

## Universal Behavior of Dielectric Responses of Glass Formers: Role of Dipole-Dipole Interactions

M. Paluch,<sup>1,2\*</sup> J. Knapik,<sup>1,2</sup> Z. Wojnarowska,<sup>1,2</sup> A. Grzybowski,<sup>1,2</sup> and K. L. Ngai<sup>3</sup>

<sup>1</sup>*Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland*

<sup>2</sup>*Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1, 41-500 Chorzow, Poland*

<sup>3</sup>*CNR-IPCF, Dipartimento di Fisica, Università di Pisa, Largo B. Pontecorvo 3, I-56127 Pisa, Italy*

(Received 8 September 2015; published 15 January 2016)

From an exhaustive examination of the molecular dynamics in practically all van der Waals molecular glass formers ever probed by dielectric spectroscopy, we found that the width of the  $\alpha$ -loss peak at or near the glass transition temperature  $T_g$  is strongly anticorrelated with the polarity of the molecule. The larger the dielectric relaxation strength  $\Delta\epsilon(T_g)$  of the system, the narrower is the  $\alpha$ -loss peak. This remarkable property is explained by the contribution from the dipole-dipole interaction potential  $V_{dd}(r) = -Dr^{-6}$  to the attractive part of the intermolecular potential, making the resultant potential more harmonic, and the effect increases rapidly with the dipole moment  $\mu$  and  $\Delta\epsilon(T_g)$  in view of the relation,  $D \propto (\mu^4/kT_g) \propto kT_g[\Delta\epsilon(T_g)]^2$ . Since the novel correlation discovered encompasses practically all van der Waals molecular glass formers studied by dielectric spectroscopy, it impacts the large dielectric research community as well as those engaged in solving the glass transition problem.

DOI: 10.1103/PhysRevLett.116.025702

In 1995, P.W. Anderson [1] made the statement that “The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition.” Since then his insightful remark has stimulated a tremendous amount of theoretical as well as experimental research activities. He added that “This could be the next breakthrough in the coming decade.” Notwithstanding, the glass transition problem remains an unsolved problem in the past two decades until the present time. Likely this is due to the diversity in dynamic properties found in glass-forming materials with different chemical and physical structures, which poses tremendous difficulty for any theory to account for and to be consistent with all of them. While the large volume of disparate data frustrates theoretical treatment, it confers the opportunity of finding trends or correlations that may provide insight into the core physics essential for solution of the problem.

In this Letter we present an outstanding correlation from the dynamic properties of the structural  $\alpha$  relaxation of practically all van der Waals molecular glass formers acquired by dielectric relaxation spectroscopy, and it should have impact on the research frontier. In addition to the literature data, isobaric dielectric measurements at ambient pressure of more glass formers were carried out using a Novo-Control GMBH Alpha dielectric spectrometer. The samples were placed between two stainless steel electrodes of the capacitor with a gap of 0.1 mm provided by a quartz ring. The temperature was controlled by the Novo-Control Quattro system, with the use of a nitrogen gas cryostat. The experimental technique probes the dynamics of a molecular glass former (MGF) via the response of the electric dipole of the MGF routinely

over many decades of frequencies in the range  $10^{-2} \leq f \leq 10^7$  Hz. The spectra are analyzed to assess the properties of the  $\alpha$  relaxation near the glass transition temperature  $T_g$ . The complex dielectric susceptibility  $\epsilon^*(f)$  measured is given by the expression,

$$\epsilon^*(f) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \int_0^\infty e^{-i(2\pi f)t} \psi(t) dt, \quad (1)$$

where  $\psi(t)$  is the response as a function of time of the polarization to applied electric field from the permanent dipoles,  $\epsilon_0$  and  $\epsilon_\infty$  are, respectively, the low and high frequency dielectric permittivity, and  $(\epsilon_0 - \epsilon_\infty)$  is the dielectric strength  $\Delta\epsilon$ . The more polar the MGF with larger dipole moment, the larger is  $\Delta\epsilon$ . The frequency dispersion of the  $\alpha$  relaxation is obtained by fitting  $\epsilon^*(f)$  with the Kohlrausch-Williams-Watts function,

$$\psi(t) = \exp[-(t/\tau_\alpha)^{\beta_{\text{KWW}}}], \quad (2)$$

for  $\psi(t)$  in Eq. (1). The fit yields values of  $\tau_\alpha$  and the fractional exponent  $\beta_{\text{KWW}}$  for each MGF. The narrower the width of the  $\alpha$ -loss peak, the larger is the value of  $\beta_{\text{KWW}}$ .

