Theory for Nanoparticle Sintering under Electrical Boundary Conditions


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A statistical model for sintering of solution-processed electrically conducting nanoparticle structures is developed. The model considers thermal expansion of the particles under Joule heating as the driving force of the process. The theory is used to explain the fast resistance transition observed for the recently-reported rapid electrical sintering process. A comparison with experimental results shows good agreement for the kinetics of the process. A heat-equation solution is also derived for a generic geometry of a printed conductor. This provides a basis for further refinements of the model to take other driving mechanisms, such as diffusion and inter-particle forces, into account. The results of this paper help in developing quantitative understanding of the physical processes that are relevant in nanoparticle sintering.

I. INTRODUCTION

The strong decrease in the melting temperature of nanoparticles as a function of their size [1, 2] has resulted in developments to utilize metals and inorganic semiconductors as nanoparticle dispersions in fabrication of printed electronics on low-temperature substrates [3]. This is motivated by the potential of the inorganic materials as compared to their printable organic counterparts to improve material properties such as conductivity and semiconductor charge-carrier mobility that are central to the performance of electric circuits. The first applications of printed electronics currently entering the market include photovoltaics, displays and lightning, RFID tags, memory cards and sensors [3, 4].

Although nanoparticle inks can be developed to sinter at low temperatures such as 100°C - 150°C by minimizing the particle size and using low-boiling ink constituents such as solvents, binders and particle encapsulations (dispersants), the conventional thermal oven sintering still has several drawbacks. In particular, oven sintering is a rather slow process and it is not area specific. Therefore, also the substrate is heated up to the sintering temperatures, which easily causes shrinkage of many low cost substrates. Consequently, alternative sintering methods have been developed such as laser sintering [5], pulsed light sintering [6], microwave sintering [7, 8] and the rapid electrical sintering (RES) [9, 10]. In this paper, we focus on the modelling of the sintering process to explain the rapid transition of the RES process for which the resistance of a printed track can drop several decades in a microsecond [9]. However, we find that the results of this paper are likely also relevant to the other sintering techniques.

Several physical processes are known to be manifested in nanoparticle sintering [11–13] such as diffusion, decrease of total surface energy, inter-particle Van der Waals forces, capillary effects, viscous flow, possible external pressure, chemical reactions and phase transitions of the different ink constituents. For nanosized particles, linear theories of diffusion become inaccurate [13]. Sintering is also affected by the statistical variations of the particle size and packing density. Furthermore, values of several process parameters such as surface and grain boundary energies and diffusion coefficients are not thoroughly tabulated. Therefore, modelling of the process is challenging and has typically been limited to few-particle systems and offered only qualitative understanding.

In the traditional theories of sintering [11, 12], the initial stage of the process is a compact structure where nearest-neighbour particles are in contact without a gap or a layer of different material in between. In those models, inter-particle neck growth is enabled by diffusion, viscous flow or vapor transport. Theories of sintering kinetics of such processes date back to 1950’s and 1960’s [11] but do not reproduce the fast dynamics observed for the electrical sintering process [9][35]. To model the electrical sintering process in this paper, the initial structure is, after printing and drying, assumed to consist of polymer-encapsulated particles packed so that the encapsulant separates nearest-neighbour particles [3, 14–18]. Consequently, the initial state is similar to that of viscous or liquid-phase sintering [11, 19]. In such a structure with small sub-nanometer sized minimum gaps that can result from using short ligand particle encapsulants [20–22], thermal expansion can be of significance. For example, assuming silver particles of 50 nm in diameter and using the bulk heat expansion coefficient of 20 ppm/K that is supported by Ref. [23] for nanoparticles, a 400°C heating results in a 0.4 nm diameter growth. For stationary particles as assumed in this paper, this reduces the inter-particle gap also by 0.4 nm which is of the same order as the shortest observed particle-particle distances in solution-processed nanoparticle layers [21, 22]. On the other hand, the diffusion effects are more likely manifested during the later steps of the RES process, when grain growth is observed and the conductivity gradually reaches its final level [9, 24].

