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APPROXIMATION OF THE EMF OF A THERMOCOUPLE
Part I. The polynomials of temperature and Runge’s phenomenon

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Approximation polynomial of temperature for the emf of a thermocouple is of high order, with low accuracy and many digits in the polynomial coefficients. These disadvantages are shown clearly in comparison with the approximation of high-temperature heat capacity. The fitting problems result from the fundamental reason, namely, the particular analytical expression for the emf as the function of temperature.

In the approximation theory, this disadvantage is known as Runge’s phenomenon. In this report, it is shown to be typical of the functions with a negative power of the variable, where the derivation produces a factorial.

Keywords: *emf, fitting, polynomials, thermocouples*

Introduction

The emf of metal thermocouples is approximated with polynomials

$$\mathrm{emf}(t,0)=\sum_{i=0}^{n}a_i t^i \qquad (1)$$

where t is the temperature in °C of the working junction, with the reference junction at 0°C. The degree of the polynomial is large enough. For the temperature interval of –270 to 0°C, n is 13 for thermocouple E, 10 for K, 8 for N and 14 for T. Notation emf(t_1,t_2) is used throughout the work to avoid the confusion between a voltage at a junction (denoted below ΔU) and the difference in voltage between two junctions (denoted in literature ΔU).

There are two reasons why the approximating polynomial is of high order. First, the function has several maximums and minimums. This is not the case for thermocouples. Figure 1 shows that the emf of thermocouple T is smooth, monotonic function, without extremums. Second, the function approximated is of the high order itself. For example, theory predicts that the electrical resistivity of metals at low temperature increases as the fifth power of temperature: $\rho\sim T^5$ [1]. It is evident that the polynomial must be of the fifth order at least. But, again, this is not the case for the emf of thermocouples. Figure 2 shows ln(emf) *vs.* ln$T$ for the data in Fig. 1, but with emf(T,0 K) and T instead of emf(t,0°C) and t, respectively. Points fit well to linear function ln(emf)=1.775ln$T$– 8.087, indicating that the emf increases with temperature even slowly than T^2.

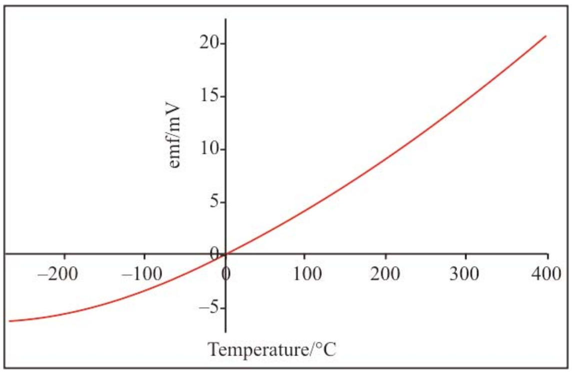

Fig. 1 The emf for thermocouple T *vs.* temperature

Thus, we face a paradox. The emf is a smooth monotonic low-order function of temperature, but is fitted to the high-order polynomial in temperature.

Recently the emf of a thermocouple was shown to obey expression

$$\Delta U(T)=\varepsilon_0\left[T-\Theta_\mathrm{V}\ln\left(1+\frac{T}{\Theta_\mathrm{V}}\right)\right] \qquad (2)$$

where ε_0 is the limiting theoretical value of the thermocouple sensitivity, and Θ_V is the characteristic temperature of a particular thermocouple, depending on the metals in the thermocouple [2]. The emf generated by a thermocouple with the junctions at tempera-

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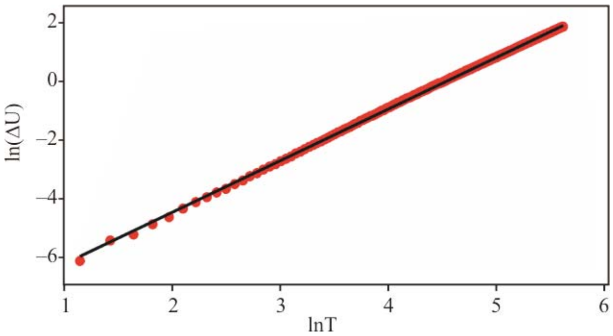

Fig. 2 Logarithm plot of the data in Fig. 1 with substitutions $t \to T$ and emf(t,0°C)→emf(T,0 K)

tures T_1 and T_2 is the difference between two voltages at these temperatures:

$$\text{emf}(T_1,T_2)=\Delta U(T_1)-\Delta U(T_2) \qquad (3)$$

Formula (2) turned out to be useful not only for metal thermocouples, but also for semiconductor ones used in new ultra-fast DSCs [3]. No conventional (and approved by metrological service) function emf(T_1,T_2) for this type of a heat flux detector exists, like the functions for the letter-designed metal thermocouples. Fortunately, formula (2) with two variable coefficients, ε_0 and Θ, fits the emf of a semiconductor thermocouple over the temperature range −170–160°C with an error less than 0.5°C [4].

