

A Relationship between Intermolecular Potential, Thermodynamics, and Dynamic Scaling for a Supercooled Ionic Liquid

M. Paluch, S. Haracz, A. Grzybowski,* and M. Mierzwa

Institute of Physics, Silesian University, ulica Uniwersytecka 4, 40-007 Katowice, Poland

J. Pionteck

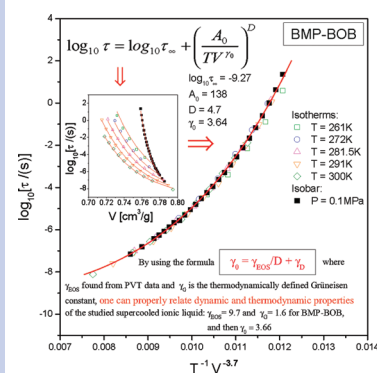
Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

A. Rivera-Calzada and C. Leon

GFMC, Departamento de Física Aplicada III, Campus de Moncloa, Universidad Complutense de Madrid, Spain

ABSTRACT In this letter, we report that an essentially extended scaling version of the Avramov model leads to a consistent relation between dynamic scaling and thermodynamic properties in the thermodynamic scaling regime, which is valid for a considered herein ionic liquid 1-butyl-1-methylpyrrolidinium bis[oxalate]borate (BMP-BOB), although the thermodynamic scaling works imperfectly for the tested ionic liquid. Taking into account that the relation is suggested to be well-grounded by an effective intermolecular potential based on the inverse power law, this finding is meaningful because it shows that benefits originating from the thermodynamic scaling idea and the newly developed Avramov model can concern a wider class of materials than only supercooled van der Waals liquids, and consequently the theoretical approach presented herein can play an important role in the description of molecular dynamics near the glass transition.

SECTION Macromolecules, Soft Matter



A liquid is typically solidified into its disordered, glassy state by sufficiently rapid cooling. An alternative way of transforming a glass-forming liquid into an amorphous state is by applying hydrostatic pressure. In the past decade, both methods were frequently exploited to study the combined temperature–pressure dependence of the structural relaxation times in the vicinity of the glass-transition. This type of study has been carried out mainly for van der Waals liquids and polymers as well as for some H-bonding systems. The obtained experimental data for relaxation times $\tau(T,P)$ are a useful benchmark for the different theories dealing with the glass transition phenomena, as it is for the entropic model proposed by Avramov.¹ The first tests revealed that the key equation of the model is appropriate to describe the dramatic slowing down of the relaxation times of only such glass-forming liquids that have a pressure independent value of the fragility parameter.² In order to include the more frequent case, when fragility depends on compression, Avramov and co-workers³ recently modified the model (eq 1).

$$\log \tau = \log \tau_{\infty} + \left(\left(\frac{T_g}{T} \right)^{F(P)} \left(1 + \frac{P}{\Pi} \right)^{\beta} \right) \log \left(\frac{\tau_g}{\tau_{\infty}} \right) \quad (1)$$

where T_g is the glass transition temperature determined at the relaxation time τ_g and zero pressure, the fitting parameter τ_{∞}

means the relaxation time in the high temperature limit, and β and Π are other fitting parameters. The exponent $F(P) = F_0[1 - C/c_{p0} \ln(1 + P/\Pi)]$ is proportional to the fragility parameter and is developed on the basis of its value F_0 at zero pressure. The development of $F(P)$ involves the isobaric heat capacity c_{p0} at zero pressure and an additional fitting parameter C .

