The Influence of the Distribution Function of Ferroelectric Nanoparticles Sizes on Their Electrocaloric and Pyroelectric Properties

Hanna V. Shevliakova, Anna N. Morozovska, Nicholas V. Morozosky, George S. Svechnikov, Senior Member, IEEE, and Vladimir V. Shvartsman

Abstract—We consider a model of a nanocomposite based on noninteracting spherical single-domain ferroelectric nanoparticles (NPs) of various sizes embedded in a dielectric matrix. The size distribution function of these NPs is selected as a part of the truncated Gaussian distribution from minimum to maximum radius. For such nanocomposites, we calculate the dependences of the reversible part of the electric polarization, the electrocaloric (EC) temperature change, and the dielectric permittivity on the external electric field, which have the characteristic form of hysteresis loops. We then analyze the change in the shape of the hysteresis loops relative to the particle size distribution parameters. We demonstrate that the remanent polarization, coercive field, dielectric permittivity maxima, and maxima and minimums of the EC temperature change depend most strongly on the most probable radius, moderately on the dispersion, and have the weakest dependence on the maximum radius of the NP. We calculate and analyze the dependences of pyroelectric figures of merit on the average radius of the NPs in the composite. The dependences confirm the presence of a phase transition induced by the size of the NPs, which is characterized by the presence of a maxima near the critical average radius of the particles, the value of which increases with an increasing dispersion of the distribution function.

Index Terms—Electrocaloric (EC) effect, ferroelectric (FE) nanoparticle (NP), nanocomposite, particle size dispersion, pyroelectric (PE) effect.

I. INTRODUCTION

From the second half of the twentieth century to the present, ferroelectric (FE) materials have been the objects of intense experimental and theoretical studies due to their use as active media in a number of converting devices, in particular in pyroelectric (PE) [1]–[3] and electrocaloric (EC) [1], [2], [4], [5] converters. For many years, PE converters have been used in many applications from gas detectors to thermal imaging [6]; however, only the recently discovered “giant” EC effect in thin films [7] opened up the prospect for using the EC effect in solid-state microcoolers. The PE and EC properties of thin FE films, multilayers, and other low-dimensional materials can differ greatly from those of bulk materials. In particular, the prospects of using FE nanocomposites for EC converters [8]–[10] and PE sensors [11] are more compelling. Therefore, the studies of low-dimensional FE materials, such as thin films and nanocomposites, are very relevant [3], [5], [11]–[13]. The study of EC cooling is of great importance to finding solutions to environmental problems [5], [12] and energy efficiency [14] of currently available cooling technologies.

Further progress in this direction is hindered by a number of technological and theoretical difficulties [15], [16]. These difficulties relate to the appearance of a practically unremovable electric field of depolarization, which is not taken into account when considering EC and PE effects [8].

Modern methods allow precise selection of nanoparticles (NPs) by size and shape; however, nanocomposites made on this basis, as a rule, contain NPs with a more or less symmetric distribution in size within certain limits around the average size [17]–[19].

As indicated in [20], it is still unclear what effect the size distribution of FE NPs has on the EC properties of nanocomposites based on them. In his case, the properties of the composite depend on the predominance of the contribution of particles of one size or another. The numerical and analytical models developed to date are mainly aimed at the description of composites with NPs of the same size and certain shape [8], [21]–[23].

This article is essentially a semianalytical and semnumerical description of the EC and PE properties of nanocomposites based on FE NPs with the most realistic Gaussian size distribution function.

The shape of FE NPs-fillers is important, because it strongly affects the critical size of the NPs, as well as their critical concentration where the long-range interaction between them becomes noticeable. The role of the distribution function for NPs of an arbitrary shape becomes very complex in the general
case, and some relatively simple conclusions can be made for single-domain ellipsoidal NPs only [24].

II. PROBLEM STATEMENT

We consider a nanocomposite consisting of an isotropic dielectric polymer matrix with permittivity \( \varepsilon_{\text{r}} \) and immersed BaTiO\(_3\) FE NPs with permittivity \( \varepsilon_{\text{p}} \). Each FE NP is surrounded by a semiconductor shell with a dielectric permittivity \( \varepsilon_{\text{IF}} \), which acts as a layer screening the FE polarization of a particle with a thickness equal to the “effective” screening length \( \Lambda \) [25]. The NP sizes vary in a range from minimum \( R_{\text{min}} \) to maximum \( R_{\text{max}} \). A schematic representation of the nanocomposite is shown in Fig. 1, modified from [26]. Due to the screening, the interaction between the NPs in a nanocomposite can be ignored if the relative fraction of the volume of the NPs is small (less than 10%). However, if the degree of screening is very high, the interaction between the NPs disappears, and the interaction of the NPs with an external electric field is weakened. It is believed that the degree of screening is independent of the particle concentration, which holds true up to very high concentrations.

FE NPs were previously polarized by a strong electric field, while the polymer was in the liquid phase and the particles could rotate in it almost freely. In this phase, the Curie temperature of FE NPs should be significantly higher than the polymer melting temperature, and the poling field should be significantly smaller than the breakdown field of the liquid polymer. After polymer solidification, all NPs are single domain with the only component of spontaneous polarization \( P_3(r) \) directed along axis 3 of the BaTiO\(_3\) unit cell.

The model structure of the core-shell NP is in accordance with the X-rays synchrotron radiation analysis [27] and scanning transmission electron microscopy observation [28] data, indicating the presence of an inner tetragonal core, gradient lattice strain layer, and surface cubic layer [29], which was used earlier [8], [29] to evaluate the efficiency of EC conversion of these NPs. The shell with a high \( \varepsilon_{\text{IF}} \) and small \( \Lambda \) is required to reduce the depolarization field inside the spherical FE NP, and, consequently, to significantly reduce the critical size of the NP. Without the shell, the critical size of BaTiO\(_3\) NPs increases up to (50–100) nm at room temperature (see, e.g., experimental work [30]).