Dielectric relaxation has been the main research tool of our group and collaborators elsewhere [2–5]. From analyses of a substantial number of MGF studied by us alone over the past twenty years or so, we have observed the remarkable trend that very polar MGFs with sizeable dipole moments invariably have narrow dielectric  $\alpha$ -loss peaks, or values of  $\beta_{\text{KWW}}$  not much less than unity at temperatures near and above  $T_g$ . Excluded from the considerations are the hydrogen-bonded glass formers, for reasons that will become clear later. This observation from us was found

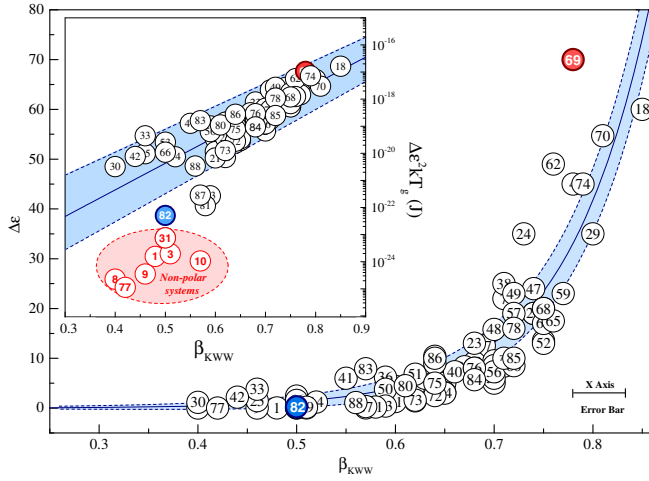


FIG. 1. Dielectric strength  $\Delta\epsilon(T_g)$  as a function of the fractional exponent  $\beta_{\text{KWW}}$  in the Kohlrausch-Williams-Watts function. The inset presents  $kT_g[\Delta\epsilon(T_g)]^2$  against  $\beta_{\text{KWW}}$ . All the values taken together with the numbers explanation and references are collected in Table I. No. 69 is propylene carbonate, No. 82 is toluene.

consistent with those in the literature. Moreover, we are not able to find any counterexample from polar MGFs, or from nonpolar or very weakly polar MGFs with narrow dielectric  $\alpha$ -loss peak. The observation has prompted us to launch a thorough examination of existing dielectric data of the MGFs to check if there is any strong correlation between  $\Delta\epsilon$  and  $\beta_{\text{KWW}}$ . This step taken is natural since these two parameters basically totally determine  $\epsilon^*(f)$  in Eqs. (1) and (2) at  $T_g$ , where  $\tau_\alpha$  is a constant  $\sim 100$  s.

The data of  $\Delta\epsilon$  and  $\beta_{\text{KWW}}$  taken from our amassed dielectric studies of MGFs and the literature that we can find, 88 from Refs. [5–46], are plotted against each other in Fig. 1. The presence of a strong correlation between  $\Delta\epsilon$  and  $\beta_{\text{KWW}}$  is evident by inspection of the plot. Data from all MGFs seem to fall near or within the shaded band in the figure, except for propylene carbonate having much larger  $\Delta\epsilon$  for its value of  $\beta_{\text{KWW}}$ . The correlation reveals that the non-exponentiality [i.e., larger  $(1-\beta_{\text{KWW}})$  or degree of departure of  $\psi(t)$  from Debye] of the  $\alpha$  relaxation is reduced increasingly in MGFs with larger dipole moments. As hallmarks of the  $\alpha$  relaxation, nonexponentiality and dynamic heterogeneity are parallel consequences of the many-body cooperative dynamics that are governed by intermolecular forces. Most of the MGFs considered are van der Waals liquids. Their intermolecular forces consist of the short range repulsion and a long range attraction contributed by the London dispersion force originating from the correlated movements of the electrons in interacting molecules [47]. These forces are the negative of the gradient of the corresponding intermolecular potential terms. The attractive potential for the London dispersion force is given by  $V_L(r) = -(3/4)h\nu(\alpha/4\pi\epsilon_v)^2/r^6$ , where  $\epsilon_v$  is the vacuum permittivity,  $h\nu$  is the energy of the

harmonic oscillator,  $\alpha$  is the polarizability of the molecule, and  $r$  is the distance between molecules. The sum of the repulsive potential and the attractive potential from the London dispersion force is formally similar to the standard Lennard-Jones potential  $V_{12,6}(r)$ , which is the special case with the choice of  $q = 12$  and  $p = 6$  of the generalized Lennard-Jones potentials [48],

$$V_{q,p}(r) = \frac{E_0}{(q-p)} \left[ p \left( \frac{r_0}{r} \right)^q - q \left( \frac{r_0}{r} \right)^p \right]. \quad (3)$$

The parameters  $r_0$  and  $E_0$  represent the position and depth of the potential well minimum, respectively.