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In this paper, a new statistical model based on thermal-expansion of the particles is developed for the sintering process (Section II) and the model is compared with experiments (Section III). The results show that the developed model can explain the observed kinetics of the electrical sintering process. The obtained values of the fitting parameters are discussed in Section IV.

II. ANALYSIS

A. Geometrical simplifications

To model the electrical heating and sintering of a printed track, the coupling of heat between the track and environment needs to be solved. A conductor track printed on a substrate is schematically shown in Fig. 1. Here $W_{tr}$, $L_{tr}$ and $H_{tr}$ are the width, length and height of the track while $W_s$, $L_s$ and $H_s$ are the width, length and height of the substrate, respectively. Probe contacts to the ends of the track are indicated, $T_{tr}$ is the track temperature and $P(t)$ is the time-dependent electrical heating power of the track. Initially, before the heat generation $P(t)$ is turned on, the whole system is at environment temperature $T_0$.

The three-dimensional geometry of Fig. 1(a) was simulated for constant heat source using the COMSOL Multiphysics® finite-elements (FEM) solver with parameter values shown in Table I. The FEM simulations indicated that convection and radiation effects can be ignored and taking into account only heat conduction from the track into the substrate and to the probe contacts well describes the dominant heat transfer processes of the system for the short time scales of electrical sintering that are considered in this paper. For the initial state of the unsintered, highly resistive track, for which $L_{tr} \gg W_{tr} \gg H_{tr}$, leakage to probes and temperature variations along the length of the track. (c) Limiting the width of the system to that of the track. (d) One-dimensional geometry that is solved analytically.

TABLE I: Parameter values used in FEM simulation.

<table>
<thead>
<tr>
<th>param. value</th>
<th>unit</th>
<th>definition</th>
</tr>
</thead>
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<td>$k_s$</td>
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<td>W/(m K)</td>
</tr>
<tr>
<td>$\rho_s$</td>
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<td>kg/(m$^3$)</td>
</tr>
<tr>
<td>$c_s$</td>
<td>1700</td>
<td>J/(kg K)</td>
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<td>$T_0$</td>
<td>300</td>
<td>K</td>
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<td>$h_{conv}$</td>
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<td>W/(m$^2$K)</td>
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</table>

FIG. 1: Approximations of the system in order to facilitate analytical solution of the heat equation. (a) Three-dimensional geometry of a printed track on top of a substrate. The electrical contacts to the track in a typical measurement setup are also shown with the series resistance $R_s$ limiting the maximum current. (b) Two-dimensional geometry ignoring temperature variations along the length of the track. (c) Limiting the width of the system to that of the track. (d) One-dimensional geometry of a printed track on top of a substrate. The three-dimensional geometry of Fig. 1(a) was simulated for constant heat source using the COMSOL Multiphysics® finite-elements (FEM) solver with parameter values shown in Table I. The FEM simulations indicated that convection and radiation effects can be ignored and taking into account only heat conduction from the track into the substrate and to the probe contacts well describes the dominant heat transfer processes of the system for the short time scales of electrical sintering that are considered in this paper. For the initial state of the unsintered, highly resistive track, for which $L_{tr} \gg W_{tr} \gg H_{tr}$, leakage to probes and temperature variations along the length of the track can be ignored and the geometry can be reduced to two dimensions as shown in Fig. 1(b). Heat conduction to the probe contacts becomes important for the sintered low-resistance state of the track and is included in the modelling later in this paper. Moreover, for short time scales, the heat conduction occurs mainly beneath the track and the two-dimensional model can further be simplified as shown in Fig. 1(c). Next, for simplicity, we assume that also temperature variations along the track width can be ignored enabling a one-dimensional model. For practical track widths, this assumption can become inaccurate as discussed in [10]. However, the assumption of uniform temperature across the track width considerably facilitates analytical solution of the heat equation and the approximation is in this paper found to result in good agreement between modelled and measured characteristics of the sintering process. Finally, due to the rapidness of the electrical sintering process, the heat conduction into the substrate during the sintering process is not affected by the bottom surface of the substrate. Therefore, the geometry of the system can be approximated by the one-dimensional semi-infinite model shown in Fig. 1(d).