If an NP shape can be approximated by an ellipsoid of revolution with semi-axes \( a = b \) and \( c \), three cases can be considered semiquantitatively. The case \( a = b \approx c \) reduces to the nanospheres already considered in this work, and the cases \( a = b \gg c \) and \( a = b \ll c \) are options for long rods or wires and thin plates, respectively. The spontaneous polarization tends to be parallel to the rod (or wire) axis to minimize the depolarization field that vanishes in the limit \( a/c \rightarrow 0 \) [31]. For this case only, the distribution function of the semi-axis \( a \) is important, and, as a rule, the critical size \( a_{\text{cr}} \) is significantly smaller than the critical radius \( R_{\text{cr}} \) for the sphere. This happens because the value of \( a_{\text{cr}} \) is determined by the free energy minimum, consisting of the negative Landau energy and positive correlation energy, while \( R_{\text{cr}} \) is determined by the minimum of the Landau, correlation, and depolarization energies. The shell is not important for polarized nanowires, since their depolarization field energy is negligibly small. In contrast to the long nanorods and nanowires with \( \bar{P} \uparrow \uparrow \hat{c} \), the nanodisks, either with \( \bar{P} \uparrow \uparrow \hat{a} \) or with \( \bar{P} \uparrow \uparrow \hat{a} \), are characterized by a much higher critical size due to the high depolarization field energy.

Experimental realizations of quasi-spherical FE perovskite NPs are abundant [32], [33], and the sizes \( \sim (5–50) \) nm are typical experimental values [34]–[36]. There are several studies of FE NPs covered with a surfactant [37], [38], or otherwise known as core-shell NPs. The core-shell structure was also noted for the bare BaTiO\(_3\) particles (see [39], [40]). In practice, the NPs obtained by for example, ball milling of a single-crystalline bulk BaTiO\(_3\) are faceted, and to regard them as perfect spheres is an approximation. Below we ignore the influence of the core nonsphericity on the stability of the polarization state and its reversal by an external electric field.

For the calculations, we assume that the radii distribution of the NPs corresponds to a distribution function \( f(R) \), which is expressed by the normal Gaussian distribution

\[
f(R) = \left(1/\sigma_R \right) \exp \left[-(R - R_m)^2/(2\sigma^2) \right]
\]

where \( \sigma^2 \) is the dispersion characterizing the spread of \( R \) around the most probable radius \( R_m \), and \( \sigma_R \) is the normalizing coefficient. Given that the particle radii vary from \( R_{\text{min}} \) to \( R_{\text{max}} \) the normalization condition is

\[
\int_{R_{\text{min}}}^{R_{\text{max}}} f(R) dR = 1
\]

where the normalizing coefficient \( \sigma_R \) is

\[
\sigma_R = \sqrt{\frac{\pi}{2}} \sigma \left[ \text{erf} \left( \frac{R_m - R_{\text{min}}}{\sqrt{2}\sigma} \right) - \text{erf} \left( \frac{R_m - R_{\text{max}}}{\sqrt{2}\sigma} \right) \right]
\]

(2b)

radii \( R_{\text{min}} \leq R_m \leq R_{\text{max}} \), and \( \text{erf}(x) = 2/\sqrt{\pi} \int_0^x \exp(-z^2)dz \) is the error function.

The average radius is calculated by the formula

\[
\bar{R}(R_m) = \int_{R_{\text{min}}}^{R_{\text{max}}} R \cdot f(R) dR = \left( \frac{\sigma^2}{\sigma_R} \right) \times \left( \exp \left[- \left( \frac{R_m - R_{\text{min}}}{\sqrt{2}\sigma} \right)^2 \right] - \exp \left[- \left( \frac{R_m - R_{\text{max}}}{\sqrt{2}\sigma} \right)^2 \right] \right) + R_m
\]

(2c)
and differs from \(R_m\) as the gausoid is “cut off” in the range from \(R_{\min}\) to \(R_{\max}\).

The dependence of the \(f(R)\) on the parameters \(R_m, \sigma\), and \(R_{\max}\) is presented in Fig. 2(a), (e), and (i), respectively.

We have previously analyzed the typical dependences of the PE parameters and EC conversion on the external electric field \(E_{\text{ext}}\), temperature, and radius of spherical single-domain FE NPs [21], using the phenomenological Landau–Ginsburg–Devonshire (LGD) theory and effective medium approximation.

It should be noted that the “bulk” LGD-coefficients, renormalized by size effects, can be used to describe the spatially confined FE micro- and nanosystems [21, 25]. Contributions of strains and polarization gradients, as well as the depolarization and screening effects, were taken into consideration by depolarization factor depending on the values of the relative dielectric permittivity of the NPs (\(\varepsilon_{NP}\)), shell (\(\varepsilon_{IF}\)), and surrounding medium (\(\varepsilon_c\)), \(R\) and \(\Lambda\) [21]

\[
\eta(R, \Lambda) = 3\varepsilon_c/[\varepsilon_b + 2\varepsilon_c + \varepsilon_{IF}(R/\Lambda)].
\]  

The expression for the NP transition temperature \(T_{\text{cr}}\) from the single-domain FE to the paraelectric phase is [21]

\[
T_{\text{cr}}(R, \Lambda) = T^*_C - \eta(R, \Lambda)/(3\alpha T_{\text{cr}} \varepsilon_0 \varepsilon_c)
\]  

where the first term \(T^*_C\) is the Curie temperature (possibly renormalized by the surface stress [24]) and \(\alpha\) is the inverse Curie–Weiss constant. The second term originates from a depolarization field. Polarization obeys the time-dependent LGD equation [21, 25]

\[
\Gamma \partial P/\partial t + \alpha T(T - T_{\text{cr}})P + \beta P^3 + \gamma P^5 = \eta E_{\text{ext}}
\]  

(5)

where \(\Gamma\) is the Khalatnikov’s kinetic coefficient.