In general, the temperature and pressure/volume dependence of the structural relaxation times can be analyzed by using an equation of state (such as eq 1), or alternatively in terms of a recently proposed concept of thermodynamic scaling. According to the idea of thermodynamic scaling, both isobaric and isothermal data can be scaled onto one master curve if they are plotted against TV^{γ} , where the exponent γ is a characteristic material constant. The importance of this idea relies on relating the exponent γ to many other key parameters characterizing the molecular dynamic behavior of glass-forming materials, such as isochoric fragility, or the ratio of E_v/E_p reflecting the relative contributions of thermal energy and density to the temperature dependence of τ . Moreover, it

Received Date: December 28, 2009

Accepted Date: February 22, 2010

Published on Web Date: March 01, 2010

is very frequently implied that the exponent γ might also be identified with the exponent appearing in the part of the soft Lennard-Jones (LJ) potential, which is responsible for the description of intermolecular repulsive interactions. However, the latter suggestion is still a matter of hot debate among various groups dealing with the concept of thermodynamic scaling.^{4–14}

The thermodynamic scaling was mainly examined in two classes of glasses: van der Waals materials and polymers, but there is no systematic study carried out in the vicinity of glass transition for ionic liquids, which incorporate the Coulombic interactions in the cohesive energy of glass formers.¹⁵ Although the thermodynamic scaling was formulated on the basis of a purely phenomenological consideration, it can be also justified on a theoretical ground. Casalini et al.¹⁶ demonstrated its validity on the basis of the Avramov model considering the effect of volume instead of pressure on the structural relaxation time τ :

$$\log \tau = \log \tau_{\infty} + \left(\frac{A}{TV^{\gamma}} \right)^D \quad (2)$$

where $D = 2c_v/ZR$, and

$$\gamma = \gamma_G = \frac{c_p/c_v - 1}{T\alpha_p} \quad (3)$$

are defined by the isobaric and isochoric heat capacities, c_p and c_v , the isobaric volume expansivity α_p , the gas constant R , and the degeneracy Z of the system, i.e., the number of escape channels for a locally moving particle. The importance of the previous equation lies in the fact that it not only enables us to parametrize the experimentally obtained relaxation times as a function of T and V , but also provides the potential relationship between dynamic and thermodynamic quantities. The validity of eq 2 was examined for a number of small molecular liquids by Casalini et al.^{16–18} Although these authors demonstrated that eq 2 satisfactorily fits the experimental data, they found significant discrepancy between the two values of the exponent γ when calculated by different means, one determined from fitting analysis to eq 2 (γ), and the other one calculated using the thermodynamic quantities according to eq 3 (γ_G).^{16,19} For instance, for the prototypic van der Waals glass-forming liquid *o*-terphenyl (OTP), they found the value of $\gamma_G = 1.2$ by the analysis of thermodynamic properties, whereas $\gamma \approx 4.0$ results from the analysis of dielectric relaxation times. The authors identified the origin of this discrepancy as nonconfigurational contributions to the Grüneisen parameter, attaining a good agreement between γ and γ_G values.^{16,19,20} Otherwise, Dyre's group²¹ suggested that the Grüneisen parameter can be indirectly related to the effective exponent of the intermolecular potential valid for strongly correlated systems by means of the isochoric specific heat and the excess (configurational) isochoric specific heat. This last result has been obtained in the limit of strong correlation between the intermolecular potential energy U and the virial W , where the effective exponent of intermolecular potential has been defined as $\gamma_{U-W} \equiv [(\Delta W)^2/(\Delta U)^2]^{1/2}$ by thermal averages of the fluctuations ΔU and ΔW of the potential energy and virial. Dyre's group showed that such U – W correlation is met if the potential function U can be well approximated by a function dominated by an inverse power

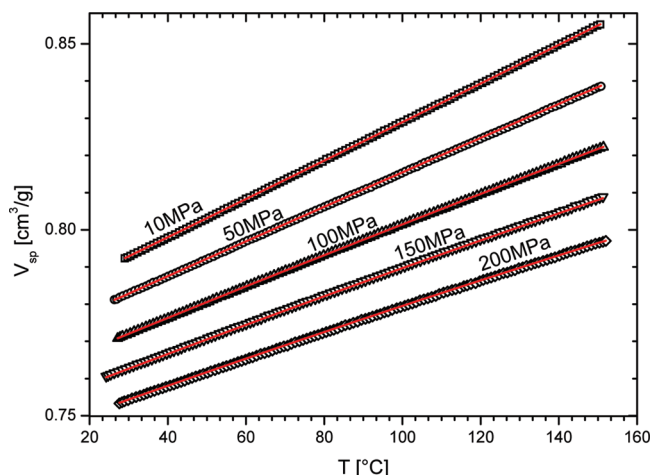


Figure 1. Plot of isobaric PVT data for BMP-BOB. Solid lines are fits to eq 4.