The objective of this work is to show that the fundamental mathematical reasons make the temperature polynomials improper for the fitting of the emf and to justify the necessity to develop another way for the approximation of the emf data.

Mathematics of the emf fitting to a power series

Any analytical function $F(x)$ can be fitted to a polynomial in x by using the Taylor series

$$F(x)=F(0)+\sum_{i=1}^{n}\frac{F^{i}(0)}{i!}x^{i}+R(x^{n}) \qquad (4)$$

where $F(0)$ is the value of the function at point x=0, $F^i(0)$ is the value of the i^{th} derivative with respect to x at point x=0, and $R(x^n)$ is the residue of the series, tending to zero when n tends to infinity. Taking $\Delta U(T)$ in Eq. (2) as $F(x)$, we have the derivatives

$$F^{\text{I}}(T)=\varepsilon_0\frac{T}{T+\Theta},\ F^{\text{II}}(T)=\frac{\varepsilon_0\Theta}{(T+\Theta)^2},$$
$$F^{\text{III}}(T)=-\frac{2\varepsilon_0\Theta}{(T+\Theta)^3},\ F^{\text{IV}}(T)=\frac{6\varepsilon_0\Theta}{(T+\Theta)^4},\ \text{etc.}$$

First derivative, $F^{\text{I}}(0)$, is equal to zero, but the rest derivatives are not. General equation for the i^{th} derivative with i>1 is

$$F^{i}(T)=(-1)^{i}\frac{(i-0)!\varepsilon_0\Theta}{(T+\Theta)^{i}} \qquad (5)$$

It is very important for further discussion that the differentiation produces factorial (i–1)! in the numerator while the term for i^{th} derivative in Eq. (4) contains factorial i! in the denominator. This case is not typical in the Taylor expansion, it occurs only for the negative power, x^{-n}. Differentiation of most functions does not produce factorial in the numerator, and the factorial in the denominator decreases the terms in sum (4) rapidly. Here we have the ratio of two factorials, and, reducing the fraction, we receive

$$\text{emf}(T_1,T_2)=\sum_{i=2}^{n}(-1)^{i}\frac{\varepsilon_0\Theta}{i}\left(\frac{T_1}{\Theta}\right)^{i}-\Delta U(T_2) \qquad (6)$$

where $\Delta U(T_2)$ is a constant. Thus, the emf is expanded to the series, equivalent to the polynomial

$$\text{emf}(T_1,T_2)=a_0+a_2T_1^2+a_3T_1^3+a_4T_1^4+\ldots+a_iT_1^i \qquad (7)$$

with the recurrence formula for coefficients

$$a_i=-a_{i-1}\frac{i-1}{i}\Theta^{-1} \qquad (8)$$

The terms of the expansion decrease due to the division of each subsequent coefficient by characteristic temperature Θ_V. Such a series is similar to the geometric series with a factor of T/Θ. Besides, the series is alternating, i.e. two neighbor terms differ in sign. For $T/\Theta<1$, the terms decrease with order i, and the series (infinite polynomial with $i\to\infty$) converges. The less the ratio T/Θ, the faster the convergence. But, for $T/\Theta>1$, the terms increase with i, and the series diverges. The residue of the series ($R(x^n)$ in Eq. (4)) does not tend to zero. The increase in the number of terms in the polynomials of this kind does not improve the fitting. This fact is known in the approximation theory as the Runge's phenomenon [5].

Practice of the emf fitting to a power series

The emf data of most important and carefully investigated thermocouples are available in the WWW (http://srdata.nist.gov/its90/main). Other national metrological surveys use the same tables [6]. Values of Θ_V for letter-designated thermocouples are listed in Table 1. They were derived from the fitting of the emf to Eq. (2). We will show below that the coefficients and terms in the NIST polynomials do agree with the mathematical results described in the previous section.