B. Solution to the heat equation

We define the time-dependent heating power $P(t)$ of the printed track as well as the normalized temperature
of the track $\theta_{tr}$ and the substrate $\theta$ as

$$P(t) \equiv P \{ R[T_{tr}(t)] \} = U^2 R(t)/ \left[ \{ R(t) + R_s \}^2 \right]$$  \hspace{1cm} (1a)$$

$$\theta_{tr} \equiv T_{tr} - T_0$$  \hspace{1cm} (1b)$$

$$\theta \equiv T - T_0$$  \hspace{1cm} (1c)$$

where $U$ is the applied voltage over the track (electrical boundary condition), $R_s$ is the external resistance in series with the track and $T_0$ is the environment temperature. The heat conduction model for the system of Fig. 1(d) with initial and thermal boundary conditions can now be expressed as

$$P(t) = c_{tr} m_{tr} \frac{d\theta_{tr}(t)}{dt} + \Phi(t)$$  \hspace{1cm} (2a)$$

$$\frac{\partial^2 \theta(x, t)}{\partial x^2} = \frac{\partial \theta(x, t)}{\partial t}$$  \hspace{1cm} (2b)$$

$$\frac{\partial \theta(x, t)}{\partial x} \bigg|_{x=0} = - \frac{\Phi(t)}{k_s A}$$  \hspace{1cm} (2c)$$

$$\theta(0, t) = \theta_{tr}(t)$$  \hspace{1cm} (2d)$$

$$\theta(x \to \infty, t) \to 0$$  \hspace{1cm} (2e)$$

$$\theta(x, 0) \to 0$$  \hspace{1cm} (2f)$$

where $c_{tr}$ and $m_{tr}$ are the heat capacity and mass of the track, $\Phi$ is the thermal current from the track to the substrate and $A$ is the area of the track-substrate interface. Equation (2a) relates the heat generation in the track to the heating of the track and to the heat current from the track to the substrate. The substrate is modelled using the one-dimensional heat equation (2b) with boundary conditions for the heat flux (2c) and temperature (2d), (2e). Equation (2f) is the initial condition.

Solution to the track temperature can be found from Eqs. (2a) - (2f) using the Laplace transform as

$$\theta_{tr}(t) = \frac{1}{c_{tr} m_{tr}} \int_0^t e^{\alpha \tau} \text{Erfc} \left[ \alpha \sqrt{\tau} \right] P(t-\tau) d\tau ,$$  \hspace{1cm} (3)$$

where

$$\alpha \equiv \frac{k_s A}{c_{tr} m_{tr} \sqrt{a}} = \frac{A}{c_{tr} m_{tr} \sqrt{k_s \rho c_s}}$$  \hspace{1cm} (4)$$

and Erfc is the complementary error function. For the numerical Simulink® implementation of the model, considered in this paper, we utilize the Laplace transform of the heat flux

$$\Phi(s) = c_{tr} m_{tr} \alpha \sqrt{s} \tilde{\theta}_{tr}(s)$$  \hspace{1cm} (5)$$

and use a continued-fraction approximation with ninth-order nominator and denominator polynomials [25] for the square-root transfer function $\sqrt{s}$, where $s$ is the Laplace variable.

C. The thermal expansion model

As supported by SEM imaging of printed nanoparticle layers [9], prior to sintering, the printed and dried structure is assumed to consist of separated polymer-encapsulated nanoparticles. Possible solvent residuals that can exist in the structure are ignored in what follows. Initial electrical conductivity of the structure is assumed to be due to inter-particle tunneling and/or nonvanishing conductivity of the encapsulant. Electrical transport in the non-sintered structure is characterized by (i) conductivity of the particles, (ii) size distribution of the particles (for simplicity, the particles are assumed to be of equal size), (iii) conductivity through the encapsulant and (iv) statistical distribution of the inter-particle gaps that are assumed to be filled by the encapsulant.