law, $ar^{-3\gamma_{U-W}}$. In real systems, the U – W correlation cannot be 100%, e.g., due to attractive forces. Therefore, they argue that the best scaling properties for real materials are achieved if the difference between the potential U and the inverse power law term is a linear function, i.e., the approximation function, $f(r) = ar^{-3\gamma_{U-W}} + b + cr$. However, the authors^{8,21} emphasize that the added linear term is justified rather with no doubts only in isochoric conditions, because rather the term does not affect the fluctuations ΔU and ΔW . If the system volume varies, the U – W correlation is expected to become weaker, and actually such a scenario has been observed for results of NPT molecular dynamics simulations compared with the corresponding NVT simulations.²¹

The purpose of this article is twofold: first, to check the validity of the thermodynamic scaling in the vicinity of the glass transition for the ionic liquid 1-butyl-1-methylpyrrolidinium bis[oxalate]-borate (BMP-BOB), and second, to further develop the Avramov model in order to remove the inconsistency often found between γ and γ_G values, without any need for excluding the nonconfigurational contributions to the parameter γ_G , such as vibrational and secondary modes, and for considering any configurational thermodynamic quantities at all.

Isobaric (at ambient pressure) and isothermal dependences of dielectric structural relaxation times of BMP-BOB reported previously in ref 22 have again been used in this work.²³ Since we are fundamentally interested in the analysis of the volume dependence of τ , it was essential to perform additional PVT studies. The collected PVT data enabled us to convert the pressure and temperature dependence of τ to the volume one. The detailed description of the apparatus for PVT measurements is presented elsewhere.²⁴ A few examples of the measured $V(T)$ isobars at labeled pressures are depicted in Figure 1. The experimental points have been parametrized by means of the Tait equation:

$$V(T, P) = (V_0 + V_1 T + V_2 T^2) \left[1 - 0.0894 \ln \left(1 + \frac{P}{b_0 \exp(-b_1 T)} \right) \right] \quad (4)$$

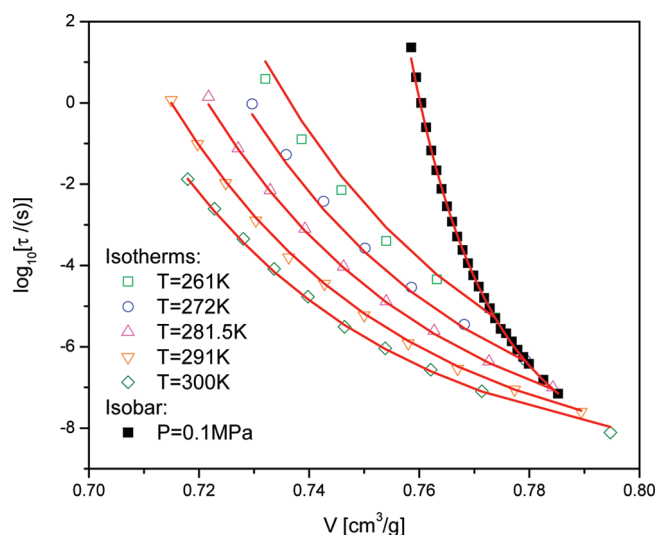


Figure 2. Plot of isothermal and isobaric relaxation data for BMP-BOB taken from ref 22. Solid lines are fits to eq 2, which has the same mathematical form as eq 11.

with the following values of the parameters: $V_0 = 0.779 \text{ cm}^3/\text{g}$, $V_1 = 5.2 \times 10^{-4} \text{ cm}^3 \cdot \text{C}^{-1}/\text{g}$, $V_2 = 7.7 \times 10^{-7} \text{ cm}^3 \cdot \text{C}^{-2}/\text{g}$, $b_0 = 287 \text{ MPa}$, and $b_1 = 4 \times 10^{-5} \text{ C}^{-1}$.

