CONDENSED MATTER

The Thermodielectric Effect in Paraffin Wax

Martin Tomas · Pavel Novotny

Abstract This paper deals with results of the thermodielectric effect measurement. A paraffin wax as a dielectric material was investigated via differential scanning calorimetry and potentiometry during a phase transition. Possible description of the thermodielectric effect based on fundamental laws of thermodynamics is shown; to be more specific, the link between the potential difference and the latent heat is presented. The thermodynamic model of thermodielectric effect based on electrochemical equilibrium and charge generation at the solid/liquid interface is introduced. Results of the thermodielectric effect measurement are used for the calculation of a molecular mass of the paraffin wax. The relation for a surface area (interface) between liquid and solid phase of the paraffin wax during solidification is derived from the presented theoretical description of the thermodielectric effect.

1 Introduction

In the 1940s, an interesting phenomenon was discovered during solidification or melting of dielectrics. This phenomenon was called "thermodielectric effect" and it was discovered by Brazilian physicist J. da Costa Ribeiro [1]. The thermodielectric effect is also known as "Costa Ribeiro

M. Tomas (✉) · P. Novotny
New Technologies - Research Centre, University of West
Bohemia, Univerzitni 8, 306 14 Plzen, Czech Republic
e-mail: mtomas@ntc.zcu.cz

effect". This effect can be measured in a dielectric which is melting or freezing. An important part of the dielectric is a phase boundary (interface) which is moving across the material during phase transition. If the phase boundary moves inside the material, electric current and potential difference between the liquid and solid phase will be observed. Thermodielectric effect was detected during the phase transition of many materials such as carnauba wax, naphthalene, paraffin wax and many other substances [2, 3]. This effect can also be linked to some electrical phenomena in the atmosphere [4, 5].

The first investigation of the thermodielectric effect was realized in a capacitor which contained a two-phase dielectric (liquid and solid phase) [1]. Costa Ribeiro used a cylindrical capacitor and the space between electrodes was filled with liquid paraffin. A very simple system of cooling was developed. An inner electrode of the capacitor was cooled by agitated air. To minimize the charging by friction, the air was filtered and its speed was very low. The electrodes were connected with an electrometer to measure the potential difference. The value of the potential difference was varied according to the dielectric material used. Costa Ribeiro also observed differences in measured values when another measuring system configuration was used.

Costa Ribeiro derived two fundamental laws of the thermodielectric effect. The first law is called "law of intensities" and can be expressed as

$$i = k_1 \frac{\mathrm{d}m}{\mathrm{d}t}, \tag{1}$$

where k_1 is the thermodielectric constant, which depends on the thermodielectric cell construction and measured material. Equation (1) describes the relation between the produced electrical current i and the rate of phase change dm/dt.

The second law of the thermodielectric effect is called "law of charges" and one can express it as

$$Q = k_2 m, \qquad (2)$$

where k_2 is also a thermodielectric constant depending on given thermodielectric cell and given material. Equation (2) means that the charge Q released from the dielectric during phase change is proportional to the mass m of the dielectric which is melting or freezing.

The thermodielectric effect was also examined in freezing water. An origin of this phenomenon in water was analysed by Reynolds and Workman [6]. The main interest of these researchers was an influence of impurities on the freezing process.

The theory of the thermodielectric effect was created by Gross [2]. His theoretical concept supposes that the phase boundary behaves like a permeable membrane. As the membrane moves across the dielectric, the charge carriers pass through it in different quantities. The phase boundary can be described as a potential barrier with a different height for each type of the charge carrier.

The properties of the charge carriers in dielectrics were the focus of many researchers. In a real dielectric material, one can find a very small quantity of the charge carriers. Particles in the dielectrics are mostly neutral, but we can consider a small amount of the positive and negative charge carriers (electrons, ions) [7]. This coincidence is attractive for an explanation of the thermodielectric effect and it is possible to set up an experiment which can monitor the ions motion in the dielectric [8].

The naphthalene vapour which condensed on the electrode was used in this experiment. The thermodielectric effect occurred during vapour condensation. Before condensation, the naphthalene vapour flowed between two electrodes of high voltage power supply. These electrodes created an electrical field which removed charged ions from the vapour. However, the ordinary thermodielectric effect was observed.

The existing theory of the thermodielectric effect is not rigorous for many types of dielectrics [2, 4, 9]. The exact origin of this effect is also unknown. The thermodielectric effect is not definitely described, but the thermodielectric effect measurement can provide important information about processes like a polymerization and polyaddition of plastic materials. The thermodielectric effect can also be used for a purity measurement of various substances.

The main goal of this paper is to theoretically describe the thermodielectric effect and to compare obtained results with experimental investigation of this phenomenon. Our description is based on a thermodynamic model of this effect assuming electrochemical equilibrium and charge generation at the solid/liquid interface. We focused on the relation of the potential difference generated during thermodielectric effect and the area of the phase boundary between solid and liquid part of measured material.

