channels is an important step from a technological point of view. We successfully obtained an output power of 4.9 mW, and a high voltage up to 3120 V. Apart from being a new energy conversion method, our approach opens up a way for charging droplets from which applications that require either charged droplets, a rotary atomizer or both such as electrostatic painting and crop dusting, can benefit.

6.2 Recommendation

Several aspects for further improvement of the experimental work as well as theoretical studies are important to be addressed in future research.

Firstly, using viscoelastic fluid in a micro-channel under actuation by a periodic pressure gradient is an interesting and promising approach for an experimental study of streaming potential energy conversion. An experimental study to verify

the theoretical prediction is not only necessary and crucial but also important for providing more insight into the AC streaming potential energy conversion system which is still in lack of experimental verification.

As for the ballistic energy conversion system on a rotary atomizer platform, smaller size, more uniform and more highly charged droplets are needed to allow harvesting a larger proportion of the kinetic energy, which is now lost on droplet impact.

The work reported in this thesis is performed in the context of investigating and improving the practical energy conversion efficiency from the streaming potential, aiming to obtain a maximal efficiency at maximal output power. Currently, high efficiencies have been reported in literature in experimental work [3–6] performed on highly charged polymer membranes but the efficiencies of such systems were calculated based on the formula of thermodynamic efficiency (application of the figure of merit, see detail in chapter 2, section 2.3). An exciting possibility is therefore to investigate these systems of highly charged polymer membranes but aim to achieve maximal efficiency at maximum output power density. Significant challenges for such a direct measurement are posed by the design of the experimental set-up so as to minimize the loss of energy at the electrodes due to concentration and polarization. Theoretical studies for designing and explaining the experimental results of such systems are also needed. To solve this, I suggest that although the Poisson-Boltzmann equation has been utilized for interpreting the experimental results and theoretical predictions with moderate surface charged density, it becomes invalid when using high surface potential or large ionic concentration. As an alternative approach, fluid Density Functional Theory (f-DFT) is an effective tool to investigate the physical phenomena in the nanoscale since it has the ability of containing detailed molecular interaction information once an appropriate intermolecular potential is given. It is able to predict the electrical double layer properties more precisely due to the coupling of the ionic size and electrical correlations. Fluid Density Functional Theory is therefore an excellent candidate for the next generation of theory for streaming potential energy conversion. This research area indeed has recently witnessed increasing interest of theoretical scientists and some nice predictions have been published such as [7–12]. So far however a combination of theory and experimental verification has been lacking.

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Nederlandse samenvatting

Dit proefschrift presenteert een studie naar de werking van systemen voor elektrokinetische energie omzetting, en in het bijzonder systemen die gebaseerd zijn op de verplaatsing van ionen in micro- en nanostructuren. Zowel experimenteel als theoretisch is het gebruik van verschillende types vloeistof, zowel in on-chip systemen als in off-chip systemen onderzocht, in combinatie met het aanbrengen van verschillende krachten: constante druk, periodieke druk en de centrifugaalkracht. Hierbij was het doel het omzetten van mechanische energie in elektrische energie. Onder de onderzochte vloeistoffen bevonden zich zowel Newtoniaanse als niet-Newtoniaanse vloeistoffen. In de studie naar het gebruik van verschillende vloeistoffen is experimenteel gekeken naar de effecten van het toevoegen van hoge polymeerconcentraties aan de oplossing in de microkanalen. Het is voor de eerste keer aangetoond dat het toevoegen van geladen polymeren aan een elektrolytoplossing de efficiëntie van de energie omzetting sterk verbeterd ten opzichte van een vloeistof zonder polymeren. Deze vinding heeft de potentie om een bijdrage te leveren aan een meer efficiënte omzetting van mechanische energie in elektrische energie. In een tweede studie gerelateerd aan het gebruik van polymeren onderzochten we theoretisch het effect van het gebruik van een Maxwell visco-elastische vloeistof in cilindrische micro- en nanokanalen, voor zowel actuatie met oscillerende druk gradiënten als met elektrische velden. We constateerden dat Onsagers wederkerige relatie in bovenstaand geval geldig is. Tijdens de implementatie van de berekening werd het duidelijk dat de efficiëntie van de energieomzetting van de stromingspotentiaal theoretisch zeer hoog is, een conclusie die in voorafgaand werk in de literatuur ook al getrokken werd voor