Isobaric and isothermal relaxation data are plotted versus specific volume in Figure 2. Having the structural relaxation times converted to a T - V representation, we can now test the usefulness of the thermodynamic scaling for the description of the molecular dynamics of ionic liquids by plotting $\log \tau$ as a function of TV^γ . The optimal value of exponent $\gamma = 3.7 \pm 0.1$ was determined from a linear regression²⁵ of $\log T_g$ on $\log V_g$, as shown in the inset of Figure 3. The glass transition T_g and V_g are defined herein as the temperature and volume, respectively, in which the relaxation time achieves a value of 1 s to limit extrapolations used to determine these parameters. It is seen from the rescaled experimental data shown in Figure 3 that they do not all collapse into a single master curve. The isothermal data measured at the lowest temperature slightly deviate from the scaling curve, i.e., the isotherm at 261 K is characterized by its mean squared deviation from the master curve, which is equal to 0.54 decades of the relaxation time. In fact, such a scenario for ionic liquids has been recently considered by Dyre's group on the grounds of both computer simulations and theoretical considerations.⁷ Dyre and co-workers suggested that the thermodynamic scaling might be broken down in the case of systems with more than only one type of intermolecular repulsive interactions. Exactly such a situation occurs in the case of ionic liquids since the effective intermolecular potential is a superposition of the soft LJ and Coulombic interactions. The authors²⁶ also suggested that the breaking down in the thermodynamic scaling in the case of more than one type of intermolecular repulsive interactions could be associated with the change of shape of the structural relaxation peak calculated for different T and P values at the same structural relaxation time τ . However, BMP-BOB does not reveal such a change,²⁷ and it could explain the fairly good scaling observed for most of the isothermal–isobaric relaxation data of BMP-BOB.

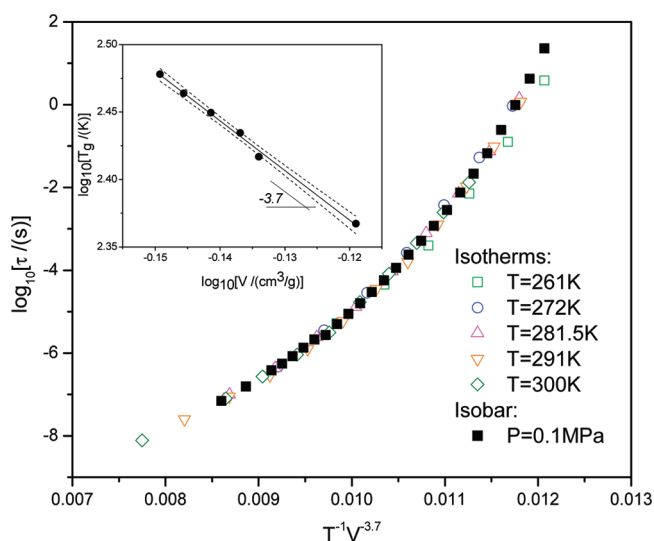


Figure 3. Scaling of isothermal and relaxation data presented herein in Figure 2. The inset shows the scaling exponent determined from the linear regression of the logarithmic dependence of glass transition temperature on volume. The solid line denotes the regression line, and the dashed lines outline its 95% confidence band.

Taking into account that the value of exponent $\gamma = 3.7$ is not so different from the values of γ for a number of typical van der Waals liquids (OTP $\gamma = 4$; PDE $\gamma = 4.5$, PC $\gamma = 3.7$), we can conclude that Coulombic interactions do not dominate close to T_g in BMP-BOB. In this context, it is also of interest to recall values of γ determined from viscosity or dielectric measurements of a few other ionic liquids: $\gamma = 2.25$ (OMIM-BF₄), $\gamma = 2.4$ (OMIM-PF₆), $\gamma = 2.9$ (BMIM-PF₆),⁴ and $\gamma = 2.45$ (Verapamil hydrochloride).²⁸ In all these cases, values of the exponent γ are smaller than 3.