2 Thermodynamics of Polarizable Materials

Gibbs' definition of the entropy s is originally formulated for local equilibrium systems. The paraffin wax is a mixture of a few compounds and two phases (liquid and solid) with the measurable electric phenomena during chemical reactions and phase transitions. Due to these phenomena the general form of the entropy has to be applied [10]. For the mixture of solids we use

$$T\dot{s} = \dot{u} - \frac{\mathbf{t}_{el}^M}{\rho}\dot{\mathbf{e}} - \sum \mu_\alpha \dot{w}_\alpha - \mathscr{E}_{eq}\overline{\left(\frac{\dot{\mathbf{P}}}{\rho}\right)} - \mathbf{B}_{eq}\overline{\left(\frac{\dot{\mathscr{M}}}{\rho}\right)} \quad (3)$$

and for the mixture of fluids

$$T\dot{s} = \dot{u} + p\overline{\left(\frac{\dot{1}}{\rho}\right)} - \sum \mu_\alpha \dot{w}_\alpha - \mathscr{E}_{eq}\overline{\left(\frac{\dot{\mathbf{P}}}{\rho}\right)} - \mathbf{B}_{eq}\overline{\left(\frac{\dot{\mathscr{M}}}{\rho}\right)}, \quad (4)$$

where $\overline{()}$ is the material (Euler) derivative, u is the internal energy, T is the temperature, p is the pressure, μ_α is the chemical potential and w_α is mass fraction of component α. The pressure is in general described by the Cauchy stress tensor $\mathbf{t}^M$ and is usually split into two parts - elastic part $t_{el}^{M\,ij}$ and dissipative part (plastic) $t_{dis}^{M\,ij}$,

$$\mathbf{t}^M = \mathbf{t}_{el}^M + \mathbf{t}_{dis}^M, \quad \text{or in components} \quad t^{M\,ij} = t_{el}^{M\,ij} + t_{dis}^{M\,ij}. \quad (5)$$

The elastic part describes the reversible phenomena (the perfect spring) and the dissipative part describes the irreversible phenomena (viscous and plastic behaviour). The elastic part of the stress tensor of mechanical forces has different forms for solids, i.e.

$$\mathbf{t}_{el}^M = p\left(e_{(1)}, T\right)\mathbf{I} + \overset{(o)M}{\mathbf{t}}_{el}\left(\overset{(o)}{\mathbf{e}}\right), \quad \text{tr}\,\mathbf{e} = e_{(1)}, \quad (6)$$

where $\mathbf{e}$ is Euler deformation tensor, $e_{(1)}$ is its volumetric part and $\overset{(o)}{\mathbf{e}}$ its deviatoric part describing the distortion (deformation without change of volume). For fluids, one can write

$$\mathbf{t}_{el}^M = -p(\rho, T)\mathbf{I} = \sum_\alpha -p_\alpha(\rho_\alpha, T)\mathbf{I}. \quad (7)$$

For fluids it is the deformation represented by the change of volume $\text{tr}\,\mathbf{e} = e_{(1)}$, which is connected with the change of density

$$e_{(1)} = \frac{v - v_0}{v_0} = \frac{\rho_0 - \rho}{\rho} \quad \text{and} \quad (8)$$

$$e_{(1)\,\alpha} = \xi_\alpha e_{(1)} = \rho_\alpha v_\alpha e_{(1)} \quad (9)$$

and is through formulas (10) and (11) correlated with the volume and mass fractions. The volume fraction is introduced analogously

$$\xi_\alpha = \frac{w_\alpha v_\alpha}{v} = \frac{w_\alpha}{\sum\limits_\beta w_\beta \frac{v_\beta}{v_\alpha}} \tag{10}$$

and is applied for deformation tensor

$$\mathbf{e} = \sum_\alpha \mathbf{e}_\alpha = \sum_\alpha \xi_\alpha \mathbf{e}, \tag{11}$$

where $v = 1/\rho$ is the specific volume of the mixture, v_α is the specific volume of component α and $w_\alpha v_\alpha$ is the partial volume occupied by component α. The definition of the chemical potential for the component α

$$\dot{\mu}_\alpha = -s_\alpha \dot{T} - \rho v_\alpha \mathbf{e} : \overline{\left(\frac{\mathbf{t}_{el}^M}{\rho}\right)} \quad \text{for solids,}$$

$$\dot{\mu}_\alpha = -s_\alpha \dot{T} + v_\alpha \dot{p} \quad \text{for fluids} \tag{12}$$

is the consequence of the definition of the Gibbs-free enthalpy for each component

$$\mu_\alpha = u_\alpha - \left(\frac{\mathbf{t}_{el}^M}{\rho}\right) : (\rho v_\alpha \mathbf{e}) - T s_\alpha =$$

$$= h_\alpha - T s_\alpha \quad \text{for solids,} \tag{13}$$

$$\mu_\alpha = u_\alpha + p v_\alpha - T s_\alpha = h_\alpha - T s_\alpha \quad \text{for fluids.} \tag{14}$$