rechthoekige micro- en nanokanalen. Voor de cilindrische kanalen is de efficiëntie zelfs hoger als voor de rechthoekige kanalen, wat te verklaren is door de lagere hydraulische weerstand van de cilindrische kanalen. De ontwikkeling van deze theorie leidde ook tot meer inzicht in het mechanisme dat de aanzienlijke efficiëntieverbetering oplevert. De efficiëntieverbetering kan worden toegeschreven aan het feit dat tijdens resonantie wanneer de efficiëntie maximaal is, de vloeistof in het kanaal bijna alleen elastisch gedrag laat zien en de stroming daardoor bijna wrijvingsloos is. Ook vonden we dat de oscillerende electroosmotische stroming in een Maxwell vloeistof een grotere toename van de maximale snelheid oplevert dan een oscillerende drukgedreven stroming, wanneer in beide gevallen vergeleken wordt met het gedrag bij frequenties ver onder de oscillatiefrequentie wanneer beide actuatiemethoden een zelfde maximale snelheid opleveren. Deze bevindingen vergroten ons begrip van AC elektrokinetische fenomenen voor visco-elastische vloeistoffen en leveren inzichten op die gebruikt kunnen worden voor het ontwerp van en de beschrijving van stromingskarakteristieken in microfluidische chips. De traditionele aanpak in energie-omzetting, die is gebaseerd op de stromingspotentiaal, volgt een enkel-staps proces, waarbij de omzetting van mechanische energie in elektrische energie plaats vindt in een continue stromende vloeistoffase. Dit heeft als nadeel dat er in de vloeistof een geleidingsstroom loopt in de tegengestelde richting van de stromingsstroom (streaming current) welke de omzettingsefficiëntie vermindert. Een nieuw ontwikkeld proces genaamd ballistische energie omzetting werkt met een tweestaps proces, waarin eerst mechanische energie wordt omgezet in kinetische energie van de vloeistof, en vervolgens de kinetische energie wordt meegedeeld aan druppeltjes die worden gelanceerd in de gasfase. Tijdens een traject naar een collector op hoge elektrische potentiaal wordt deze kinetische energie vervolgens omgezet in elektrische energie. Dit versnellings-afremmings mechanisme werd voor het eerst gerapporteerd in de BIOS groep door Yanbo Xie in een drukgedreven systeem dat gebruik maakte van een membraan met een enkele microporie. Een van de mogelijke nadelen van dit systeem was dat deze porie verstopt kan raken. Als gevolg hiervan is er een filter met hoge kwaliteit nodig in het systeem, en ook zal het systeem meer kwetsbaar zijn. Bovendien is het uitgangsvermogen van het systeem met een enkele microporie laag.

Daarom ontwikkelden we een nieuw platform voor ballistische energie-omzetting dat is gebaseerd op het gebruik van de centrifugaalkracht en een groot oppervlak van een glazen schijf. De resulterende energie-omzetter die is gebaseerd op de stromingsstroom (streaming current) zonder gebruik van een poreus membraan of microkanalen is een belangrijke stap bekeken vanuit een technologisch gezichtspunt. We waren succesvol in het verkrijgen van een uitgangsvermogen van 4.9 mW en een hoogspanning tot 3120 V. Naast een nieuwe energie-omzettingsmethode, biedt onze aanpak ook de mogelijkheid tot het vormen van geladen druppeltjes. Toepassingen die gebruik maken van geladen druppeltjes zoals een rotatieverstuiver, elektrostatische verfspuiten en crop-dusting apparatuur kunnen daarmee profijt hebben van de nieuw ontwikkelde methode.

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List of Publications

Peer-reviewed journal publications

- **T. Nguyen**, Y. B. Xie, L. J. de Vreede, A. van den Berg, and J. C. T. Eijkel, "Highly enhanced energy conversion from the streaming current by polymer addition," *Lab on a Chip*, vol. 13, pp. 3210-3216, 2013.
- **T. Nguyen**, T. Tran, H. de Boer, A. van den Berg, and J. C. T. Eijkel, "Rotary-Atomizer Electric Power Generator," *Physical Review Applied*, vol. 3, p. 034005, 03/16/ 2015.
- **T. Nguyen**, et al., "Viscoelastic Fluid Flow in Circular Narrow Confinements Driven by Periodic Pressure and Potential Gradients", in preparation

International conferences

- **T. Nguyen**, Y. B. Xie, L. J. de Vreede, A. van den Berg, and J. C. T. Eijkel (2012) Polymer-enhanced energy harvesting from streaming potential. In: ***MicroTAS 2012***, 16th International Conference on Miniaturized Systems for Chemistry and Life Sciences, October 28 November 1, 2012, Okinawa, Japan
- **T. Nguyen**, Y. B. Xie, L. J. de Vreede, A. van den Berg, and J. C. T. Eijkel, Enhanced Energy Conversion from the Streaming Potential by Polymer Addition, 1st international conference on ***Microfluidic Handling Systems, 2012***, Enschede, The Netherlands.
- **T. Nguyen**, H.de Boer, T. Tran, A. van den Berg, and J. C. T. Eijkel (2013) Streaming current of a rotary atomizer for energy harvesting. In:

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