For BaTiO\(_3\), the coefficients \(\alpha\), \(\beta\), and \(\gamma\) are temperature-dependent in a similar linear way as \(\alpha = \alpha_T (T - T_0)\), \(\beta = \beta_T (T - T_0)\), and \(\gamma = \gamma_T (T - T_0)\). Coefficient \(\beta\) is negative in the considered case of the first-order FE phase transition. Subsequently, positive gradient coefficients \(g_{44}\) and \(g_{11}\) are regarded either small enough, or already included in the renormalization of \(T^*_C\). This allows us to ignore the last two gradient terms in (5).

The dynamic dielectric susceptibility, defined as \(\chi_{33} = \partial P/\partial E_{\text{ext}}\), obeys the equation [21]

\[
\Gamma \partial \chi_{33}/\partial t = [\alpha T(T - T_{\text{cr}}(R, \Lambda))] + 3\beta P^2 + 5\gamma P^4]\chi_{33} = \eta.
\]  

(6)

The analytical expression for the PE coefficient is [21]

\[
\Pi(R, \Lambda) = \frac{\alpha_T P + \beta_T P^3 + \gamma_T P^5}{\alpha_T T_{\text{cr}}(R, \Lambda)] + 3\beta P^2 + 5\gamma P^4}
\]  

(7)

In the case of an FE with the linear temperature dependence of coefficient \(\alpha\) in LGD-expansion (5), the EC temperature change \(\Delta T_{\text{EC}}\) can be calculated from the expression [21]

\[
\Delta T_{\text{EC}} \approx T/(\eta \rho C_P)(\alpha T/2 \cdot [P^2(E) - P^2(0)]) + \beta_T/4 \cdot [P^4(E) - P^4(0)] + \gamma_T/6 \cdot [P^6(E) - P^6(0)]\).
\]  

(8a)

This equation is valid in the quasi-static case only.

| Symbol and unit | Value\(^a\) |
|----------------|-------------|
| \(\alpha_2\) (C\(^{-2}\) m J/K) | 6.68 \cdot 10\(^3\) |
| \(T_c\) (K) | 381 |
| \(\beta\) (C\(^{-4}\) m\(^3\) J) | \(\beta_T = (T - 393) - 8.09 \cdot 10^4, \beta_T = 18.76 \cdot 10^3\) |
| \(\gamma\) (C\(^{-6}\) m\(^3\) J) | \(\gamma_T = (T - 393) + 16.56 \cdot 10^2, \gamma_T = -33.12 \cdot 10^3\) |

\(^a\) \(p = 6.02 \cdot 10^5\) kg/m\(^3\), \(\varepsilon_f = 4.6 \cdot 10^3\) V/Kg (K) and \(C_P = \rho C_P\) in l/(m\(^3\) K) at room temperature.

b These parameters are valid until \(\gamma > 0\), i.e. for \(T < 445\) K.

Since the nanocomposite contains NPs of different sizes, the required parameters should be averaged with the distribution function \(f(R)\)

\[
\Delta T_{\text{EC}}(\Lambda, E_{\text{ext}}) = \int_{R_{\min}}^{R_{\max}} \Delta T_{\text{EC}}(R, \Lambda, E_{\text{ext}}) f(R) dR.
\]  

(8b)

The EC coefficient \(\Sigma(E_{\text{ext}})\) is defined as the derivative of the \(\Delta T_{\text{EC}}(E_{\text{ext}})\) with respect to \(E_{\text{ext}}\)

\[
\Sigma = d\Delta T_{\text{EC}}/dE_{\text{ext}}.
\]  

(9)

Relative dielectric permittivity is

\[
\varepsilon_{33} = 1 + \chi_{33}/\varepsilon_0
\]  

(10a)

\[
\varepsilon_{NP}(\Lambda, E_{\text{ext}}) = \int_{R_{\min}}^{R_{\max}} \varepsilon_{33}(R, \Lambda, E_{\text{ext}}) f(R) dR.
\]  

(10b)

The heat capacity is [21]

\[
C_P = C_P^0 + \delta C_P
\]  

(11a)

\[
\delta C_P = T(\alpha_T P + \beta_T P^3 + \gamma_T P^5)\Pi(R, \Lambda).
\]  

(11b)

LGD parameters for a bulk BaTiO\(_3\) are given in Table I. The critical radius of the size induced FE-paraelectric phase transition, \(R_{\text{cr}} \approx 8\) nm, was calculated in [41].

## III. RESULTS AND DISCUSSION

### A. Polarization Hysteresis Loops, EC Temperature Changes, and Dielectric Permittivity

The obtained dependences of \(P\), \(\Delta T_{\text{EC}}\), and \(\varepsilon_{NP}\) on \(E_{\text{ext}}\) shown in Fig. 2(b)–(d), (f)–(h), and (j)–(l) have the form of hysteresis loops.

Hysteresis loops \(P(E_{\text{ext}})\), \(\Delta T_{\text{EC}}(E_{\text{ext}})\), and \(\varepsilon_{NP}(E_{\text{ext}})\), shown in Fig. 2(b)–(d), correspond to different values of the most probable \(R_m\) in \(f(R)\), varying in the interval 5 nm \(\leq R_m \leq 17\) nm [see Fig. 2(a)]. Other parameters of \(f(R)\) were fixed at \(R_{\min} = 1\) nm, \(R_{\max} = 40\) nm, and \(\sigma = 5\) nm.