To take the randomness of the nanoparticle structure into account, a percolation-based model is adopted for the conductivity of the printed track [15, 16]

$$\sigma = \sigma_0 e^{-\beta L_{cd}} ,$$  \hspace{1cm} (6)$$

where $\sigma_0$ is the maximum conductivity, $\beta$ is a fitting parameter depending on the encapsulant and $L_{cd}$ is defined through the gap size distribution $h_L(L)$ as

$$p_{cd} = \int_0^{L_{cd}} h_L(L) dL ,$$  \hspace{1cm} (7)$$

where $p_{cd}$ is the bond percolation threshold for a conductor-network layer of thickness $d$ [16]. The gap size distribution is assumed to consist of three parts as shown in Fig. 2: (i) a sintered zero-gap component of weight $q$, (ii) a dynamic distribution of gaps of sizes between $0 < L_1 \leq L \leq L_2$ and (iii) a static fraction $f_v$ of pores. Before sintering, we have $q = 0$. During sintering, the gap distribution for $L_1 \leq L \leq L_2$ evolves towards smaller gaps such that when $L_1$ vanishes, the degree of sintering ($q$) is irreversibly increased. The gap distribution for $L_1 \leq L \leq L_2$ is here assumed to be uniform to simplify the analysis. Using (7), we find

$$L_{cd} = \begin{cases} L_1 + \frac{(p_{cd} - q)(L_2 - L_1)}{1 - f_v - q} & \text{if } q \leq p_{cd} \\ 0 & \text{otherwise} \end{cases}$$  \hspace{1cm} (8)$$

The size reduction of the uniformly distributed gaps during sintering is in this paper assumed to be due to
thermal expansion of the particles. Other possible mechanisms are discussed in Sec. IV.

We define the sintering power as

$$P_{\text{sint}} = \frac{W_{tr}H_{tr}}{L_{tr}} \left[ U_{\text{eff}}^2 - WF \right] \sigma - \Phi,$$  \hspace{1cm} (9)

where the first term is the heating power of (1a) with $U_{\text{eff}} \equiv UR(t)/(R(t) + R_s)$ as the voltage over the track and $WF \equiv 4s \cdot 2.4 \cdot 10^{-8} \Omega W/(K^2) \cdot T_{tr}(T_{tr} - T_0)$ is a Wiedemann-Franz term describing thermal leakage into the probe contacts at the ends of the track. This term was not included in the one-dimensional model in (2a) to simplify the analysis above. The factor 4 in (9) is introduced assuming heat generation at the center of the track length and conduction towards both ends over distance $a$ of $L_{tr}$. For the weak convection and radiation assumed here, the FEM analysis with heat sinks at track ends to represent the probes result in constant temperature over the track length except for narrow regions close to the ends. This enhances the Wiedemann-Franz leakage and is taken into account by the parameter $s$ above in (9). In what follows, we call the parameter $s$ as “Wiedemann-Franz enhancement”.

For the thermal expansion model of sintering, the process is divided into five stages as:

1. Solid polymer suppresses particle expansion
   $$T_{tr} < T_{\text{mp}}, \quad \phi_p = 0, \quad \phi_m = 0.$$

2. Polymer melts / softens
   $$T_{tr} = T_{\text{mp}}, \quad 0 \leq \phi_p \leq 1, \quad \phi_m = 0.$$

3. Particles expand freely
   $$T_{\text{mp}} < T_{tr} < T_{\text{mm}}, \quad \phi_p = 1, \quad \phi_m = 0.$$

4. Particles melt
   $$T_{tr} = T_{\text{mm}}, \quad \phi_p = 1, \quad 0 \leq \phi_m \leq 1.$$

5. Melted particles expand
   $$T_{tr} > T_{\text{mm}}, \quad \phi_p = 1, \quad \phi_m = 1.$$

Here $T_{\text{mp}}$ is the melting/softening temperature of the polymer encapsulant and $T_{\text{mm}}$ is the melting temperature of the metal particles while $m_p$ and $m_m$ are the masses of the melted encapsulant and metal, respectively. The melted mass fractions are defined as $\phi_p = m_p/m_{tr}$ and $\phi_m = m_m/m_{tr}$ with $m_p$ and $m_m$ the total polymer and metal masses in the structure, respectively.