One should emphasize that the development of the polynomial is rather intricate problem. The whole temperature interval of the emf is divided into two or three parts with a separate polynomial for each part. The polynomials must fit to one another at the points bordering the intervals. The first and second derivatives of the polynomials must be equal as well. It means that the three first coefficients in two neighbor polynomials are calculated after special procedure, not following the conventional mathematical procedure discussed in the previous section. Next derivatives have a discontinuity at the border point, but their coefficients depend on the previous coefficients. The polynomials derived by metrological surveys of different countries from identical emf(t) tables may differ from one another. Below, we will compare the Taylor expansion only with the NIST polynomials. GOST polynomials are different [6], but the analysis of their coefficients leads up to the same conclusions.

Table 1 Low-temperature intervals of the letter-designated thermocouples (NIST polynomials) and Θ_V values [2]

Type	metal(alloy) 1 *metal(alloy) 2*	T range of a polynomial/°C	Polynomial order, n	Θ/K
E	Chromel *Constantan*	–270–0	13	159
J	Fe *Constantan*	–210–760	8	197
K	Chromel *Alumel*	–270–0	10	325
N	Nicrosil *Nisil*	–270–0	8	564
R	13%Rh/Pt *Pt*	–50–1064	9	4097
S	10%Rh/Pt *Pt*	–50–1064	8	4180
T	Cu *Constantan*	–270–0	14	340

For type E thermocouple, polynomial coefficients for $-273<t<0$°C are listed in Table 2. These are used for the calculation of the emf at two temperatures, –25 and –250°C. For –25°C, the terms of the polynomial decrease rapidly with i, and become negligible for $i>8$. One can omit the last terms, one by one, and the accuracy of the fitting will become worse gradually. The increase in the number of coefficients, i.e., the degree of the polynomial, will not affect the result. This is a ‘good’ approximation. The result is completely different for –250°C. The terms increase with i, becoming greater than the final sum. The last term (516.4421) is fifty times greater than the value of the whole polynomial (–9.7185). The omission of the last term will corrupt the result drastically. On the other hand, the increase in the degree of polynomial (n+1) will add new significant terms and change all previous coefficients. Such an approximation is ‘bad’.

This drastic difference between –25 and –250°C is explained easily by the mathematics of the approximation. Terms in the Taylor expansion for the emf of a thermocouple change with the term’s power as $(t/\Theta_V)^{-i}$. Characteristic temperature for E type thermocouple is 159 K (Table 1). For t=–25°C absolute value of t/Θ is less than 1, and the series converges readily, as a geometric series with the factor less than 1. For

Table 2 Calculation of the emf (in mV) for E type thermocouple

i	Coefficients	–25 °C		–250 °C	
	a_i	t^i	a_it^i	t^i	a_it^i
0	0	0	0	0	0
1	$5.8665508708\cdot10^{-2}$	–25	–1.4666	–250	–14.6664
2	$4.5410977124\cdot10^{-5}$	625	0.0284	62500	2.8382
3	$-7.7998048686\cdot10^{-7}$	–15625	0.0122	–15625000	12.1872
4	$-2.5800160843\cdot10^{-8}$	390625	–0.0101	3906250000	–100.7819
5	$-5.9452583057\cdot10^{-10}$	–9765625	0.0058	$-9.765625\cdot10^{11}$	580.5916
6	$-9.3214058667\cdot10^{-12}$	244140625	–0.0023	$2.441406\cdot10^{14}$	–2275.7339
7	$-1.0287605534\cdot10^{-13}$	–6103515625	0.0006	$-6.103516\cdot10^{16}$	6279.0561
8	$-8.0370123621\cdot10^{-16}$	$1.52588\cdot10^{11}$	–0.0001	$1.525879\cdot10^{19}$	–12263.5076
9	$-4.3979497391\cdot10^{-18}$	$-3.81470\cdot10^{12}$	0.0000	$-3.814697\cdot10^{21}$	16776.8468
10	$-1.6414776355\cdot10^{-20}$	$9.53674\cdot10^{13}$	0.0000	$9.536743\cdot10^{23}$	–15654.3506
11	$-3.9673619516\cdot10^{-23}$	$-2.38419\cdot10^{15}$	0.0000	$-2.384186\cdot10^{26}$	9458.9280
12	$-5.5827328721\cdot10^{-26}$	$5.96046\cdot10^{16}$	0.0000	$5.960464\cdot10^{28}$	–3327.5681
13	$-3.4657842013\cdot10^{-29}$	$-1.49012\cdot10^{18}$	0.0000	$-1.490116\cdot10^{31}$	516.4421
			$\sum a_it^i$=–1.4321		$\sum a_it^i$=–9.7185