Both the isobaric and isothermal structural relaxation times plotted as a function of volume in Figure 2 have been fitted to eq 2. Except for the isotherm at the lowest measured temperature, all other experimental data are reasonably well represented by the fitting curves. From the numerical fitting procedure characterized by a quite good adjusted coefficient of determination equal to 0.9969, the following set of parameters was obtained: $\log \tau_0 = -9.27$, $A = 138$, $D = 4.7$, and $\gamma = 3.64$. It can be noted that the value of exponent γ is very close to the one previously determined from linear regression. The non-Arrhenius character of the temperature dependence of τ observed in the vicinity of T_g in BMP-BOB reflects the changes both in thermal energy and molecular packing. The role played by both effects can be quantified by calculating the ratio E_V/E_P . This ratio characterizes the relative effects of density and temperature on variation of the structural relaxation time with temperature. In order to determine the ratio E_V/E_P we use the following equation derived in ref 29, which relates the ratio to the exponent γ :

$$\left. \frac{E_V}{E_P} \right|_{T_g} = \frac{1}{1 + T_g \alpha_P \gamma} \quad (5)$$

The value of E_V/E_P calculated from the previous equation is equal to 0.63. The fact that this value for BMP-BOB is larger

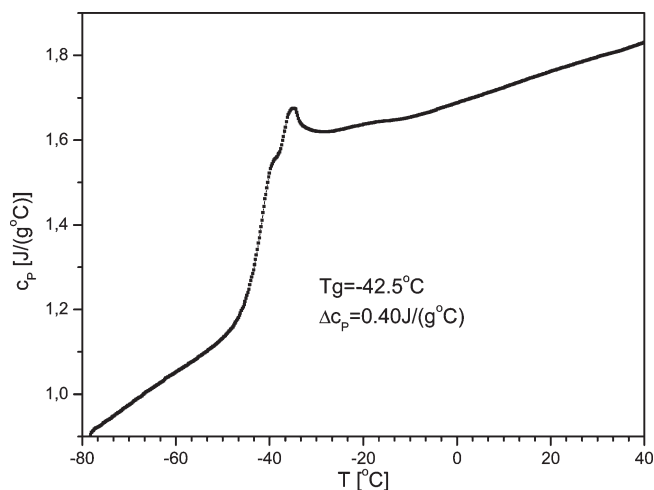


Figure 4. Plot of the temperature dependence of heat capacity for BMP-BOB, showing the glass transition.

than one-half indicates that the temperature exerts a somewhat greater effect on molecular dynamics than density does. A similar result has been obtained for a protic ionic liquid Verapamil hydrochloride,²⁸ where the thermodynamic scaling also does not work properly.

Additionally, we have carried out measurements of the specific heat capacity of BMP-BOB in order to be able to check whether the identity $\gamma = \gamma_G$ in eq 3 is valid or not. The result of this measurement is presented in Figure 4. It is worth noting that the value of $T_g = 233$ K determined at $\tau = 1$ s from dielectric measurements is in very good agreement with $T_g = 230.6$ K from the heat capacity measurements. From the data in Figure 4, we estimate a value of the isobaric heat capacity $c_p = 1.6$ J/g°C in the vicinity of glass transition temperature. Since in eq 3 the heat capacity is defined at constant volume, we also use the well-known thermodynamic relationship to convert c_p to c_v :

$$c_v = c_p - \frac{TV\alpha_p^2}{\kappa_T} \quad (6)$$

where α_p is the isobaric volume expansivity and κ_T is the isothermal compressibility. Having already determined all quantities appearing in eq 3, we calculated the value of exponent $\gamma_G = 1.5$. This value is more than two times smaller than the value of scaling exponent γ in eq 2 determined from relaxation times. Thus, we found similar discrepancy between γ and γ_G as in the case of van der Waals liquids.