For the isotropic stress tensor $\mathbf{t}_{et}^M = p\mathbf{I}$ it is possible to write $\left(\frac{\mathbf{t}_{el}^M}{\rho}\right) : (\rho v_\alpha \mathbf{e}) = v_\alpha p e_1$, where $v_\alpha e_{(1)}$ describes the volume compressibility. The specific enthalpies for each component are

$$h_\alpha = u_\alpha - \left(\frac{\mathbf{t}_{el}^M}{\rho}\right) : (\rho v_\alpha \mathbf{e}) \quad \text{and} \tag{15}$$

$$h = \sum_\alpha h_\alpha w_\alpha =$$

$$= \sum_\alpha (u_\alpha w_\alpha - \left(\frac{\mathbf{t}_{el}^M}{\rho}\right) : (\underbrace{\rho_\alpha v_\alpha}_{\xi_\alpha} \mathbf{e})) \quad \text{for solids,} \tag{16}$$

$$h_\alpha = u_\alpha + p v_\alpha \quad \text{and} \quad h = \sum_\alpha h_\alpha w_\alpha \quad \text{for fluids.} \tag{17}$$

The above definitions are valid when the Gibbs-Duhem condition (describing the dependence of the quantities α on the concentration β, for $\alpha \neq \beta$) is satisfied [12]. In our case, the equilibrium magnetic induction $\mathbf{B}_{eq}$ is zero and the equilibrium electric field intensity $\mathscr{E}_{eq}$ can be induced by the phase transition and will be investigated later. The electromagnetic interaction is formulated in the classical form (non-relativistic approximation, i.e. all terms of order v^2/c^2

are neglected). The electric field intensity $\mathscr{E}$ and magnetization $\mathscr{M}$ in the moving material point are influenced by its velocity, but in our case, we concentrate on the system at rest. The electric field induced by the phase transition will be included in the electrochemical potential. The balance laws of mass, energy and entropy applied for the following formulation are mentioned, e.g. in the book by de Groot and Mazur [10] or papers by Pavelka and Marsik [11] or Marsik [13].

3 Description of the Thermodielectric Effect

The thermodielectric effect represents the connection between electrical and thermodynamic properties of materials. All the relevant processes which contribute to the entropy production are [14]

$$\sigma_{TD}(S) = \sum_\rho \frac{\mathscr{A}_\rho \dot{\zeta}_\rho}{T} -$$

$$- \sum_\alpha \mathbf{j}_{D\alpha} \cdot \left(\nabla\left(\frac{\mu_\alpha}{T}\right) - \frac{z_\alpha F}{M_\alpha T}\mathscr{E}\right) +$$

$$+ \rho\frac{(\mathscr{E} - \mathscr{E}_{eq})}{T} \cdot \overline{\left(\frac{\mathbf{P}}{\rho}\right)} \geq 0. \tag{18}$$

The first term describes the steady-state phase transition for which the affinity $\mathscr{A} = M_l \mu_l - M_s \mu_s = 0$. The phase transition $\alpha = l, s$ is an isothermal process (i.e., $T = $ const.), and with respect to the chemical potential definitions (13) and (14)

$$M_l \mu_l - M_s \mu_s = M_l h_l - M_s h_s - T(M_l s_l - M_s s_s) = 0,$$
$$\text{and for} \quad M = M_l = M_s,$$
$$h_{ls} = T(s_l - s_s) \; [\text{J} \cdot \text{kg}^{-1}], \tag{19}$$

where h_{ls} is the latent heat.

In the second term in (18), the electric field intensity $\mathscr{E} = \mathbf{E} = -\nabla\phi$, which is induced by the phase transition. The corresponding entropy production for the whole system with the volume $\mathscr{V} = \mathscr{V}_l + \mathscr{V}_s$ is (see Fig. 4)

$$- \int_{\mathscr{V}} \left(\sum_\alpha \mathbf{j}_{D\alpha} \cdot \nabla\left(\frac{\mu_\alpha}{T}\right) + \frac{z_\alpha F}{M_\alpha T}\nabla\phi\right) dv =$$

$$= -\frac{1}{T} \int_{\partial\mathscr{V}} (\mu_\alpha + \frac{z_\alpha F\phi}{M_\alpha})\mathbf{j}_{D\alpha} \cdot \mathbf{da} =$$

$$= +\frac{1}{T} \int_{\mathscr{V}} \left(\sum_\alpha \mu_\alpha \text{div}\mathbf{j}_{D\alpha} + \frac{F\phi}{M}\text{div}\mathbf{j}_e\right) dv \geq 0 \tag{20}$$

for $\alpha = l, s$, $\mathbf{j}_e = z_l\mathbf{j}_{Dl} + z_s\mathbf{j}_{Ds}$.