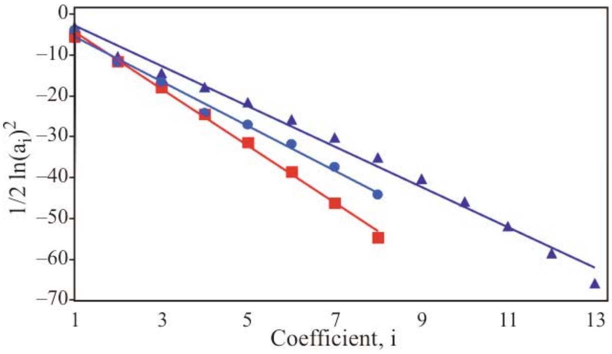

Fig. 3 Polynomial coefficients in the low-temperature range for thermocouples ▲ – E, ● – N and ■ – S, fitted to their linear regressions

$t=-250$°C, the absolute value of t/Θ is greater than 1, and the series diverges. The greater the power of a term in the series, the greater the term itself.

In applying the results of the mathematical evaluations to the practical fitting, one can see that the terms in the polynomials are alternative in sign, i.e., negative for even *i* and positive for odd. This is valid for $i>2$, because three first coefficients a_i ($i=0, 1, 2$) are used for the fitting of two polynomials at the border between their temperature intervals. It is interesting, that the term's alteration in sign is obtained not by the alteration in sign of a coefficient, but of the powers of the variable. Temperature in °C is negative itself, and its odd and even powers differ in sign.

And finally, it is interesting to check whether the values of the polynomial coefficients do decrease with the number as Θ^{-i}. Logarithms are most suitable way to analyze productions and geometric series. In applying logarithm to Eq. (6) for the terms in the Taylor series for the emf, we have

$$\ln a_i = \ln\frac{\varepsilon_0\Theta}{i} - i\ln\Theta \qquad (9)$$

Here, we omitted only term $(-1)^i$. To proceed both positive and negative coefficients, we calculate $0.5\ln(a_i)^2$. The results are shown in Fig. 3, fitted to linear regression

$$0.5\ln(a_i)^2 = 2.50 - 4.93i \qquad (10)$$

Exponent of 4.93 is 138, very close to 159 of Θ_V for type E thermocouple. Similar evaluations for thermocouples N ($0.29-5.46i$) and S ($2.88-6.96i$) are also shown in Fig. 4. Thus, one can conclude that the properties of the fitting polynomial for the emf of thermocouples do agree with those derived from the Taylor expansion of Eq. (2).

Approximation of high-temperature heat capacity

Merits and demerits of the polynomial fitting for the emf are seen better in the comparison with other examples. Fitting Debye function $D(x)$ is the most relevant topic. According to the Debye model, heat capacity as a function of temperature is

$$C = 3R\left[\frac{12}{x^3}\int_0^x \frac{y^3\mathrm{d}y}{\mathrm{e}^y - 1} - \frac{3x}{\mathrm{e}^x - 1}\right] \qquad (11)$$

where R is the gas constant, $x=\Theta_D/T$ and Θ_D is the characteristic temperature of the vibrational spectrum of a solid (Debye temperature). Formula in the brackets, $D(x)$, ranges from 0 ($T=0$, $x=\infty$) to 1 ($T=\infty$, $x=0$) and cannot be expressed in an analytical equation. It is calculated and tabulated instead. Nevertheless, for practical use we have to approximate table $D(x)$ and then calculate the Debye function after the fitting function (polynomial). In his original report, Debye has considered himself the expansion of function $D(x)$ for high- and low-temperature limits [7]. Cubic function $C=aT^3$ for the low-temperature limit is the most important and well-known result. It is used in low-temperature calorimetric works for the extrapolation of heat capacity to zero temperature and calculation of thermodynamic functions [8].