Next we show that the above-mentioned inconsistency can be resolved if a more realistic assumption concerning the distribution of energetic barriers in the Avramov model is assumed. In the original Avramov model¹ it is assumed that the distribution of the activation barrier energies E for molecular rearrangements can be approximately described by an exponential dependence,

$$\varphi(E) \sim \exp\left(\frac{E - E_{\max}}{\sigma}\right) \quad (7)$$

with a constant value of E_{\max} , where σ is the width of distribution. The assumption that the maximal activation

barrier E_{\max} is independent of density is not physically justified. In fact, one should rather expect an increase of E_{\max} when the molecular packing is increased by compression or by cooling of a liquid. Consequently, we suggest the following dependence of E_{\max} on density:

$$E_{\max} \sim \left(\frac{\rho}{\rho_0}\right)^{\gamma_{\text{EOS}}} \quad (8)$$

The exponent γ_{EOS} can be determined directly from the analysis of PVT data by using the following equation of state (EOS),¹¹

$$P \cong \frac{RT\rho}{M} + P_0 + B(T) \left[\left(\frac{\rho}{\rho_0}\right)^{\gamma_{\text{EOS}}} - 1 \right] \quad (9)$$

where $B(T)$ is some temperature dependent parameter, M is the molar mass, and (ρ_0, P_0) denote density and pressure in a chosen reference state. The meaning of this EOS in context of the thermodynamic scaling relies on deriving^{30,31} it directly from the generalized LJ potential³² or rather from its approximation mainly dependent on an inverse power law reflecting repulsive interactions dominant between small-distanced molecular species in viscous systems. Such an inverse power law approximation for non van der Waals systems can also include other intermolecular interactions, e.g., Coulomb interactions, and it can work well for each system which obeys the thermodynamic scaling. It is interesting that it is also possible to estimate the value of the exponent γ_{EOS} from the fitting analysis applying another EOS recently derived by Papathanassiou:³⁵

$$\left(\frac{\rho}{\rho_0}\right)^{\gamma_{\text{EOS}}} \cong 1 + \frac{\gamma_{\text{EOS}}}{B_T(0)} P \quad (10)$$

where $B_T(0)$ should be treated as the isothermal bulk modulus at zero pressure.¹⁴ It turns out that both methods provide very similar values of $\gamma_{\text{EOS}} \approx 9.7$.

Taking into account the assumption we have made for E_{\max} (eq 8), one can easily derive a new formula for $\tau(T, P)$:

$$\log \tau = \log \tau_{\infty} + \left(\frac{A_0}{TV\gamma_0}\right)^D \quad (11)$$

This relationship has basically the same mathematical form as eq 2, but there is a fundamental difference in the meaning of exponent γ_0 :

$$\gamma_0 = \frac{\gamma_{\text{EOS}}}{D} + \gamma_G \quad (12)$$

The primary benefit resulting from eq 12 is the explanation of the difference often found between the scaling exponent γ_0 and the Grüneisen parameter γ_G , which is determined by the scaling exponent γ_{EOS} characterizing the repulsive part of the intermolecular potential. To check the validity of this new relationship we calculated from eq 12 a value of $\gamma_G = 1.6$. As we have already herein reported a very similar value of γ_G was determined from eq 3 using thermodynamic quantities, showing the validity of the formalism presented. Thus, a new important relationship has been established correlating

molecular dynamic and thermodynamic properties of supercooled liquids.