The attractive London dispersion force is present in polar and nonpolar MGFs, but present in polar MGFs it is an additional attractive force originating from interacting between the permanent dipoles in the molecules. The tendency for their dipoles to align to minimize energy is opposed by randomization of orientations of the dipoles through rotations effected by thermal energy. It was shown [50,51] that when the thermal energy  $kT$  is greater than the dipole-dipole interaction energy, the rotationally averaged energy of interaction between two identical dipoles with moment  $\mu$  and separated by a distance  $r$ , is given by the Boltzmann-weighted average of

$$V_{dd}(r) = -\frac{2}{3kT} (\mu^2/4\pi\epsilon_v)^2 \left( \frac{1}{r^6} \right). \quad (4)$$

The total intermolecular potential in polar MGFs is the sum  $V_{q,p}(r) + V_{dd}(r)$ .

The dipole-dipole energy term  $V_{dd}(r)$  acts in concert with the energy term from the London dispersive force in enhancing the overall attractive part of the intermolecular potential. The enhancement increases with the polarity of the molecules or  $\Delta\epsilon$  of the MGF. Since the intermolecular potential determines the  $\alpha$ -relaxation dynamics [48] and  $\beta_{\text{KWW}}$ , correlation of  $V_{dd}$  with  $\beta_{\text{KWW}}$  can be expected to be as good as  $\Delta\epsilon$  with  $\beta_{\text{KWW}}$  and may be even better because intermolecular potential is fundamental. The magnitude of  $V_{dd}$  in Eq. (4) is proportional to  $\mu^4/kT$ , while  $\Delta\epsilon \propto \mu^2/kT$ . Combining these two, we have the following series of proportionality relations,

$$V_{dd} \propto \mu^4/kT \propto kT(\Delta\epsilon)^2. \quad (5)$$

When applying this relation to different MGFs for comparisons, temperature in Eq. (5) should be taken at  $T_g$  as well as  $(\Delta\epsilon)^2$  to be evaluated at  $T_g$  for each MGF. Thus, the more fundamental correlation of  $V_{dd}$  with  $\beta_{\text{KWW}}$  in effect can be demonstrated by plotting  $kT_g[\Delta\epsilon(T_g)]^2$  against  $\beta_{\text{KWW}}$ . Carried out in a semilogarithmic plot in the inset to Fig. 1, the same data of the MGFs show a strong linear correlation suggested by the shaded band. Propylene carbonate no longer exhibits a deviation. Shown also in this plot and outside the shaded band are data from some typical nonpolar MGFs having  $\Delta\epsilon$  close to zero. Obviously,

TABLE I. Parameters of molecular glass formers included in Fig. 1. Glass temperature defined as  $T_g = T(\tau_\alpha = 100 \text{ s})$ , dielectric strength at  $T_g$  ( $\Delta\epsilon$ ),  $\beta_{\text{KWW}}$  parameter, and fragility ( $m_p$ ) are listed. For the materials taken from literature, the reference number is provided. The parameters marked by (\*\*) were measured in the present work. The values of  $\beta_{\text{KWW}}$  with (\*) were calculated using the shape parameters in the Havriliak-Negami function, i.e.,  $\alpha_{\text{HN}} \cdot \beta_{\text{HN}} = \beta_{\text{KWW}}^{1.23}$  [49]. The compound number is equivalent with the data presented in Fig. 1.