The surface of the mixture of solid and liquid paraffin wax is $\partial\mathscr{V} = \partial\mathscr{V}_l + \partial\mathscr{V}_s$. To evaluate the volume integral, we take into account the balance of mass in the form $\text{div}\mathbf{j}_{D\alpha} = \rho(\omega_\alpha - \dot{w}_\alpha)$, where $\mathbf{j}_{D\alpha}$ is the diffusion flux and

$\rho\omega_\alpha$ [kg · m^{-3} · s^{-1}] is the production (sink or source) of the component α. The balance of the electric charge in the form div$\mathbf{j}_e = -\dot{z} = -(z_l\dot{w}_l - z_s\dot{w}_s)$ evaluates the production of the solid phase and electric charge, respectively. The phase transition process takes place on the moving interface surface $A(t)$ only, whose volume $\mathscr{V}_{PT} = \delta l A(t) \to 0$ and in the rest of volume $\mathscr{V}$ the production terms $\rho\omega_\alpha$, $\dot{z}$ equal zero. Due to this assumption the volume integral in the entropy production (20) equals zero.

The phase transition (solidification of dielectrics, e.g. paraffin wax etc.) is accompanied by the Red-Ox reaction (adding or loosing of electrons), i.e.

$$P_l \to P_s^{-z_s} + z_s \quad \text{oxidation or} \tag{21}$$

$$P_l^{-z_l} + z_l \to P_s \quad \text{reduction,}$$
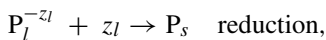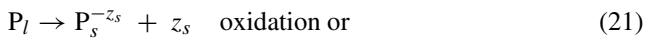
so that the electron transfer participates in this process. The surface integral in the term (20) describes the entropy transfer (at T = const. it corresponds to energy) through the phase transition interface A, see Fig. 4. Taking into account the surface orientation $\mathbf{da} = \mathbf{n}\mathrm{d}a$ the mass flux balance through surface is $\mathbf{j}_{Ds} \cdot \mathbf{n}_s \mathrm{d}a + \mathbf{j}_{Dl} \cdot \mathbf{n}_l \mathrm{d}a = 0$, and the surface integral over the interface is

$$\int_{\partial\mathscr{V}_s + \partial\mathscr{V}_l} (\mu_\alpha + \frac{z_\alpha F\phi}{M_\alpha})\mathbf{j}_{D\alpha} \cdot \mathbf{da} =$$
$$= \int_A ((\mu_l + \frac{z_l F\phi}{M_l})\mathbf{j}_{Dl} + (\mu_s + \frac{z_s F\phi}{M_s})\mathbf{j}_{Ds})\mathbf{da} =$$
$$= \int_A \left[(\mu_l + \frac{z_l F\phi}{M_l}) - (\mu_s + \frac{z_s F\phi}{M_s})\right] \mathbf{j}_{Dl}\mathbf{n}_l \mathrm{d}a =$$
$$= \left[\mu_l - \mu_s + \left(\frac{z_l}{M_l} - \frac{z_s}{M_s}\right)F\phi\right]\mathbf{j}_{Dl}A \geq 0. \tag{22}$$

For the steady state, when the process is so slow that the entropy production goes to zero, we obtain the so-called Nernst equation, which expresses the equality of the electrochemical potentials (23) at the interfaces (membranes). Its consequence is the electrochemical interaction between particles, which contains the corresponding amount of the electric energy. The electrochemical potential is defined

$$\mu_{es} = \mu_s + \frac{z_s F\phi}{M_s} \quad \text{for solids,}$$
$$\mu_{el} = \mu_l + \frac{z_l F\phi}{M_l} = \mu_s + T(s_l - s_s) +$$
$$+ (\mathcal{V}_l - \mathscr{V}_s)p + \frac{z_l F\phi}{M_l} \quad \text{for fluids.} \tag{23}$$

The Clausius-Clapeyron relation can be derived from this (23). Alternative definition of $\mu(T, p, \phi)$ for a mixture is (according to 12)

$$\mathrm{d}\mu_\alpha = \underbrace{\frac{\partial\mu_\alpha}{\partial T}}_{-s_\alpha} \mathrm{d}T + \underbrace{\frac{\partial\mu_\alpha}{\partial p}}_{\mathscr{V}_\alpha} \mathrm{d}p + \underbrace{\frac{\partial\mu_\alpha}{\partial\phi}}_{\frac{z_\alpha F}{M}} \mathrm{d}\phi. \tag{24}$$

When the molecular mass of solid and liquid phases are equal ($M_s = M_l = M$) the equilibrium at the phase transition surface can be described by the condition

$$M\mathrm{d}\mu = -T(s_l - s_s)\frac{\mathrm{d}T}{T} + (\mathscr{V}_l - \mathscr{V}_s)\mathrm{d}p + \frac{(z_l - z_s)F}{M}\mathrm{d}\phi. \tag{25}$$