In summary, we have found that the thermodynamic scaling works well but not perfect for the studied ionic liquid BMP-BOB. Nevertheless, we have been able to establish a consistent relation (eq 12) between the scaling exponent γ_0 and the thermodynamically defined Grüneisen constant γ_G . It has been achieved by developing the Avramov model, where we implemented the exponent γ_{EOS} that has been previously suggested (mainly on the basis of investigations of van der Waals liquids)¹¹ to be related to the exponent of the repulsive part of the generalized LJ potential or its inverse power law approximation. In this way, we showed that the important relation (eq 12) between the scaling of molecular dynamics and the thermodynamic properties, both based on the same effective intermolecular potential dominated by an inverse power law term, is valid for the herein analyzed ionic liquid BMP-BOB. This meaningful finding leads to the conclusion that the relation given by eq 12, which has been very recently successfully verified for supercooled van der Waals liquids,³⁴ can be appropriate for a wider class of materials, and thus it can have a more general character, i.e., it can work properly at least in such cases where the total effective intermolecular potential (including Coulomb and LJ interactions for ionic liquids) can be approximated by a function of one inverse power law term giving a dominant contribution to the total intermolecular force field. It is worth noting that such an approximated scenario looks justified if the thermodynamic scaling is valid, because one can expect that the inverse power law potential term is still responsible for the thermodynamic scaling, although its exponent straightforwardly corresponds to $3\gamma_{\text{EOS}}$ and is only indirectly related to the scaling exponent γ_0 according to our approach, i.e., otherwise as it is in works of other authors^{4–10,21,26} who rather relate the exponent of the inverse power law approximation to the exponent that enables to scale structural relaxation times or viscosity data. Consequently, the proposed extension of the Avramov model finally represented by eq 11 can play an important role in the theoretical description of molecular dynamics near the glass transition.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed.

ACKNOWLEDGMENT M.P., A.G., and M.M. are deeply thankful for the financial support received from the Polish Ministry of Science and Higher Education in 2010–2013. A.R.-C. acknowledges financial support from the Ramon y Cajal program.