No	Compound name:	$\beta_{\text{KWW}}$	$\Delta\epsilon$	$m_p$	$T_g/\text{K}$	Ref.	No.	Compound name:	$\beta_{\text{KWW}}$	$\Delta\epsilon$	$m_p$	$T_g/\text{K}$	Refs.
1	2,3-dimethylpentane	0.48*	0.04	50	88	[5]	45	Ezetimib	0.70	9.5**	93	333	[27]
2	2,3-Epoxypropyl Phenylether	0.70	5		193	[6]	46	Fenofibrate	0.70	8.5	94	251	[28]
3	2,4,6-trimethylheptane	0.51*	0.03	63	123	[5]	47	Glibenclamide	0.74	24*	78	339	[29]
4	2-Methylpentane-2,4-diol	0.78	45		187	[6]	48	Isocyanocyclohexane	0.70	15.8		134	[17]
5	2-phenyl-5-acetomethyl-5-ethyl-1,3-dioxocyclohexane	0.64	8		222	[6]	49	Indapamid	0.72	23	76	374	[30]
6	2-Picoline	0.74	19		133	[7,8]	50	Indomethacin	0.59	3.8	83	314	[31,32]
7	3-bromopentane	0.71	22	53	108	[9–11]	51	Iso-eugenol	0.62	6.8*	73	220	[26]
8	3-methylheptane	0.40*	0.02	47	97	[5]	52	Isooctylcyanobiphenyl	0.75	13	86	221	[33]
9	3-methylpentane	0.46*	0.02	46	79	[5]	53	Itraconazol	0.50	2.4*	134	326	[34]
10	4-methylheptane	0.57*	0.03	46	99	[5]	54	KDE	0.75	20	73	313	[35]
11	DTNB	0.50	0.04	86	345	[12]	55	Ketoprofen	0.70	6*	87	267	[36]
12	$\alpha$ -pentaacetylglucose	0.62	4	88	289	[13]	56	Methyl-m-toluate	0.70	7.3		165	[6]
13	$\alpha$ -phenyl-o-cresol	0.6	3.4		219	[6]	57	Methyl-tetrahydrofuran	0.72	19		91	[6]
14	Azithomycin	0.52	1.2*	117	375	[14]	58	M-fluoroaniline	0.64	9		172	[37]
15	$\beta$ -adenosine	0.60	4.34	90	369	[15]	59	N,N-diethyl-3-methylbenzamide	0.77	23	73	198	[38]
16	Benzophenone	0.75	13.5*	125	212	[16]	60	Nimesulide	0.72	8.5	82	291	**
17	Benzoyl butylether	0.69	12.5		223	[17]	61	N-Methyl-caprolactam	0.75	17		172	[6]
18	Bicalutamide	0.85	60		328	**	62	N-methyl-e-caprolactam	0.76	49		172	[25]
19	Biphenyl-2-isobutylate	0.60	2		210	[6]	63	N-Propylbenzene	0.59	0.4		122	[6]
20	BMPC	0.62**	1.45**	72	241	[18]	64	PCB62	0.65	3		274	[17]
21	$\beta$ -pentaacetylglucose	0.60	1.3	88	288	[13]	65	Phenolphthalein dimethylether (PDE)	0.76**	17.5**	75	294	[39]
22	$\beta$ -thymidine	0.68	9.16	83	327	[15]	66	Posaconazole	0.50	1.55**	150	330	[40]
23	$\beta$ -uridine	0.68	13	89	336	[15]	67	PPG 400	0.64	10.4		73	[6]
24	Butyronitrile	0.73	35	47	100	[19,39]	68	Prilocaina	0.75	20		217	**
25	Carvedilol	0.46	1.5	129	310	[20]	69	Propylene carbonate (PC)	0.78	70	93	157	[41]
26	Celecoxib	0.67	8.3	110	331	[21]	70	Propylene Glycol	0.81	54.7		73	[6]
27	Chlorpropamide	0.74	19	64	286	**	71	Ranolazyna	0.71	10	118	292	**
28	Clarithomycin	0.62	2.7	118	382	[14]	72	Rofecoxib	0.64	2.5	104	324	**
29	Cymetydyna	0.80**	35**	69	316	[22]	73	Roxithromycin	0.62	1.6	121	356	[14]
30	Decahydroisoquinoline	0.40	1.14	156	180	[12,23]	74	ROY	0.79**	45	71	259	[42]
31	HTNB	0.50	0.04	83	343	[12]	75	Salol	0.64**	5**		221	[43]
32	Dibutyl phthalate	0.65	5.6**	60	182	[24]	76	Sildenafil	0.68	8	85	329	[44]
33	Dicyclohexyl-2-methylsuccinate	0.46	3.8		222	[6]	77	Squalane	0.42	0.007	75	167	[12]
34	Diethyl Phthalate	0.71	8.4**		187	[6]	78	Sumatriptan	0.72	16	88	309	**
35	Di-iso-butyl-phthalate	0.64	3		191	[6]	79	TDMSPS	0.51	0.15		125	[17]
36	Dimethyl Phthalate	0.59	6.2		193	**	80	Telimisartan	0.61	4.5	87	400	[45]
37	Diocetyl Phthalate	0.65	5		189	[6]	81	Tetraphenyl tetramethyl trisiloxane	0.58	0.2		211	[6]
38	Diphenyl-vinylene carbonate	0.71	25		253	[25]	82	Toluene	0.50**	0.25**	126	59	[39]
39	Dipropyleneglycol Dibenzoate	0.65	3.1		223	[17]	83	Tributylacetyl citrate	0.57	7.9	85	186	**
40	Dipropylene dimethyl glycol dimethylether	0.66	7.3		137	[6]	84	Tricresyl Phosphate	0.68	5.7		211	[6]
41	EPON828	0.55**	6**	158	257	[35]	85	Quinaldine	0.72	10		180	[46]
42	Ethylbenzene	0.44	2.2		115	[17]	86	Triethylacetyl citrate	0.64	10	84	200	**
43	Etoricoxib	0.63	6	98	328	**	87	Trimethyl pentaphenyl trisiloxane	0.57	0.3		230	[6]
44	Eugenol	0.68	8	90	192	[26]	88	Triphenyl phosphite	0.56	1.1		204	[6]