With such a change in parameters of \(f(R)\), with decreasing \(R_m\), the number of particles with a radius \(R < R_m\) decreases, and the number of particles with \(R > R_m\) practically does not change [compare the curves 1–4 in Fig. 2(a)]. It is noted that different \(R_m\) correspond to different \(R_{\text{cr}}\), namely, \(R_m = 6.84, 9.59, 13.11,\) and 17.01 nm for \(R_{\text{cr}} = 5, 9, 13,\) and 17 nm. Therefore, in Fig. 2(a), the inscriptions for the same curves 1–4 indicate both quantities, \(R_m\) and \(R_{\text{cr}}\).

It should be noted that the characteristic features of the hysteresis loops associated with the proximity of the most
Fig. 2. Dependences of the (b), (f), and (j) polarization, (c), (g), and (k) EC temperature change, according to (8a) and (d), (h), and (l) relative dielectric permittivity on external electric field for an ensemble of noninteracting BaTiO₃ NPs, which radii are distributed as shown in plots (a), (e), and (i). The calculations are performed for different parameters of the distribution functions. (a)–(d) $R_m = 5, 9, 13,$ and $17$ nm (curves 1–4), fixed $R_{\text{max}} = 40$ nm, and $\sigma = 5$ nm. (e)–(h) $\sigma = 7, 5, 3,$ and $1$ nm (curves 1–4), fixed $R_m = 5$ nm, and $R_{\text{max}} = 40$ nm. (i)–(l) $R_{\text{max}} = 25, 20, 15,$ and $10$ nm (curves 1–4), fixed $\sigma = 5$ nm, and $R_m = 5$ nm. Other parameters are: $R_{\text{min}} = 1$ nm, $T = 293$ K, $\varepsilon_{\text{IF}} = 300,$ $\Lambda = 2$ nm, $\varepsilon_e = 15,$ $\Gamma = 10^2$ $\Omega$/m, and $\omega = 2 \times 10^4$ s⁻¹. BaTiO₃ parameters are listed in Table I.
probable particle radius to $R_{\text{cr}} \approx 8$ nm, are best observed for $R_m = 9$ nm on loops $\varepsilon_{\text{NP}}(E_{\text{ext}})$ (see red loops 2). When $R_m = 5$ nm, most particles are in the paraelectric phase, and when $R_m = 17$ nm—in the FE phase.

An increase in $R_m$ leads to a decrease in the average slope of the polarization hysteresis loop $P(E_{\text{ext}})$, an increase in the remanent polarization $P_r$, and coercive field $E_c$, and also to a slight decrease in the maximum polarization $P_{\text{max}}$ [see Fig. 2(b)].

In this case, the $\Delta T_{\text{EC}}(E_{\text{ext}})$ loop is deformed in such a way that the negative maxima $\Delta T_{\text{EC}}$ expand near $E_c$ and their absolute value $\Delta T_{\text{EC}}^{\text{max}}$ increases, while the positive value $\Delta T_{\text{EC}}$ on the “shoulders” of the $\Delta T_{\text{EC}}(E_{\text{ext}})$ loop decreases [see Fig. 2(c)].

With an increase in $R_m$, the height of the $\varepsilon_{\text{NP}}(E_{\text{ext}})$ loop maxima near $E_c$ monotonously increases [see Fig. 2(d)], and the expansion of the maxima is similar to the expansion of the maxima $\Delta T_{\text{EC}}$, and corresponds to a decrease in the slope of the $P(E_{\text{ext}})$ loop in Fig. 2(b).

The hysteresis loops $P(E_{\text{ext}})$, $\Delta T_{\text{EC}}(E_{\text{ext}})$, and $\varepsilon_{\text{NP}}(E_{\text{ext}})$, shown in Fig. 2(f)–(h), correspond to different $\sigma$ values, varying in the interval $1 \text{ nm} \leq \sigma \leq 7 \text{ nm}$ [see Fig. 2(e)]. Other parameters of $f(R)$ were fixed at: $R_{\text{min}} = 1$ nm, $R_m = 5$ nm, and $R_{\text{max}} = 40$ nm. Note that different $\sigma$ correspond to different $R_m$ values, namely $R_m = 8.31, 6.84, 5.54$, and $5.00$ nm for $\sigma = 7, 5, 3, \text{ and 1 nm}$. Therefore, in Fig. 2(e), the inscriptions for the same curves 1–4 indicate both values, $R_m$ and $\sigma$.

With a decreasing $\sigma$, $f(R)$ becomes much better localized near the maximum at $R = R_m$. Since $R_m$ is smaller than $R_{\text{cr}}$, there are features for loops 4 associated with most of the particles in the composite being in the paraelectric phase. This is why a decrease in $\sigma$ leads to a decrease in the $P_r$, and $E_c$ with a slight change in $P_{\text{max}}$ and an increase in the average slope of the narrow $P(E_{\text{ext}})$ loop, characteristic of small $R_m < R_{\text{cr}}$ [see Fig. 2(f)]. In this case, the $\Delta T_{\text{EC}}(E_{\text{ext}})$ loop is deformed in such a way that the negative maxima of $\Delta T_{\text{EC}}$ near $E_c$ become narrow with a decrease in their absolute value $\Delta T_{\text{EC}}^{\text{max}}$ and change sign, and the positive value $\Delta T_{\text{EC}}$ on the “shoulders” of the $\Delta T_{\text{EC}}(E_{\text{ext}})$ loop increases [see Fig. 2(i)].