The second term on the right side of this (25) is neglected. In case of negligible volume change or pressure change, this term can be assumed to be zero. We consider the chemical potential of the solid phase μ_s as the reference value and then the specific chemical potential of the liquid phase is sum of μ_s and latent heat h_{ls}. The phase equilibrium condition at the interface (25) can be written in the following form

$$z_{el} - z_{es} = -h_{ls}\frac{M}{F\phi}, \tag{26}$$

where $h_{ls} > 0$ is the added latent heat needed for the paraffin wax melting. This latent heat is responsible for the generated electric potential ϕ[V = J · C^{-1}], which is connected through Faraday constant ($F = 96,485$ C · mol^{-1}) with the phase transition heat. Denoting the change of the electric charge during the phase transition as $-z_e = z_{el} - z_{es}$, the measured potential is equal to

$$\phi = \frac{Mh_{ls}}{z_e F}. \tag{27}$$

With the known free charge number of electrons z_e (negative charge) and the measured latent heat we have the relation for the unknown molecular mass M

$$M = \frac{z_e F\phi}{h_{ls}}. \tag{28}$$

The above result (27) is the consequence of the electrochemical potentials' equality (23). Considering the electrochemical potential is constant through the phase transition interface, the question is the second term in the integrand on the left hand side of the inequality (20). The electric current is generated by the diffusion fluxes $\mathbf{j}_e = z_{el}\mathbf{j}_{Dl} + z_{es}\mathbf{j}_{Ds} = \sigma_{eP}\mathbf{E}$. However, this electric current is by the experiment very small (paraffin wax conductivity σ_{eP} is very low) [16], so that this term is close to zero.

3.1 Solid-Liquid Interface Analysis

The difference of the electric potential at the interface between solid and liquid, see Figs. 4, 1 and 2, is calculated from the Maxwell equation (see Appendix), especially from div$\mathbf{D}_\alpha = z_\alpha\rho_\alpha = z_\alpha M_\alpha c_\alpha$, where z_α is the number of the free electric charges per 1 mol and c_α is the molar concentration, for $\alpha = l, s$.

Fig. 1 Thermodielectric cell
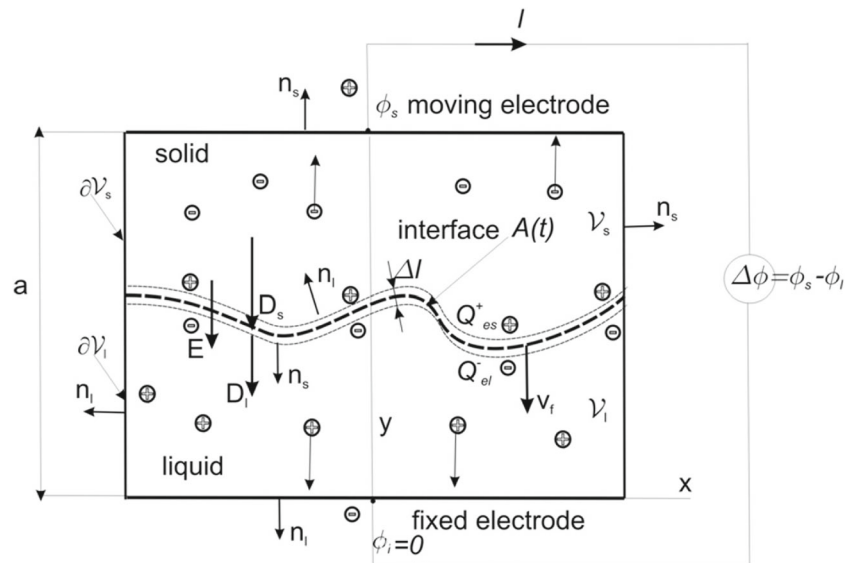
We consider that *the charge is generated* at the interface only. Under that assumption the total charge during solidification is equal to

$$
Q_e = \int_{\mathcal{V}_s(t)} \mathbf{D}_s \, dv + \int_{\mathcal{V}_l(t)} \mathbf{D}_l \, dv =
$$
$$
= \int_{\partial \mathcal{V}_s(t)} \mathbf{D}_s \mathbf{n} \, da + \int_{\partial \mathcal{V}_l(t)} \mathbf{D}_l \mathbf{n} \, da =
$$
$$
= -A_{FE} D_{sFE} + A D_{sf} - A D_{lf} + A_{ME} D_{lME} =
$$
$$
= A_E (D_{lME} - D_{sFE}) + A(D_{sf} - D_{lf}). \quad (29)
$$

Here, we take the surface of the fixed electrode A_{FE} and the moving electrode A_{ME} of the same magnitude and equal to A_E. Assuming that the free charge is at the interface

$A(t)$ only, we set $A_E(D_{lME} - D_{sFE}) = 0$ and the total electric charge is

$$
Q_e(t) = A(t)(D_{sf} - D_{lf}) = A(t)\varepsilon_0(\varepsilon_{rs} - \varepsilon_{rl})E =
$$
$$
= \frac{A(t)\varepsilon_0(\varepsilon_{rs} - \varepsilon_{rl})}{\Delta l}(\phi_l - \phi_s). \quad (30)
$$