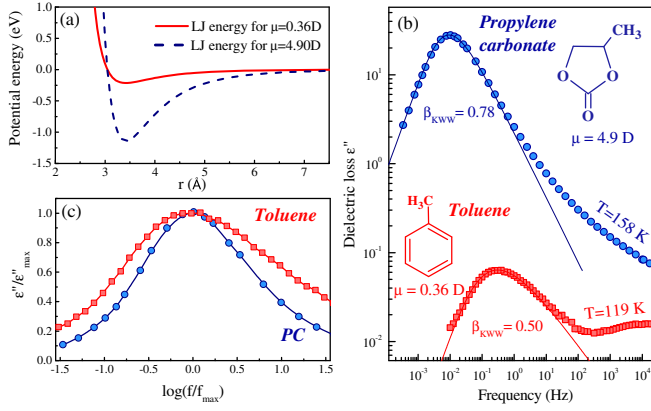


FIG. 2. Panel (a) intermolecular potentials calculated using Eq. (6) with all other parameters the same except for values of  $\mu$  equal to 0.36 and 4.9 D for toluene and propylene carbonate, respectively. Panel (b) presents the dielectric spectra of toluene and propylene carbonate recorded at 119 and 158 K, respectively, parametrized by means of the KWW function. Panel (c): rescaled data of toluene and PC.

the data of these nonpolar MGFs do not conform to the correlation established by the polar MGFs. The nonconformity can be understood from the vanishing of  $V_{dd}$  and  $\Delta\epsilon$  in the nonpolar MGFs. Then, only the potential from the London dispersive force contributes to the attractive part of the intermolecular potential, which, in conjunction with the repulsive part, determines the dynamics of the  $\alpha$  relaxation and the value of  $\beta_{\text{KWW}}$ . Thus, one can expect that the correlation between the width of the  $\alpha$ -loss peak and the polarity or  $\Delta\epsilon$  of the molecule is violated in MGFs where  $V_{dd}$  is negligible compared with  $V_L(r)$ .

Among the nonpolar MGFs in the inset to Fig. 1 is toluene having a small value of  $\mu = 0.36$  D. Its broad ( $\beta_{\text{KWW}} = 0.50$ ) but weak  $\alpha$ -loss peak is contrasted in Figs. 2(b) and 2(c) with the narrow ( $\beta_{\text{KWW}} = 0.78$ ) but intense  $\alpha$ -loss peak of propylene carbonate with large  $\mu = 4.9$  D. The  $\alpha$ -loss peak of toluene is 3 orders of magnitude lower but its full-width at half-maximum is 1.46 times wider than propylene carbonate (full-width at half-maximum is equal to 1.55 and 2.27 for PC and toluene, respectively). The qualitative discussion given above has indicated that the difference in the width of the  $\alpha$ -loss peak is due to the large disparity in the size of  $\mu$  and the dipole-dipole interaction energy term  $V_{dd}$ , which is proportional to  $\mu^4$ . In general, the total intermolecular potential is the sum of the repulsive term  $a/r^{12}$ , the London term  $V_L(r)$ , and  $V_{dd}$ , given by

$$V(r) = \frac{a}{r^{12}} - \frac{1}{r^6} \left[ \frac{2}{3kT} \frac{\mu^4}{(4\pi\epsilon_\nu)^2} + \frac{3}{4} (h\nu) \frac{\alpha^2}{(4\pi\epsilon_\nu)^2} \right]. \quad (6)$$