The governing equations for the process stages are

- **heating**: $c_{tr}m_{tr}\frac{dT_{tr}}{dt} = \Gamma_\text{a}P_{\text{sint}}$  \hspace{1cm} (10a)
- **melting polymer**: $h_p\frac{dm_{\text{mp}}}{dt} = \Gamma_\text{b}P_{\text{sint}}$  \hspace{1cm} (10b)
- **melting particles**: $h_m\frac{dm_{\text{mm}}}{dt} = \Gamma_\text{c}P_{\text{sint}}$  \hspace{1cm} (10c)
- **gap shrinkage**: $\frac{dL_{L2}}{dt} = -\Gamma_\text{d}c_{tr}m_{tr}P_{\text{sint}}$  \hspace{1cm} (10d)

where the stage-dependent parameters are defined in Table II. The latent heats of phase transitions (process stages 2 and 4, above) for the encapsulant and particles are denoted by $h_p$ and $h_m$, respectively. For a polymer glass transition, one uses $h_p = 0$. In this paper we ignore the influence of the change of the polymer heat capacity in glass transition on the track heat capacity $c_{tr}$. The particle radius is denoted with $r$ while $\delta^-$, $\delta$ and $\delta^+$ are the suppressed (encapsulant limited), normal and enhanced [26] (for melting and the melted state) heat expansion coefficients of the metal particles.

<table>
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<th>stage</th>
<th>$\Gamma_\text{a}$</th>
<th>$\Gamma_\text{b}$</th>
<th>$\Gamma_\text{c}$</th>
<th>$\Gamma_\text{d}$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
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<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
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<td>4</td>
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<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The expansion of the particles reduces the minimum and maximum gaps ($L_1$ and $L_2$) of the uniform distribution according Eq. (10d). At each time step of the simulation of the model, if $L_1$ becomes negative, the weight of the negative part of the gap distribution is irreversibly summed to the sintered weight $q$ that measures the size of the connected (percolating) cluster in the system. Thermal expansion is further enhanced for the percolating cluster because the reduction rate of a gap depends on size $r$ of the expanding structure. Grain growth that is assumed to occur after the particles come to contact is not modelled in this paper.

### III. COMPARISON TO EXPERIMENTS

As in Ref. [10], the electrical sintering method was applied to rectangular test tracks printed using the Silverjet DGP–30LT–15C and DGP–45LT–15C inks of Advanced Nano Products (ANP). The inks contain 34.5 wt% and 40.4 wt% of silver nanoparticles, respectively, with particle diameters of 40 - 60 nm, dispersed in triethylene glycol monoethyl ether solvent. The particle encapsulation used in the ink is not disclosed by the manufacturer but the sintering temperatures of about 150°C suggests a small capping molecule that also enables small initial interparticle distances [20–22]. The structures were printed at room temperature onto a Siena 250G photopaper using a Microdrop Autodrop inkjet printer with a 40-μm head. The sintering experiments were performed using a standard computer-controlled DC power supply and data were recorded using a Tektronix DPO 4034 oscilloscope at 10^7 samples/s. In order to obtain information on the track temperature during the process, thermal images were acquired with a Cedip Titanium 560M infrared ($\lambda = 1.5 - 5.1 \mu m$) camera having a frame rate of 870 fps at 160 x 128 pixels. The IR camera was equipped with a microscope lens providing a pixel size of 5 μm.
A. Heating during the presintering time