With a decreasing $\sigma$, the height of the $\varepsilon_{\text{NP}}(E_{\text{ext}})$ loop maxima near $E_c$ changes nonmonotonously [see Fig. 2(h)], and the narrowing of the $\varepsilon_{\text{NP}}(E_{\text{ext}})$ maxima is similar to the narrowing of the $\Delta T_{\text{EC}}(E_{\text{ext}})$ maxima, and corresponds to an increase in the slope of the $P(E_{\text{ext}})$ loop in Fig. 2(c).

### B. Correlation of the Shape and Characteristic Features of EC and PE Hysteresis

The dependence of the PE $\Pi$ and EC $\Sigma$ coefficients on $E_{\text{ext}}$, are shown in Fig. 3 and have the form of hysteresis loops. According to $P(E_{\text{ext}})$ and $\Delta T_{\text{EC}}(E_{\text{ext}})$ presented in Fig. 2, $\Pi$ and $\Sigma$ hysteresis loops are symmetrical with respect to the zero point. The shape of the hysteresis loops and $E_c$ values depend on the parameters of the particle radius distribution function ($R_m$, $\sigma$, and $R_{\text{max}}$) in accordance with (7)–(9).

The loops in Fig. 3(a) and (b) correspond to different $R_m$ in the $f(R)$, varying in the interval $5 \text{ nm} \leq R_m \leq 17 \text{ nm}$, and fixed $R_{\text{min}} = 1$ nm, $R_{\text{max}} = 40$ nm, and $\sigma = 5$ nm [see Fig. 2(a)]. With these changes in the $f(R)$, both the PE and EC coefficients are characterized by the presence of double maxima, which increase with increasing $R_m$, and expand and shift toward the large fields (see curves 2–4). When $R_m = 5$ nm, that is less than $R_{\text{cr}} \approx 8$ nm, the appearance of an additional maximum in both dependences $\Pi(E_{\text{ext}})$ and $\Sigma(E_{\text{ext}})$ is observed (see curves 1). The double maxima at both the dependences $\Pi(E_{\text{ext}})$ and $\Sigma(E_{\text{ext}})$ for $R_m = 5$ nm (curves 1) are related to the peculiarities of the dependences $P(E_{\text{ext}})$ and $\Delta T_{\text{EC}}(E_{\text{ext}})$ at the balance of particles with $R < R_{\text{cr}}$ and $R > R_{\text{cr}}$ at $\sigma = 5$ nm [see curves 1 in Fig. 2(a)–(c)]. As $R_m$ increases, the dependences $\Pi(E_{\text{ext}})$ and $\Sigma(E_{\text{ext}})$ are characterized by the existence of maxima, which, moving toward the larger $E_{\text{ext}}$ (that also correspond to the increase of $E_c$, increase and expand.

Field dependences $\Pi(E_{\text{ext}})$ and $\Sigma(E_{\text{ext}})$ shown in Fig. 3(c) and (d) correspond to different $\sigma$ varies in the interval $1 \text{ nm} \leq \sigma \leq 7 \text{ nm}$, and fixed $R_{\text{min}} = 1$ nm, $R_m = 5$ nm and $R_{\text{max}} = 40$ nm [Fig. 2(e)]. Since $R_m$ is smaller than $R_{\text{cr}}$, some of the $\Pi$ and $\Sigma$ loops are characterized by the presence of two positive and two negative maxima corresponding to positive and negative electric field. Other loops have only two maxima, one for the positive, and one for the negative $E_{\text{ext}}$. The shape of the loop for $\sigma = 1$ nm is significantly different from the shape of the loops for $3 \text{ nm} \leq \sigma \leq 7 \text{ nm}$. A decrease in $\sigma$ (as well as a decrease of $R_m$) corresponds to a decrease in the
height of one maximum, its “splitting” into 2 maxima, and then to an increase in the height of the other maximum (compare curves 1–4 in different plots). It is noted that the shift of the maxima toward higher fields with $R_m$ (or $\sigma$) increase. The maxima splitting is the result of the increasing contribution of the NPs with $R < R_{cr}$.

Hysteresis loops $\Pi(E_{ex})$ and $\Sigma(E_{ex})$ shown in Fig. 3(e) and (f) correspond to different $R_{\text{max}}$, varying in the interval $10 \text{ nm} \leq R_{\text{max}} \leq 25 \text{ nm}$, and fixed $R_{\text{min}} = 1 \text{ nm}$, $R_m = 5 \text{ nm}$, and $\sigma = 5 \text{ nm}$ [Fig. 2(j)]. An increase in $R_{\text{max}}$ leads to the shift and splitting of the $\Pi$ and $\Sigma$ maxima, which is associated with a decrease in the fraction of small NPs with $R < R_{cr}$ for parameters $R_{\text{min}} = 1 \text{ nm}$, $R_m = 5 \text{ nm}$, and $\sigma = 5 \text{ nm}$. For instance, on curves 4, the splitting of the maxima has already begun, and the two maxima (for each E-sign) become clear for curves 1.

C. Nanocomposite Figures of Merit

In [21], the following functions were considered for NPs in the form:

$$
\begin{align*}
F_I &= \Pi/\epsilon_{\text{NP}}, \\
F_f &= \Pi/(\epsilon_0\epsilon_{\text{NP}}), \\
F_{EQ} &= \Pi^2/(\epsilon_0\epsilon_{\text{NP}}), \\
K_{PE} &= \Pi^2/(\epsilon_0\epsilon_{\text{NP}}^2), \\
F_{EU} &= \Pi^2/(\epsilon_0\epsilon_{\text{NP}}^2). 
\end{align*}
\tag{12}
$$

The absolute values of the functions $F_I$, $F_f$ correspond to the PE figures of merit (FoM) in the radiation detector mode [1], [6], [42]–[44], the absolute values of functions $F_{EQ}$, $F_{EU}$ are the PE FoM in the energy conversion mode [6], [45], and the function $K_{PE}$ is the PE coupling constant [1], [44], [45]. For the theoretical study, not only the amplitude, but also the sign of the functions (12) are important.