With all other parameters in Eq. (6) the same except for two different values of  $\mu$  equal to 0.36 and 4.9 D for toluene and propylene carbonate, respectively, the correspondingly

different intermolecular potentials are shown in Fig. 2(a) in the upper left corner. The shapes of the two potentials are drastically different. Supposedly, the potential of propylene carbonate is a deep well and distinctly more harmonic than the standard LJ potential  $V_{12,6}(r)$ , while the hypothetical potential of toluene is a shallow well that is flat and exceedingly anharmonic. Polar MGF with value of  $\mu$  smaller than that of propylene carbonate is expected to have a potential well not as deep and less harmonic, but nevertheless not as anharmonic as that for toluene. In other words, harmonicity of the intermolecular potential in MGF is enhanced by the dipole-dipole interaction potential  $V_{dd}(r)$ , and, therefore, it is an increasing function of  $\mu^4/kT_g$  or  $kT_g[\Delta\epsilon(T_g)]^2$ .

Intuitively, it seems reasonable to expect that increased harmonicity of the intermolecular potential reduces the capacity of intermolecular coupling, which in turn reduces the nonexponentiality parameter  $n_\alpha = (1 - \beta_{\text{KWW}})$  as well as the length scale of cooperativity and heterogeneity of the  $\alpha$  relaxation. This expectation had been confirmed by Bordat *et al.* [48] by performing molecular dynamics simulations of binary Lennard-Jones systems with three different potentials [derived from the formula given here in Eq. (3)] by three different choices of the exponents,  $q$  and  $p$ , of the potential. The choice of  $q = 12$  and  $p = 11$ , made by the authors [48] for the generalized LJ potential, has given rise to the potential which is more harmonic than the classical LJ potential  $V_{12,6}(r)$ , with  $q = 12$  and  $p = 6$ . Whereas the most anharmonic potential corresponds to  $q = 8$  and  $p = 5$ . For the three potentials, the self-intermediate scattering functions  $F_s(Q_0, t)$ , calculated for the wave vector  $Q_0 = 2\pi/r_m$  at the position  $r_m$  determined at the maximum of the collective static structure factor  $S(Q)$ , have been fitted to the KWW function [given here in Eq. (2)]. For the same relaxation time  $\tau_\alpha$ , the results have shown that  $\beta_{\text{KWW}}$  is the largest for the most harmonic potential with ( $q = 12, p = 11$ ), and the smallest for the most anharmonic potential with ( $q = 8, p = 5$ ) [48].

The considerations in the previous two paragraphs on harmonicity of the intermolecular potential have shown the following properties. (i) Harmonicity increases with the value of  $kT_g[\Delta\epsilon(T_g)]^2$ , which follows from the proportionality relations (5) and results in Fig. 2(a). (ii) MGF with more harmonic intermolecular potential has a narrower  $\alpha$ -loss peak or larger value of  $\beta_{\text{KWW}}$ , which follows from Figs. 2(a) and 2(c) as well as from results of simulations [48]. On combining these results, we finally arrive at a rationalization of the correlations between  $kT_g[\Delta\epsilon(T_g)]^2$  and  $\beta_{\text{KWW}}$ , found and exhibited in Fig. 1.

In conclusion, a novel correlation between the frequency dispersion of the  $\alpha$  relaxation and the dielectric strength of molecular van der Waals glass formers has been established. The correlation is supposedly universal because data from practically all studies by dielectric relaxation in the past decades are included into the consideration. This



remarkable property is explained by the contribution from the dipole-dipole interaction potential to the attractive part of the intermolecular potential, making the resultant intermolecular potential more harmonic, and the frequency dispersion of the  $\alpha$  relaxation narrower. The findings presented should have impact on the glass transition research community, and, particularly, the multitude of researchers using dielectric relaxation techniques as a tool.

M. P., Z. W., and A. G. are deeply grateful for the financial support by the National Science Centre within the framework of the Maestro2 project (Grant No. DEC-2012/04/A/ST3/00337).