During the presintering time (time before the fast resistance transition), the track resistance stays essentially at constant level [9]. Therefore, the sintering power is also constant ($P(t) = P_0$) and defining the presintering power density as $P_0 = P_0/V_{tr}$, where $V_{tr}$ is the volume of the track, (3) can be simplified as:

$$\theta_{tr}(t) \approx \frac{P_0}{c_{tr} p_r \alpha^2} \left\{ e^{-\alpha^2 t \text{Erfc} \left[ \alpha \sqrt{t} \right]} + \frac{2 \alpha \sqrt{t}}{\sqrt{\pi}} - 1 \right\}, \quad (11)$$

which for large times ($\alpha \sqrt{t} \to \infty$) further reduces as

$$\theta_{tr}(t) \approx \frac{P_0}{c_{tr} p_r \alpha^2} \left\{ \frac{1}{\alpha \sqrt{\pi} t} + \frac{2 \alpha \sqrt{t}}{\sqrt{\pi}} - 1 \right\}. \quad (12)$$

Using (11) and (12), the presintering time as a function of power density can be solved as the time needed for the track temperature to rise to a value $T_{th}$ that is independent of the track geometry or other parameters. Consequently, on logarithmic scale, a linear dependency of the presintering time on the power density is predicted. Figure 3 collects the observed presintering times as a function of applied power density and a linear fit for times below 100 ms.

![FIG. 3: Measured presintering times as a function of applied power density and a linear fit for times below 100 ms.](image)

TABLE III: Model parameter values in addition to those of Table I that are common to all simulated track geometries of this paper.

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<thead>
<tr>
<th>param.</th>
<th>value</th>
<th>unit</th>
<th>definition (notes)</th>
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<tr>
<td>$H_{tr}$</td>
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<td>µm</td>
<td>track height (typical for an inkjet-printed layer)</td>
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<td>$L_{tr}$</td>
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<td>track length</td>
</tr>
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<td>$\sigma_0$</td>
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<td>S/m</td>
<td>reference conductivity ((6)) (half of bulk value (= \text{best obtained using RES} \ [9]))</td>
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<tr>
<td>$\delta$</td>
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<td>1/K</td>
<td>heat expansion coefficient (\text{(bulk value [23])})</td>
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<tr>
<td>$\delta^*$</td>
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<td>1/K</td>
<td>suppressed $\delta$ due to encapsulant (\text{(assumed to vanish)})</td>
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<td>packing ratio of particles (fcc)</td>
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<td>$s$</td>
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<td>Wiedemann-Franz enhancement (\text{(constant $T_{th}$ except close to the ends of the track as supported by FEM, fitted)})</td>
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<td>initial particle radius (SEM)</td>
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<td>nm</td>
<td>initial mean gap (SEM / fitted)</td>
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<td>nm</td>
<td>initial minimum gap (fitted)</td>
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<td>initial maximum gap (fitted)</td>
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<td></td>
<td>volume fraction of pores (fitted)</td>
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<td></td>
<td>bond percolation threshold ([16]) (\text{(fcc value)})</td>
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<tr>
<td>$T_{imp}$</td>
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<td>°C</td>
<td>polymer transition temperature (\text{(reasonable value, fitted)})</td>
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<tr>
<td>$T_{mm}$</td>
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<td>°C</td>
<td>particle melting temperature (\text{(in this paper $T_{th} &lt; T_{mm}$ so $T_{mm}$ is unimportant)})</td>
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<tr>
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<td>kJ/kg</td>
<td>particle latent heat (\text{(bulk value [2])})</td>
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<td>$h_p$</td>
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<td>J/kg</td>
<td>polymer latent heat (\text{(assumed insignificant)})</td>
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<td>heat conduction parameter (\text{(4)}) (\text{(fitted, see Sec. IV)})</td>
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<td>1/nm</td>
<td>attenuation parameter (\text{(5)}) (\text{(fitted, see Sec. IV)})</td>
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</table>