In (30), we apply the free charge conservation law (electroneutrality condition) in the form $Q_{es}^+ = -Q_{el}^- = Q_e(t)$. The amount of free charge is small and the electric field E can be assumed as continuous. The free charge $Q_e(t)$ depends on time, due to the interface surface evolution $A(t)$. Not all free electric charge released during solidification is bounded to the solid phase and this unbound charge moves to the anode and generates the current I, see Fig. 4. This generated current is small, but it is possible to measure it [15]. However, the released charge is also stored in a solid part of dielectric material [3, 8]. The area of the phase boundary depends on time, because the interface firstly evolves near the moving

Fig. 2 Potential difference between liquid and solid phase during thermodielectric effect
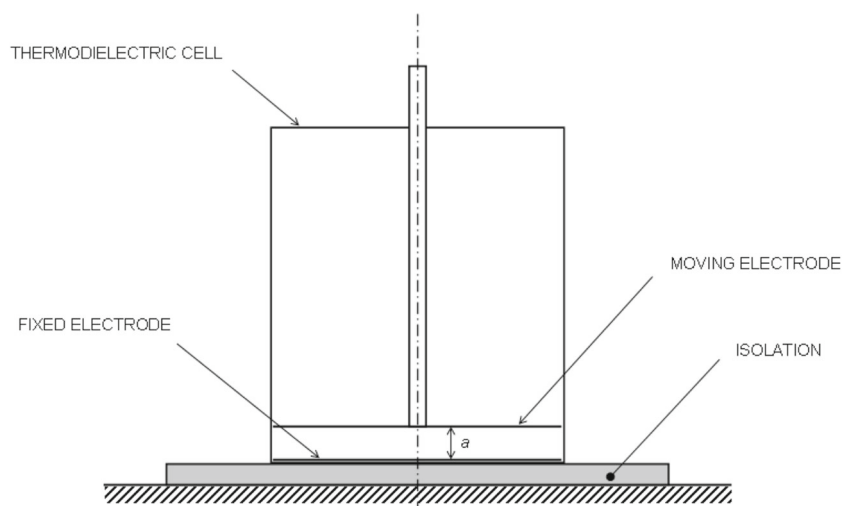
electrode and the sides of the thermodielectric cell. These components of the cell are in direct contact with an ambient atmosphere. The concave shape of the phase boundary was observed.

Formula (30) can be used to estimate the change of the free charge corresponding to the change of temperature. The chemical potential (12) for the solid part with the isotropic stress $\mathbf{t}_{el}^M = -p\mathbf{I}$ can be simplified to $\rho v_\alpha \mathbf{e} : \overline{\left(\frac{\mathbf{t}_{el}^M}{\rho}\right)} = -\rho v_\alpha e_{(1)} \overline{\left(\frac{p}{\rho}\right)} \to 0$. For incompressible material (liquid part) it is $e_{(1)} = (\rho_0 - \rho)/\rho \to 0$ and pressure terms are negligible. Now we can apply this simplification to the formula for the phase transition surface (23) and we obtain

$$d(\mu_{el} - \mu_{es}) = -(s_l - s_s)dT + \\ + v_s dp + \left(\frac{z_l F}{M_l} - \frac{z_s F}{M_s}\right)d\phi = 0. \quad (31)$$

For the isobaric process follows the relation

$$-\frac{h_{ls}}{T_C}dT + (z_l - z_s)\frac{F}{M}d\phi = 0, \quad (32)$$

which combines the change of temperature of the system dT with the generated electric potential (T_C is assumed as a phase transition temperature). Equation (32) can be used for a general description of the thermodielectric effect. However, we can obtain a more precise relation respecting the influence of the area of the phase boundary and the difference of dielectric constant of liquid and solid phase. Considering the continuity of the gradient $\nabla(\mu_{el} - \mu_{es}) \cdot \mathbf{n} = \frac{\partial(\mu_{el} - \mu_{es})}{\partial l} = 0$ of the electrochemical potentials through the phase transition interface and using the relation (30) one can write

$$\frac{h_{ls}}{T_C}\nabla T = -(z_l - z_s)\frac{F}{A(t)M\varepsilon_0(\varepsilon_{rs} - \varepsilon_{rl})}Q_e(t). \quad (33)$$

So that

$$A(t) = -\frac{Q_e(t)F(z_l - z_s)}{\varepsilon_0(\varepsilon_{rs} - \varepsilon_{rl})Mh_{ls}}\left(\frac{T_C}{\nabla T}\right), \quad (34)$$

or alternatively

$$Q_e(t) = -\frac{A(t)\varepsilon_0(\varepsilon_{rs} - \varepsilon_{rl})Mh_{ls}}{F(z_l - z_s)}\left(\frac{\nabla T}{T_C}\right). \quad (35)$$

This formula can be used for the estimate of the electric charge generation induced by the temperature gradient during solidification (freezing). Besides the charge generation $z_l - z_s$ and difference of relative permittivities $\varepsilon_{rs} - \varepsilon_{rl}$ the size of the phase transition surface $A(t)$ is important (34). The influence of the surface size for the charge (electric potential) generation is evident in Fig. 2, the area of the phase transition interface shrinks during the solidification.