The other result is less known. In considering the high-temperature limit for his heat capacity model, Debye expanded Eq. (11) to a series in x for $x\to 0$ [7] and received

$$D(x) = 1 - \frac{x^2}{20} + \frac{x^4}{560} - \frac{x^6}{18144} + \frac{x^8}{633600} - \frac{x^{10}}{23063040} + \ldots \qquad (12)$$

Relation between this expansion and fitting polynomial is tested in this work using $D(x)$ over the interval of $0\le x\le 2.5$, with $D(x)$ decreasing from 1 down to 0.745853. Tabulated points with the increment of 0.01 (total 251) [9] were fitted to a temperature polynomial of the 6th order using QuattroPro software with built-in

Table 3 Calculation of the Debye function at $x=\Theta_D/T=2.5$ after the fitting polynomial

i	Coefficients, a_i	x^i	$a_i x^i$
0	1.0000012	1	1.0000012
1	–0.00002989	2.5	–0.0000747
2	–0.04983574	6.25	–0.3114734
3	–0.000363107	15.625	–0.0056736
4	0.002175987	39.0625	0.0849995
5	–0.000211513	97.65625	–0.0206555
6	–0.0000052082	244.1406	–0.0012715
			$\sum a_i x^i = 0.7458520$

fitting procedures. The coefficients for the polynomial are listed in Table 3. In comparing a_i of the fitting polynomial with expansion (12), we see that three first coefficients in the expansion (+1, –0.05 and +0.00179) agree well with corresponding coefficients (i=0, 2 and 4) of the polynomial (+1.00, –0.0498 and +0.00218). Their contribution into the calculated value is very large, about 90% of the change in $D(x)$. Next coefficients of the expansion ($5.5\cdot10^{-5}$, $1.6\cdot10^{-6}$ and $4.3\cdot10^{-8}$ for x^6, x^8 and x^{10}, respectively) do not affect the coefficients of the polynomial.

Fitting function for the high-temperature heat capacity was a problem 75 years ago. At that time heat capacity was described by a polynomial of temperature

$$C_P=a+bT+cT^2 \tag{13}$$

This form of equation was not particularly satisfactory for the purpose because a reasonable number of terms cannot be made to fit the data with sufficient accuracy. Meier and Kelley [10] suggested empirical equation

$$C_P=a+bT-cT^{-2} \tag{14}$$

which describes the experimental data better than Eq. (13). The term with T^{-2} improves the approximation significantly, and Eq. (14) is widespread in present-day reports [11, 12]. More Debye's terms in high-temperature heat capacity are combined again with a linear term [13]

$$C_P=3R\left(1-\frac{\Theta^2}{20T^2}+\frac{\Theta^4}{560T^4}\right)+aT \tag{15}$$

In comparing polynomials for the emf (Table 2) and $D(x)$ (Table 3), we see that the former *i*) contains more coefficients (13 *vs.* 6), *ii*) with more digits (11 *vs.* 8), and *iii*) fits the table values with worse accuracy (0.005 *vs.* 0.0005%). We wouldn't discuss here in detail the number of digits in the coefficients, because this point is explained partly by subjective reasons. Suffice to point out that three terms (8th, 9th and 10th) in the emf polynomial at 250°C (Table 2) are reported with nine digits. They are all necessary in order to calculate the sum accurately, not decreasing its accuracy after rounding. It means that the corresponding coefficients (a_8, a_9 and a_{10}) must also be with nine digits at least. In the $D(x)$ polynomial, the second term is printed with seven digits, and coefficient a_2 also must have seven digits.

Accuracy of the approximation is considered here as the ratio of the deviation of polynomial values from tabulated ones (d) to the amplitude of the function approximated (A). For the emf polynomial, d=0.0005 mV and A=9.835 mV with $d/A\approx5\cdot10^{-5}$. For the $D(x)$ polynomial, d=0.0000012 and A=1–0.745853=0.254147 with $d/A\approx5\cdot10^{-6}$.

Canonical example of Runge's phenomenon

It has long been known that the increase in the order of a polynomial sometimes does not improve the approximation of tabulated data. This phenomenon is usually exemplified with conformal functions $(a^2+x^2)^{-1}$ [14], $(1+x^2)^{-1}$ [15, 16], $(1+16x^2)^{-1}$ [17], $(1+25x^2)^{-1}$ [18]. These are discussed in lectures, monographs and practical courses as 'a special class of functions'. Unfortunately, we did not find any relevant explanation of why is exactly this function so outstanding, how many functions do demonstrate the Runge's phenomenon, and how should we recognize a function of Runge's phenomenon type. The problem is considered very difficult because 'a complete and rigorous development ... requires some subtle analysis as well as evaluation of complex integrals via the theory of residues ... beyond the comprehension of most students in undergraduate numerical analysis courses' [19].