B. Dynamics of sintering

The thermal expansion model of Sec. II C was numerically implemented in Simulink®. The model parameter values that were common in all simulations are shown in Table III. Figure 4 shows the simulation results for resistance and power dissipation compared to the measurements of sintering of three tracks of different parameter values given in Table IV. From a set of 22 similar samples, relative standard deviation of 25 % was obtained for the presintering time. Consequently, also for the Sample 2, the simulated presintering time is within the experimental variation. The final resistance level below 10 Ω is not accurately predicted by the model. This is expected because the model does not include effects such as diffusion, Van der Waals, and capillary forces \([11]\) that
TABLE IV: Parameter values for the sintering of the samples of Fig. 4. Here $T_{\text{sim}}$ is the simulated presintering time, $R_{\text{init}}$ is the initial resistance, $P_{\text{max}}$ is the maximum power at transition, $t_{\text{end}}$ is the total duration of the process and $R_{\text{final}}$ is the final track resistance measured as a two-point measurement after the process at time $t_{\text{end}}$.

<table>
<thead>
<tr>
<th>param.</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
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<td>35</td>
</tr>
<tr>
<td>$R_{\text{init}}$ / [kΩ]</td>
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<td>156</td>
<td>216</td>
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<tr>
<td>$U$ / [V]</td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$I_c$ / [A]</td>
<td>198.2</td>
<td>198.2</td>
<td>490.8</td>
</tr>
<tr>
<td>$P_{\text{max}}$ / [W]</td>
<td>12.6</td>
<td>10.2</td>
<td>5.1</td>
</tr>
<tr>
<td>$t_{\text{end}}$ / [ms]</td>
<td>1050</td>
<td>1050</td>
<td>250</td>
</tr>
<tr>
<td>$R_{\text{final}}$ / [Ω]</td>
<td>2.26</td>
<td>1.79</td>
<td>3.47</td>
</tr>
</tbody>
</table>

become important in the final stages of the process resulting in significant grain growth [9]. Therefore, in order to reasonably fit to the final track temperature, after the simulated track resistance reduces below 10 Ω, it is set below the final experimental value by an estimated contact resistance of $\approx 1$ Ω. Figure 5 shows the zoomed-in view of the fast transitions in Fig. 4 for the Sample 3. The time constant of the transition is correctly produced by the simulation.

The temperature of the track during the sintering process is estimated in various ways as shown in Fig. 6 for the Sample 3 of Fig. 4. Results obtained using IR camera are shown with red curves. The camera was focused on the track (see Ref. [10]). The dashed and dotted red curves in Fig. 6 are calculated using the emissivities of $\epsilon = 0.17$ and $\epsilon = 0.64$ obtained for sintered and non-sintered tracks, respectively [10]. The solid red curve combines the two IR camera results assuming that the emissivity of the track changes stepwise from that of the non-sintered to that of the sintered state at the time of the transition. However, the frame rate of the camera limited the time resolution to about 1 ms which is too coarse to observe the maximum temperature during the fast transition. Furthermore, the camera was calibrated for temperatures between 90°C - 150°C and therefore results outside this range, especially at the earliest time instants, are not reliable. The solid blue curve shows the simulated temperature and the dashed blue curve...
is calculated using the measured power dissipation of Fig. 4 in (3). Here the thermal leakage to the probes is treated self-consistently by subtracting the Wiedemann-Franz term of (9) from the measured power and iterating (3) for a relative accuracy of $10^{-4}$. The two theoretical estimates reach temperatures of about 250°C and 300°C, respectively, that are higher than obtained based on the IR camera measurement but do not become close to the melting temperature of the silver particles. However, the estimated maximum temperatures are higher than the oven sintering temperature of the ink of 150°C.