4 Experimental Setup

The measurement of the thermodielectric effect was divided into two parts. As a measured material, paraffin wax (Penta chemicals, CAS no. 8002-74-2, EINECS 232-315-6) was used. A heat flow during the solidification of the paraffin wax was measured via differential scanning calorimetry (MDSC Q200, TA Instruments).

An improved thermodielectric cell was used for potential difference measurement. The thermodielectric cell was built from a polyvinyl chloride vessel. There were two horizontal copper electrodes in this vessel. One of them was fixed to the bottom of the vessel. The second one was connected to a fine metric thread. This thread was attached to the nut which was fastened to the PVC cell. This thermodielectric cell can be used for the thermodielectric effect measurement with respect to the distance of the electrodes, see Fig. 1. The electrodes were connected to the Solartron Analytical 1287A Potentiostat/Galvanostat.

Measurement was started by melting of the paraffin wax in the thermodielectric cell which was immersed in the water bath. When the thermodielectric cell was filled with liquid paraffin wax, electrodes were connected to the potentiostat. A polystyrene shielding was placed to overlay the cell. This shielding provided the generation of phase boundary between the electrodes.

5 Results and Discussion

A potential difference between electrodes was measured during the thermodielectric effect. The distance of the electrodes was $a = 3$ mm and the calculated mass of paraffin wax was $m = 18.31$ g. Density of the paraffin wax was supposed as $\rho = 0.777$ g $\cdot$ cm^{-3} [16]. The thermodielectric effect was measured for 1 h and the sampling frequency of potential difference was set as one value per second. The raw data were numerically reduced to 120 values (mean value was calculated from every 30 steps, see Fig. 2). The temperature of the fixed electrode was measured and is plotted in Fig. 2.

The paraffin wax was also investigated in the calorimeter (MDSC Q200, TA Instruments) to obtain the value of the heat of fusion. The heat of fusion obtained in our sample was $h_{ls} = 192.7$ J $\cdot$ g^{-1} and this value corresponds to literature [16–18].

Rate of temperature change was set to $\Delta t = 10\,°C \cdot$ min^{-1} and the measurement was realized in a nitrogen atmosphere (constant flow rate 50 mL $\cdot$ min^{-1}). Obtained results show the behaviour which is typical for multi-component materials. The minor peak in Fig. 3 is related to solid-solid transition [19]. This solid-solid transition is understood as the lattice transformation
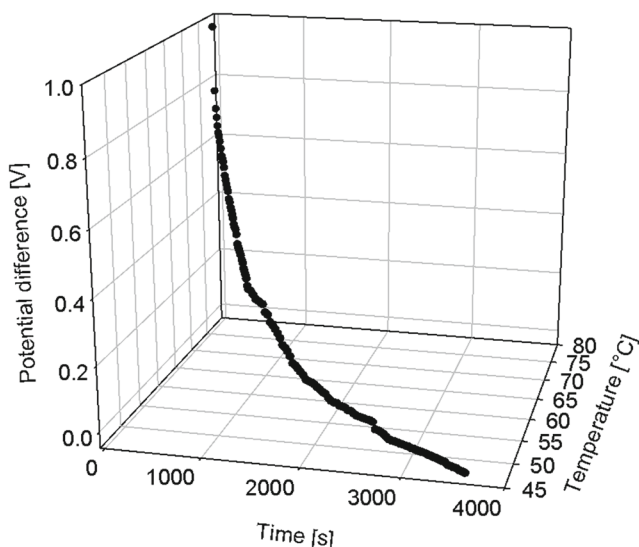
Fig. 3 The time dependence of heat flow during solidification of paraffin wax

from hexagonal close-packed to orthorhombic structure of some hydrocarbons and others from hexagonal to monoclinic or triclinic structure [20]. Equation (28) can be modified as

$$M = \frac{zF\Delta\Phi}{h_{ls}} \qquad (36)$$

and one can estimate the molar mass of the paraffin wax. If the value of potential difference at the beginning of thermodielectric effect is $\Delta\Phi = 0.7$ V (Fig. 2) and the number of transferred electrons per ion is $z_e = 1$, molar mass of paraffin wax will be approximately $M = 350.5$ g · mol^{-1}. This obtained value can be considered as plausible [16] (Fig. 4).
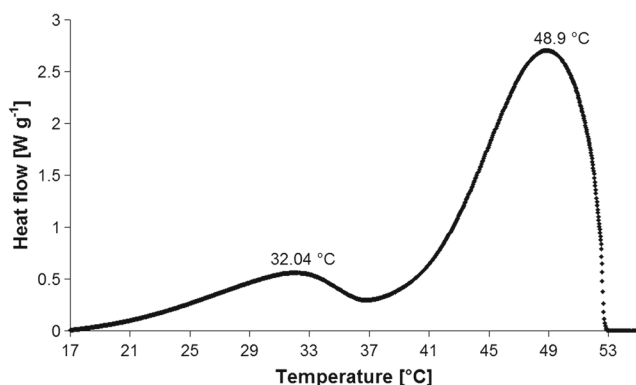