In functions (12), the PE coefficient $\Pi$ and permittivity of NPs $\epsilon_{\text{NP}}$, as well as their bulk heat capacity $c_{\text{NP}} = \rho C_{\text{NP}} P$, are size-dependent [21]. This is due to the dependence of the transition temperature $T_{cr}$ between the FE and paraelectric phases on the size $R$ of the NPs [see (1), (2), and (4)]. The estimates of FoM for BaTiO$_3$ are given in the note.\footnote{At room temperature $T \sim 2 \times 10^{-4}$ C/m$^2$K; $\epsilon_{\text{NP}} \epsilon_0 \sim 2 \times 10^{-9}$ F/m; $\epsilon_{\text{NP}} \sim 2 \times 10^{9}$ J/m$^3$K; $F_I \sim 2 \times 10^{-4}$ C/m$^2$K/2-10$^{10}$ J/m$^3$K$ \sim 10^{-10}$ m$^3$ = $10^{-10}$ A.m$^2$/V(W/m); $F_f \sim 2 \times 10^{-4}$ C/m$^2$K/2-10$^{-11}$ F/m$ \sim 10^{5}$ V/K.m$ = 10^{6}$ (V/m)/K; $K_{PE} \sim 4 \times 10^{-5}$ C$^2$/m$^2$K$^2$/2-10$^{11}$ V/m$ \cdot 2 \times 10^{6}$ J/m$^3$K$ \sim 10^{-5}$ K$^{-1}$; $F_{EU} \sim 4 \times 10^{-5}$ C$^2$/m$^2$K$^2$/2-10$^{11}$ F/m$ \sim 2 \times 10^{1}$ J/K$^2$-m$^3$ = 2 \cdot 10^{12}$ (J/m$^3$K$^{2}$); $F_{EQ} \sim 4 \times 10^{-5}$ C$^2$/m$^2$K$^2$/2-10$^{11}$ F/m$ \sim 2 \times 10^{12}$ J/m$^2$K$^2$ $\sim 0.5 \times 10^{-12}$ m$^3$/J.}

To show the effect of NP size on FoM, we build dependences (12) on $R_m$, the expression for which is given by (2c). Fig. 4 shows the size dependences of the values (12) calculated for different $R_m$ and $\sigma$.\footnote{At room temperature $T \sim 2 \times 10^{-4}$ C/m$^2$K; $\epsilon_{\text{NP}} \epsilon_0 \sim 2 \times 10^{-9}$ F/m; $\epsilon_{\text{NP}} \sim 2 \times 10^{9}$ J/m$^3$K; $F_I \sim 2 \times 10^{-4}$ C/m$^2$K/2-10$^{10}$ J/m$^3$K$ \sim 10^{-10}$ m$^3$ = $10^{-10}$ A.m$^2$/V(W/m); $F_f \sim 2 \times 10^{-4}$ C/m$^2$K/2-10$^{-11}$ F/m$ \sim 10^{5}$ V/K.m$ = 10^{6}$ (V/m)/K; $K_{PE} \sim 4 \times 10^{-5}$ C$^2$/m$^2$K$^2$/2-10$^{11}$ V/m$ \cdot 2 \times 10^{6}$ J/m$^3$K$ \sim 10^{-5}$ K$^{-1}$; $F_{EU} \sim 4 \times 10^{-5}$ C$^2$/m$^2$K$^2$/2-10$^{11}$ F/m$ \sim 2 \times 10^{1}$ J/K$^2$-m$^3$ = 2 \cdot 10^{12}$ (J/m$^3$K$^{2}$); $F_{EQ} \sim 4 \times 10^{-5}$ C$^2$/m$^2$K$^2$/2-10$^{11}$ F/m$ \sim 2 \times 10^{12}$ J/m$^2$K$^2$ $\sim 0.5 \times 10^{-12}$ m$^3$/J.}
Fig. 4. Dependences of (a) specific heat variation \(\delta C_P \equiv C_P - C_0\), and PE performances (b) \(F_i\), (c) \(F_f\), (d) \(K_{PE}\), (e) \(F_{EQ}\), and (f) \(F_{EU}\) on the average radius \(R_m\) of BaTiO\(_3\) NPs (curves 1–4) in the ensemble, calculated for different \(\sigma = 7, 5, 3,\) and 1 nm, \(E_{ext} = 0.01\) V/nm, and \(R_{max} = 40\) nm. Other parameters are the same as in Fig. 2.

The \(R_m\)-dependences of \(\delta C_P\), \(F_i\), \(F_f\), \(K_{PE}\), \(F_{EQ}\), and \(F_{EU}\) are shown in Fig. 4(a)–(d). This case corresponds to the same values \(R_{min} = 1\) nm and \(R_{max} = 40\) nm, and different values of \(\sigma = 7, 5, 4, 3\) nm—curves 1–4, with a change in the shape of \(f(R)\) specified by the change in the \(R_m\) value. A decrease in \(\sigma\) leads to a narrowing and an increase in the maxima of the \(\delta C_P\), \(F_i\), \(F_f\), \(K_{PE}\), \(F_{EQ}\), and \(F_{EU}\). The shift of these maxima to the smaller \(R_m\) is the largest for \(F_f\), and can be associated with the deformation of \(f(R)\) with a \(\sigma\) change [Fig. 2(e)]. It is worth noting, that with a decrease in \(\sigma\), the position of the \(R_m\) maxima approaches \(R_m = R_{cr} = 8\) nm [21].