Table 4 Expansion to the Taylor series and the polynomial approximation over intervals [min,max] for the Runge function $(1+x^2)^{-1}$

i	Taylor series		Approximation polynomials			
			[–0.5,+0.5]	[–1,+1]	[–5,+5]	[–5,+5]
	$F^i(0)$	$F^i(0)/i!$	a_i	a_i	a_i	$a_i\cdot5^i$
0	1	1	1.0000	0.9998	0.8499	0.850
1	0	0	$-2\cdot10^{-17}$	$-5\cdot10^{-17}$	$-8\cdot10^{-16}$	0.000
2	–2	–1	–0.9998	–0.9880	–0.2870	–7.175
3	0	0	$-9\cdot10^{-16}$	$7\cdot10^{-16}$	$4\cdot10^{-16}$	0.000
4	24	1	0.9936	0.8823	0.0367	22.949
5	0	0	$1\cdot10^{-14}$	$-2\cdot10^{-15}$	$-4\cdot10^{-17}$	0.000
6	–720	–1	–0.9207	–0.5603	–0.0019	–29.683
7	0	0	$-4\cdot10^{-14}$	$1\cdot10^{-15}$	$1\cdot10^{-18}$	0.000
8	40320	1	0.5736	0.1665	$3\cdot10^{-5}$	13.203
						$\sum a_it^i=0.143$

Fortunately, undergraduate students comprehend the functional analysis (differentiation), polynomials, and the Taylor series. Polynomials for the emf demonstrate the Runge's phenomenon because of the negative power of the variable in the initial function (in fact, logarithm, but transforming into the negative power after the differentiation). Now we can check whether this reason is also valid for the canonical function demonstrating the Runge's phenomenon.

First, the derivatives ($F^i(x)$) of function $(1+x^2)^{-1}$ up to the 8th order were calculated. Then the coefficients ($F^i(0)/i!$) in the Taylor series (Eq. (4)) were calculated. Coefficients for the approximation polynomial were calculated using software QuattroPro for the intervals $-5<x<+5$, $-1<x<+1$ and $-0.5<x<+0.5$. The results are shown in Table 4. Again, like it was in the emf and $D(x)$ fitting, the coefficients of the Taylor series and approximation polynomial agree with one another in the number of significant coefficients (i=2, 4, 6 and 8) and their sign. The coefficients of the approximation depend extremely on the number of node points and the approximation interval. The greater the interval, the greater the error of the approximation. The standard deviation between the function and its approximation polynomial is <0.000001 for $-0.5<x<+0.5$, 0.00016 for $-1<x<+1$ and 0.059 for $-5<x<+5$. It is because the coefficients of the Taylor expansion in Table 4 do not decrease with increasing their number, and terms $a_i x^i$ increase with i for large x values, like it was for the emf fitting. One may conclude that the Runge's phenomenon is typical of the functions with a negative power of a variable (x^{-n}).

Conclusions

Mathematical analysis of the equation for the emf of a thermocouple revealed that the expansion to the Taylor series of temperature produces an alternating polynomial with coefficients a_i decreasing inversely with Θ_V^i, where Θ_V is the thermoelectric characteristic temperature of the couple of metals and i is the number of the coefficient.

NIST polynomials for the emf of letter-designated thermocouples do conform the mathematical results.

Comparison between the emf polynomial and that for the approximation of the Debye function shows evidently that the emf polynomial is much worse if $T/\Theta_V>1$. The emf polynomial reproduces the divergent series, with the terms increasing with i.

Such a problem is known in the approximation theory as Runge's phenomenon. It is typical of the function with negative powers of a variable. Differentiation of such a function produces the factorial, which increases drastically the terms in the Taylor expansion, making the series diverge. There are several strategies, each employing a single polynomial over the entire interval, to wholly or partially defeat Runge's phenomenon. Unfortunately, each of them has liabilities including various permutations of inefficiency, ill-conditioning and a lack of theory [20].

We will show in the next report how to evade this problem and approximate the emf accurately with polynomials having 3–4 coefficients instead of 10–14.

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