IV. DISCUSSION

The size reduction of the inter-particle gaps during sintering was in this paper assumed to be due to thermal expansion of the particles. Other possible mechanisms for the gap reduction are (i) inter-particle neck growth induced by diffusion [11, 13, 24, 27], (ii) electromigration of Ag [28], (iii) surface melting of the particles [13] or (iv) particle movement caused by capillary forces that are induced by melting / softening / release (from the particle surface) of the polymer [11, 29, 30], Van der Waals forces [11], capacitive forces caused by the voltage bias or surface-melting-induced slippage [13]. As noted above, conventional linear diffusion theories are not in agreement with the fast time evolution of the electrical sintering of silver nanoparticles [9]. Inter-particle van der Waals forces could result in particle movements at the time scales of the process as can be seen by simulating the two-particle dynamics. However, in the particle structure, a resultant of the forces exerted on a particle by all its neighbours is nonzero only at the surface layer and due to the randomness of the structure. This considerably complicates the modelling of the force effects for the system. Therefore, in this paper, we focused on thermal expansion for which a tractable statistical model was developed. Generalization of the model for the other sintering mechanisms is left for future work.

The obtained model parameter values that provide the good fit with the experiments as shown above are rather reasonable as discussed in Table III with a few further points to note. In particular, (i) the Wiedemann-Franz enhancement parameter of $s \gg 1$ is supported by FEM simulations for the initial highly resistive track assuming a constant heat source along the track and fixed-temperature boundary conditions at the ends of the track due to probe contacts. Namely, the FEM simulations result in constant temperature of the track except for narrow regions close to the ends with large thermal gradients. Such temperature profile is also supported by the IR camera measurements. Furthermore, (ii) The exact value of the particle melting temperature, $T_{\text{mm}}$, plays no role here because the track temperature stays much lower during the simulations of this paper. Moreover, (iii) The polymer latent heat, $h_p$, is assumed to be insignificant (glass transition). For a first-order melting phase transition with a significant latent heat, a period of constant temperature should show up during the heating in the process, which is not observed using the IR camera. Finally, (iv) The fitted value of the attenuation parameter of $\beta = 22.7 \, (nm)^{-1}$, is between the measured values previously reported in literature of $1 < \beta < 15 \, (nm)^{-1}$ [16, 18, 31, 32] for different organic molecules and theoretical estimates of $29 < \beta < 34 \, (nm)^{-1}$ that are based on tunneling through a rectangular barrier in vacuum [31]. Furthermore, because we multiply with $\beta$ the statistical percolation length $L_1 \leq L_{cd} \leq L_2$ of (7) in (6) and not the actual polymer chain length, we find also the obtained value of the attenuation parameter $\beta$ to be well justified.

V. CONCLUSIONS

A model for sintering of conducting nanoparticles in a randomly distributed structure has been presented. Such structures result in solution processes such as printing that are used in low-cost fabrication of electronics. The model introduces thermal expansion as a significant driving force in the rapid electrical sintering (RES) of conducting nanoparticle structures. A good quantitative agreement between the theory and experiments is obtained with the values of the fitting parameters of the model within reasonable limits. The paper contributes to the understanding of the relevant physical processes of nanoparticle sintering. The model can be generalized to include also other commonly recognized driving mechanisms of sintering. The results can be used in developing low temperature sintering technologies for conductive and semiconductive nanoparticle inks that are of central interest of printed electronics.

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[35] Assuming that the junction resistance between well-conducting particles behaves classically and scales inversely proportional to the neck area, the equations for the kinetics of neck growth given on page 491 of [11], give for the resistance (R) of the particle structure as a function of time (t): \( R(t)/R(t + \Delta t) = (t + \Delta t)/t (2/m) \), where m is an exponent of 2 < m < 7. The observations of [9] for a resistance dropping two decades in a microsecond with a roughly constant rate at logarithmic scale do not fit this prediction. Namely, although for small initial times (t -> 0, t \( \ll \Delta t \)), the resistance change can be very fast as supported also by molecular-dynamics (MD) simulations [33, 34], the relative resistance drop during a following equal-sized timestep is limited to a maximum ratio of two (t = 0, m = 2).