We calculated and analyzed the dependences of the FoM on \(R_m\). The characteristics indicate the presence of a phase transition induced by a change in particle size, which is characterized by the presence of a maxima near the critical radius. The value of this radius increases (in the range of 8–12 nm) with an increase in the standard deviation (in the range of 1–7 nm). More details of FoM calculations can be found in [46].

**IV. CONCLUSION**

For noninteracting spherical FE NPs of various sizes embedded in a dielectric matrix, we calculated the hysteresis loops of polarization EC temperature change, PE and EC coefficients, and dielectric permittivity. We then analyzed the change in the shape of the loops for various parameters of the truncated Gaussian size distribution.

1) We have demonstrated that for the same dispersion, the remanent polarization, coercive field, maximums of dielectric permittivity, and minimums of the EC temperature changes strongly depend on the most probable radius, and weakly depend on the maximum radius.

2) For NPs with the most probable radius less than the critical radius \(R_{cr}\) of the size-induced phase transition, the dielectric permittivity maximums change slightly, but the remanent polarization, coercive field and negative maxima of the EC temperature change decrease significantly with a decreasing dispersion of the size distribution function at the constant minimal and maximal radii.

3) In an external electric field much smaller than the coercive field and at a constant minimal and maximal radii, the maxima of the size dependences of the PE FoM in the vicinity of \(R \approx R_{cr}\) increase, narrow, and shift to smaller average radius values with a decrease in the dispersion of the size distribution function.

**REFERENCES**

[1] M. Lines and A. Glass, *Principles and Applications of Ferroelectrics and Related Materials*. London, U.K.: Oxford Univ. Press, 2001.

[2] J. Burfoot and G. Taylor, *Polar Dielectrics and Their Applications*. Berkeley, CA, USA: Univ. of California Press, 1979.

[3] H. Huang and J. Scott, Eds., *Ferroelectric Materials for Energy Applications*. Weinheim, Germany: Wiley, 2018.

[4] J. F. Scott, “Electrocaloric materials,” *Ann. Rev. Mater. Res.*, vol. 41, no. 1, pp. 229–240, Aug. 2011, doi: 10.1146/annurev-matsci-062910-100341.
A. N. Morozovska, Y. M. Fomichov, P. Maksymovych, A. N. Morozovska, M. D. Glinchuk, and E. A. Eliseev, “Phase transitions in barium titanate nanoparticle with core–shell model,” Phys. B, Condens. Matter, vol. 415, pp. 14–17, Apr. 2013, doi: 10.1016/j.physb.2013.01.033.

G. Zhang et al., “Colossal room-temperature electrocaloric effect in ferroelectric polymer nanocomposites using nanostructured barium strontium titanates,” ACS Nano, vol. 9, no. 7, pp. 7164–7174, Jul. 2015, doi: 10.1021/acsnano.5b03517.

I. Zhang, X. Huang, and J. Wang, “Direct and indirect methods based on effective Hamiltonian for electrocaloric effect of BaTiO3 nanoparticle,” J. Phys., Condens. Matter, vol. 31, no. 25, Jun. 2019, Art. no. 255402, doi: 10.1088/1361-648X/ab191b.

M. Dietze and M. Es-Souni, “Dielectric and pyroelectric properties of thick and thin film relaxor-ceramic/PVDF-TrFE composites,” Funct. Compos. Struct., vol. 1, no. 3, Sep. 2019, Art. no. 030505, doi: 10.1088/2631-6331/ab3d7a.

J. Shi et al., “Electrocaloric cooling materials and devices for zero-global-warming-potential, high-efﬁciency refrigeration,” Joule, vol. 3, no. 5, pp. 1200–1225, May 2019, doi: 10.1016/j.joule.2019.03.021.

J. Quyang, Ed., Nanostuctures in Ferroelectric Films for Energy Applications: Domains, Grains, Interfaces and Engineering Methods. Amsterdam, The Netherlands: Elsevier, 2019.

Y. Bai, G.-P. Zheng, K. Ding, L. Qiao, S.-Q. Shi, and D. Guo, “The giant electrocaloric effect and high effective cooling power near room temperature for BaTiO3 thick ﬁlm,” J. Appl. Phys., vol. 110, no. 9, 2011, Art. no. 094103, doi: 10.1063/1.3658251.

I. U. Idehenre, Y. A. Barnakov, S. A. Basun, and D. R. Evans, “Spectroscopic studies of the effects of mechanochemical synthesis on BaTiO3 nanoparticles prepared using high-energy ball-milling,” J. Appl. Phys., vol. 124, no. 16, Oct. 2018, Art. no. 165501, doi: 10.1063/1.5046682.

Y. A. Barnakov, I. U. Idehenre, S. A. Basun, T. A. Tyson, and D. R. Evans, “Uncovering the mystery of ferroelectricity in zero dimensional nanoparticles,” Nanoscale, Adv., vol. 1, no. 2, pp. 664–670, Feb. 2019, doi: 10.1039/C8NA00131F.

F. Varenne, A. Makky, M. Gaucher-Delmas, F. Violleau, and C. Vauthier, “Multimodal dispersion of nanoparticles: A comprehensive evaluation of size distribution with 9 size measurement methods,” Pharmaceutical Res., vol. 33, no. 5, pp. 1220–1234, May 2016, doi: 10.1007/s11095-016-1867-7.

J. D. Robertson et al., “Puriﬁcation of nanoparticles by size and shape,” Sci. Rep., vol. 6, no. 1, Jun. 2016, Art. no. 27494, doi: 10.1038/srep27494.