\*To whom all correspondence should be addressed.  
marian.paluch@us.edu.pl

- [1] P. W. Anderson, *Science* **267**, 1615 (1995).
- [2] F. Kremer and A. Schönhal, *Broadband Dielectric Spectroscopy* (Springer, Berlin, Heidelberg, New York, 2003).
- [3] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, *Contemp. Phys.* **41**, 15 (2000).
- [4] R. Böhmer, G. Diezemann, G. Hinze, and E. Rössler, *Prog. Nucl. Magn. Reson. Spectrosc.* **39**, 191 (2001).
- [5] S. Shahriari, A. Mandanici, L. M. Wang, and R. Richert, *J. Chem. Phys.* **121**, 8960 (2004).
- [6] A. I. Nielsen, T. Christensen, B. Jakobsen, K. Niss, N. B. Olsen, R. Richert, and J. C. Dyre, *J. Chem. Phys.* **130**, 154508 (2009).
- [7] T. Blochowicz and E. A. Rössler, *Phys. Rev. Lett.* **92**, 225701 (2004).
- [8] T. Blochowicz, *Broadband Dielectric Spectroscopy in Neat and Binary Molecular Glass Formers. Frequency and Time Domain Spectroscopy, Non-Resonant Spectral Hole Burning*. (Logos Verlag, Berlin, 2003).
- [9] W. Huang, S. Shahriari, and R. Richert, *J. Chem. Phys.* **123**, 164504 (2005).
- [10] J. G. Berberian and R. H. Cole, *J. Chem. Phys.* **84**, 6921 (1986).
- [11] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
- [12] R. Richert, K. Duvvuri, and L. T. Duong, *J. Chem. Phys.* **118**, 1828 (2003).
- [13] K. Kaminski, K. Adrjanowicz, Z. Wojnarowska, M. Dulski, R. Wrzalik, E. Kaminska, A. Kasprzycka, and M. Paluch, *J. Phys. Chem. B* **115**, 11537 (2011).
- [14] K. Adrjanowicz, D. Zakowiecki, K. Kaminski, L. Hawelek, K. Grzybowska, M. Tarnacka, M. Paluch, and K. Cal, *Mol. Pharmaceutics* **9**, 1748 (2012).
- [15] K. Adrjanowicz, Z. Wojnarowska, K. Grzybowska, L. Hawelek, K. Kaminski, M. Paluch, A. Kasprzycka, and K. Walczak, *Phys. Rev. E* **84**, 051507 (2011).
- [16] P. Lunkenheimer, L. C. Pardo, M. Köhler, and A. Loidl, *Phys. Rev. E* **77**, 031506 (2008).
- [17] K. L. Ngai, *Relaxation and Diffusion in Complex Systems*. (Springer, New York, Dordrecht Heidelberg, London, 2011).
- [18] S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, *J. Chem. Phys.* **117**, 2317 (2002).
- [19] N. Ito, K. Duvvuri, D. V. Matyushov, and R. Richert, *J. Chem. Phys.* **125**, 024504 (2006).
- [20] Z. Wojnarowska, Y. Wang, J. Pionteck, K. Grzybowska, A. P. Sokolov, and M. Paluch, *Phys. Rev. Lett.* **111**, 225703 (2013).
- [21] K. Grzybowska, M. Paluch, A. Grzybowski, Z. Wojnarowska, L. Hawelek, K. Kolodziejczyk, and K. L. Ngai, *J. Phys. Chem. B* **114**, 12792 (2010).
- [22] U. Sailaja and M. Shahin Thayyil, *Transl. Med.* **4**, 1000138 (2014).
- [23] M. Paluch, S. Pawlus, S. Hensel-Bielowka, E. Kaminska, D. Prevosto, S. Capaccioli, P. A. Rolla, and K. L. Ngai, *J. Chem. Phys.* **122**, 234506 (2005).
- [24] M. Sekula, S. Pawlus, S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, *J. Phys. Chem. B* **108**, 4997 (2004).
- [25] S. Capaccioli, M. Shahin Thayyil, and K. L. Ngai, *J. Phys. Chem. B* **112**, 16035 (2008).
- [26] E. Kaminska, K. Kaminski, M. Paluch, and K. L. Ngai, *J. Chem. Phys.* **124**, 164511 (2006).
- [27] J. Knapik, Z. Wojnarowska, K. Grzybowska, L. Hawelek, W. Sawicki, K. Wlodarski, J. Markowski, and M. Paluch, *Mol. Pharmaceutics* **11**, 4280 (2014).
- [28] U. Sailaja, M. Shahin Thayyil, N. S. Krishna Kumar, and G. Govindaraj, *J. Pharm. Biomed. Anal.*, doi: 10.1016/j.jpba.2014.09.003 (2015).
- [29] Z. Wojnarowska, K. Grzybowska, K. Adrjanowicz, K. Kaminski, M. Paluch, L. Hawelek, R. Wrzalik, M. Dulski, W. Sawicki, J. Mazgalski, A. Tukalska, and T. Bieg, *Mol. Pharmaceutics* **7**, 1692 (2010).
- [30] Z. Wojnarowska, K. Grzybowska, L. Hawelek, M. Dulski, R. Wrzalik, I. Gruszka, M. Paluch, K. Pienkowska, W. Sawicki, P. Bujak, K. J. Paluch, L. Tajber, and J. Markowski, *Mol. Pharmaceutics* **10**, 3612 (2013).
- [31] K. Adrjanowicz, A. Grzybowski, K. Grzybowska, J. Pionteck, and M. Paluch, *Cryst. Growth Des.* **13**, 4648 (2013).
- [32] Z. Wojnarowska, K. Adrjanowicz, P. Wlodarczyk, E. Kaminska, K. Kaminski, K. Grzybowska, R. Wrzalik, M. Paluch, and K. L. Ngai, *J. Phys. Chem. B* **113**, 12536 (2009).
- [33] S. Pawlus, M. Mierzwa, M. Paluch, S. J. Rzoska, and C. M. Roland, *J. Phys. Condens. Matter* **22**, 235101 (2010).
- [34] M. Tarnacka, K. Adrjanowicz, E. Kaminska, K. Kaminski, K. Grzybowska, K. Kolodziejczyk, P. Wlodarczyk, L. Hawelek, G. Garbacz, A. Kocot, and M. Paluch, *Phys. Chem. Chem. Phys.* **15**, 20742 (2013).
- [35] M. Paluch, K. L. Ngai, and S. Hensel-Bielowka, *J. Chem. Phys.* **114**, 10872 (2001).
- [36] U. Sailaja, M. Shahin Thayyil, N. S. Krishna Kumar, and G. Govindaraj, *Eur. J. Pharm. Sci.* **49**, 333 (2013).
- [37] S. Hensel-Bielowka, M. Paluch, and K. L. Ngai, *J. Chem. Phys.* **123**, 014502 (2005).
- [38] P. J. Griffin, J. R. Sangoro, Y. Wang, A. P. Holt, V. N. Novikov, A. P. Sokolov, Z. Wojnarowska, M. Paluch, and F. Kremer, *Soft Matter* **9**, 10373 (2013).
- [39] Q. Qin and G. B. McKenna, *J. Non-Cryst. Solids* **352**, 2977 (2006).