Fig. 4 Solidification process-"solid-liquid" interface moves with the velocity $\mathbf{v}_f$. Free charge generated during phase transition is partially bounded at the interface $A(t)$, part of the charge is stored in the solid phase

6 Conclusions

The measurement of the electric potential difference during thermodielectric effect and calorimetric measurement can be useful for the determination of the molar mass of the paraffin wax. Theoretical explanation of the thermodielectric effect can be based on fundamental laws of thermodynamics. Presented results show the possible application of non-equilibrium thermodynamics. The thermodielectric effect is relatively easy to demonstrate and can be used in an educational process.

Appendix: Basic assumption of the material and the electromagnetic interaction - Maxwell equations

The basic quantities needed for the description of the polarizable and magnetizable materials are the *electric field intensity* $\mathbf{E}$ [V · m^{-1} = N · C^{-1}] and *magnetic field density (magnetic induction)* $\mathbf{B}$ [T = Wb · m^{-2} = kg · s^{-2} · A^{-2}]. Both of these quantities do not depend on the material properties (are the same in the free space) and they can be taken as the qualitative quantities, similarly as the temperature in an equilibrium system. To evaluate the polarization and magnetization, we need to formulate Maxwell's equations (37, 38, 39) by means of the polarization $\mathbf{P}$ and the magnetization $\mathbf{M}$ vectors [10],

$$\varepsilon_0 \mathrm{div}\,\mathbf{E} = \rho_e \underbrace{-\mathrm{div}\,\mathbf{P}}_{+\rho_b}, \qquad (37)$$

$$\frac{1}{\mu_0}\mathrm{rot}\,\mathbf{B} - \varepsilon_0 \frac{\partial\mathbf{E}}{\partial t} = \rho_e\mathbf{v} + \mathbf{j}_e + \underbrace{\frac{\partial\mathbf{P}}{\partial t} + \mathrm{rot}\,\mathbf{M}}_{\mathbf{j_b}}, \qquad (38)$$

$$\mathrm{div}\,\mathbf{B} = 0, \quad \mathrm{rot}\,\mathbf{E} + \frac{\partial\mathbf{B}}{\partial t} = 0. \qquad (39)$$

The righthand sides of Eqs. (37, 38) depend on the material composition, expressed by the mass fraction $w_\alpha = M_\alpha c_\alpha/\rho$, where M_α is molecular mass, c_α is molar concentration [mol · m^{-3}] and $\rho = \sum_\alpha \rho_\alpha$ is density of the mixture, in our case for $\alpha = s, l$ (s - solid part, l - liquid part of the mixture) [10, 11]. The electric induction and the magnetic field intensity connected with the component α are defined as follows:

$$\mathbf{D}_\alpha = \varepsilon_0\mathbf{E} + \mathbf{P}_\alpha \left[\mathrm{C}\cdot\mathrm{m}^{-2}\right], \quad \mathbf{H}_\alpha = \frac{\mathbf{B}}{\mu_o} - \mathbf{M}_\alpha \left[\mathrm{A}\cdot\mathrm{m}^{-1}\right]. \ (40)$$

It is possible to write $\mathrm{div}\mathbf{D} = \rho_e$, where ρ_e is the density of free electric charge, so that $\mathrm{div}(\varepsilon_0\mathbf{E}) = \rho_e + \rho_b$ is the

density of total charge. Provided that the polarization and magnetization are equal to zero for the vacuum, follow from the (37, 38) very important relations for *the bounded charge* and corresponding *bounded electric flux*, which is especially relevant for unsteady processes

$$-\text{div}\,\mathbf{P} = \rho_b, \qquad \frac{\partial \mathbf{P}}{\partial t} + \text{rot}\,\mathbf{M} = \mathbf{j_b}. \qquad (41)$$

In many practical applications, especially for homogeneous and isotropic materials, simplified relations are used

$$\mathbf{P} = \mathbf{D} - \varepsilon_0 \mathbf{E} = \chi_e \varepsilon_0 \mathbf{E}, \qquad \mathbf{M} = \frac{\mathbf{B}}{\mu_0} - \mathbf{H} = \chi_m \mathbf{H}. \qquad (42)$$

Then, the effects of electric and magnetic fields on the material body are represented by the electric susceptibility χ_e and by the magnetic susceptibility χ_m. Alternatively, this interaction can be formulated by the relative permittivity ε_r and relative permeability μ_r as follows

$$\varepsilon_r = \chi_e + 1, \qquad \mu_r = \chi_m + 1, \qquad (43)$$

so that

$$\mathbf{D} = \varepsilon_r \varepsilon_0 \mathbf{E}, \qquad \mathbf{B} = \mu_r \mu_0 \mathbf{H}. \qquad (44)$$

These equations are important for the formulation of the momentum and energy balance equations in the presence of electromagnetic phenomena.

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