D. V. Karpinsky et al., “Ferromagnetic-like behavior of Bi3La4Fe3O2–KBr nanocomposites,” Sci. Rep., vol. 9, no. 1, Dec. 2019, Art. no. 105417, doi: 10.1038/s41598-019-46834-0.

R. Hercig, C.-M. Chang, B. K. Mani, and I. Ponomareva, “Electrocaloric effect in ferroelectric nanowires from atomic simulations,” Sci., Rep., vol. 5, no. 1, Dec. 2015, Art. no. 17929, doi: 10.1038/srep17929.

A. N. Morozovska et al., “Analytical description of the size effect on pyroelectric and electrocaloric properties of ferroelectric nanoparticles,” Phys. Rev. Mater., vol. 3, no. 10, Oct 2019, Art. no. 104414, doi: 10.1103/PhysRevMaterials.3.104414.

H.-H. Wei, J. Zhu, and T.-Y. Zhang, “Size-dependent ultrahigh electrocaloric effect near pseudo-first-order phase transition temperature in barium titanate nanoparticles,” RSC Adv., vol. 5, no. 47, pp. 37476–37484, 2015, doi: 10.1039/C5RA05008A.

H. Huang et al., “Size effects of electrocaloric cooling in ferroelectric nanowires,” J. Amer. Ceram. Soc., vol. 101, no. 4, pp. 1566–1575, Apr. 2018, doi: 10.1111/jace.15304.

A. N. Morozovska, M. D. Glinchuk, and E. A. Eliseev, “Phase transitions induced by confinement of ferroic nanoparticles,” Phys. Rev. B, Condens. Matter, vol. 76, no. 1, Jul. 2007, Art. no. 014102, doi: 10.1103/PhysRevB.76.014102.

A. N. Morozovska, Y. M. Fomichev, P. Maksymovych, Y. M. Vysochanski, and E. A. Eliseev, “Analytical description of domain structure and phase diagrams of ferroelectric nanoparticles,” Acta Mater., vol. 160, pp. 109–120, Nov. 2018, doi: 10.1016/j.actamat.2018.08.051.
[44] A. Thakre, A. Kumar, H.-C. Song, D.-Y. Jeong, and J. Ryu, “Pyroelectric energy conversion and its applications—flexible energy harvesters and sensors,” *Sensors*, vol. 19, no. 9, p. 2170, May 2019, doi: 10.3390/s19092170.

[45] C. R. Bowen, J. Taylor, E. Le Boulbar, D. Zabek, and V. Y. Topolov, “A modified figure of merit for pyroelectric energy harvesting,” *Mater. Lett.*, vol. 138, pp. 243–246, Jan. 2015, doi: 10.1016/j.matlet.2014.10.004.

[46] H. V. Shevliakova, A. N. Morozovska, N. V. Morozosky, G. S. Svechnikov, and V. V. Shvartsman, “The influence of the distribution function of ferroelectric nanoparticles sizes on their electrocaloric and pyroelectric properties,” 2020, arXiv:2004.10871. [Online]. Available: http://arxiv.org/abs/2004.10871

Hanna V. Shevliakova received the Bachelor of Science degree in micro- and nano-electronics and the Master of Science degree in micro- and nano-system technology from the Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine, in 2016 and 2018, respectively, where she is currently pursuing the Ph.D. degree.

Her research interests include solid-state electronics and the theory of size effects in ferroelectrics.

Anna N. Morozovska received the Master of Science degree in physics and the Ph.D. degree in optics and laser physics from the Physics Faculty, Taras Shevchenko Kyiv National University, Kyiv, Ukraine, in 1999 and 2004, respectively, and the Doctor of Sciences degree in solid-state physics from the Institute of Semiconductor Physics, National Academy of Sciences of Ukraine (NASU), Kyiv, in 2009.

She is currently a Leading Scientific Researcher with the Department of Physics of Magnetic Phenomena, Institute of Physics, NASU. She has coauthored over 250 scientific articles and three books. Her research is devoted to the theory of size effects in nanoscale ferroics.

Nicholas V. Morozosky received the Doctor of Sciences degree in solid-state physics from the Institute of Problems for Material Sciences, National Academy of Sciences of Ukraine (NASU), Kyiv, Ukraine, in 1996.

He is currently a Leading Scientific Researcher with the Laboratory of Applied Ferroelectricity, Institute of Physics, NASU. He has coauthored over 60 scientific articles and two books. His research is devoted to the electrophysical and polar-active properties of macroscale and nanoscale ferroelectrics and pyroelectrics.

George S. Svechnikov (Senior Member, IEEE) received the Ph.D. degree in physics of semiconductors and dielectrics from the Institute of Semiconductors Physics, National Academy of Sciences of Ukraine (NASU), Kyiv, Ukraine, in 1981.

He is currently an Associate Professor with the Igor Sikorsky Kyiv Polytechnic Institute, Kyiv. He has published more than 150 scientific articles. He is a Fellow of SPIE. His research interests include physics and devices in nanophotonics, ferroelectric materials, and quantum well optoelectronics.

Vladimir V. Shvartsman received the Diploma degree in solid state physics from Moscow Engineering Physical, Moscow, Russia, in 1995, the Ph.D. degree in physical chemistry from the Karpov Institute of Physical Chemistry, Moscow, in 2000, and the Habilitation degree in materials science from the University of Duisburg-Essen, Duisburg, Germany, in 2015.

He is currently a Docent with the Faculty of Engineering, University of Duisburg-Essen. He has coauthored over 160 scientific articles and three book chapters. His research interests include experimental studies of ferroelectric and multiferroic materials, magnetoelectric and electrocaloric effects, and scanning probe microscopy of functional materials.