- [40] K. Adrjanowicz, K. Kaminski, P. Włodarczyk, K. Grzybowska, M. Tarnacka, D. Zakowiecki, G. Garbacz, M. Paluch, and S. Jurga, *Mol. Pharmaceutics* **10**, 3934 (2013).
- [41] P. Lunkenheimer, in *Habilitation* (Augsburg, 1999).
- [42] Y. Sun, H. Xi, M. D. Ediger, R. Richert, and L. Yu, *J. Chem. Phys.* **131**, 074506 (2009).
- [43] R. Casalini, M. Paluch, and C. M. Roland, *J. Phys. Chem. A* **107**, 2369 (2003).
- [44] K. Kolodziejczyk, M. Paluch, K. Grzybowska, A. Grzybowski, Z. Wojnarowska, L. Hawelek, and J. D. Ziolo, *Mol. Pharmaceutics* **10**, 2270 (2013).
- [45] K. Adrjanowicz, Z. Wojnarowska, P. Włodarczyk, K. Kaminski, M. Paluch, and J. Mazgalski, *European Journal of pharmaceutical sciences* **38**, 395 (2009).
- [46] R. Kahlau, T. Gnutzmann, F. Emmerling, K. Rademann, and E. A. Rössler, *J. Chem. Phys.* **137**, 054505 (2012).
- [47] F. London, *Trans. Faraday Soc.* **33**, 8 (1937).
- [48] P. Bordat, F. Affouard, M. Descamps, and K. L. Ngai, *Phys. Rev. Lett.* **93**, 105502 (2004).
- [49] F. Alvarez, A. Alegria, and J. Colmenero, *Phys. Rev. B* **44**, 7306 (1991).
- [50] M. Rigby, E. B. Smith, W. A. Wakeham, and G. C. Maitland, *The Forces between Molecules*, (Oxford University Press, Oxford, 1986).
- [51] A. J. Stone, *The Theory of Intermolecular Forces* (Oxford University Press, Oxford, 1997).