REFERENCES

- Avramov, I. Pressure Dependence of Viscosity of Glassforming Melts. *J. Non-Cryst. Solids* **2000**, *262*, 258–263.
- Paluch, M.; Hensel-Bielowka, S.; Psurek, T. Analysis of “Equation of State” for Supercooled Liquid. *J. Chem. Phys.* **2000**, *113*, 4374–4378.
- Avramov, I.; Grzybowski, A.; Paluch, M. A New Approach to Description of the Pressure Dependence of Viscosity. *J. Non-Cryst. Solids* **2009**, *355*, 733–736.
- Roland, C. M.; Bair, S.; Casalini, R. Thermodynamic Scaling of the Viscosity of van der Waals, H-Bonded, and Ionic Liquids. *J. Chem. Phys.* **2006**, *125*, 124508.
- Alba-Simionesco, C.; Tarjus, G. Temperature versus Density Effects in Glassforming Liquids and Polymers: A Scaling Hypothesis and Its Consequences. *J. Non-Cryst. Solids* **2006**, *352*, 4888–4894.
- Pedersen, U. R.; Bailey, N. P.; Schröder, T. B.; Dyre, J. C. Strong Pressure-Energy Correlations in van der Waals Liquids. *Phys. Rev. Lett.* **2008**, *100*, 015701-1–015701-4.
- Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Schröder, T. B.; Dyre, J. C. Pressure–Energy Correlations in Liquids. I. Results from Computer Simulations. *J. Chem. Phys.* **2008**, *129*, 184507-1–184507-13.
- Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Schröder, T. B.; Dyre, J. C. Pressure–Energy Correlations in Liquids. II. Analysis and Consequences. *J. Chem. Phys.* **2008**, *129*, 184508-1–184508-20.
- Coslovich, D.; Roland, C. M. Thermodynamic Scaling of Diffusion in Supercooled Lennard-Jones Liquids. *J. Phys. Chem. B* **2008**, *112*, 1329–1332.
- Coslovich, D.; Roland, C. M. Pressure–Energy Correlations and Thermodynamic Scaling in Viscous Lennard-Jones Liquids. *J. Chem. Phys.* **2009**, *130*, 014508-1–014508-5.
- Grzybowski, A.; Paluch, M.; Grzybowska, K. Consequences of an Equation of State in the Thermodynamic Scaling Regime. *J. Phys. Chem. B* **2009**, *113*, 7419–7422.
- Berthier, L.; Tarjus, G. Nonperturbative Effect of Attractive Forces in Viscous Liquids. *Phys. Rev. Lett.* **2009**, *103*, 170601-1–170601-4.
- Xu, N.; Haxton, T. K.; Liu, A. J.; Nagel, S. R. Equivalence of Glass Transition and Colloidal Glass Transition in the Hard-Sphere Limit. *Phys. Rev. Lett.* **2009**, *103*, 245701-1–245701-4.
- Grzybowski, A.; Paluch, M.; Grzybowska, K. Comment on “Density Scaling of the Diffusion Coefficient at Various Pressures in Viscous Liquids”. *Phys. Rev. E*, in press.
- Rivera, A.; Brodin, A.; Pugachev, A.; Roessler, E. A. Orientational and Translational Dynamics in Room Temperature Ionic Liquids. *J. Chem. Phys.* **2007**, *126*, 114503-1–114503-7.
- Casalini, R.; Mohanty, U.; Roland, C. M. Thermodynamic Interpretation of the Scaling of the Dynamics of Supercooled Liquids. *J. Chem. Phys.* **2006**, *125*, 014505-1–014505-9.
- Casalini, R.; Roland, C. M. An Equation for the Description of Volume and Temperature Dependences of the Dynamics of Supercooled Liquids and Polymer Melts. *J. Non-Cryst. Solids* **2007**, *353*, 3936–3939.
- Casalini, R.; Capaccioli, S.; Roland, C. M. What Can We Learn by Squeezing a Liquid? *J. Phys. Chem. B* **2006**, *110*, 11491–11495.
- Roland, C. M. In *Current Topics in Elastomers Research*; Bhowmick, A. K., Ed.; CRC Press in Taylor & Francis Group: Boca Raton, FL, 2008; Chapter 24.
- Roland, C. M.; Casalini, R. Entropy Basis for the Thermodynamic Scaling of the Dynamics of o-Terphenyl. *J. Phys.: Condens. Matter* **2007**, *19*, 205118-1–205118-8.
- Schröder, T. B.; Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Dyre, J. C. Pressure-Energy Correlations in Liquids. III. Statistical Mechanics and Thermodynamics of Liquids with Hidden Scale Invariance. *J. Chem. Phys.* **2009**, *131*, 234503-1–234503-17.
- Rivera-Calzada, A.; Kaminski, K.; Leon, C.; Paluch, M. Ion Dynamics under Pressure in an Ionic Liquid. *J. Phys. Chem. B* **2008**, *112*, 3110–3114.
- Since isothermal and atmospheric isobaric data have been measured by means of different apparatuses in different

laboratories, temperatures collected in the both experiments are rescaled to adjust them mutually.

- (24) Roland, C. M.; Hensel-Bielowka, S.; Paluch, M.; Casalini, R. Supercooled Dynamics of Glass-Forming Liquids and Polymers under Hydrostatic Pressure. *Rep. Prog. Phys.* **2005**, *68*, 1405–1478.
- (25) Paluch, M.; Grzybowska, K.; Grzybowski, A. Effect of High Pressure on the Relaxation Dynamics of Glass-Forming Liquids. *J. Phys.: Condens. Matter* **2007**, *19*, 205117-1–205117-12.
- (26) Gnan, N.; Schröder, T. B.; Pedersen, U. R.; Bailey, N. P.; Dyre, J. C. Pressure–Energy Correlations in Liquids. IV. “Iso-morphs” in Liquid Phase Diagrams. *J. Chem. Phys.* **2009**, *131*, 234504-1–234504-18.
- (27) Rivera-Calzada, A.; Kaminski, K.; Leon, C.; Paluch, M. Elucidating the Existence of the Excess Wing in an Ionic Liquid on Applying Pressure. *J. Phys.: Condens. Matter* **2008**, *20*, 244107-1–244107-4.
- (28) Wojnarowska, Z.; Paluch, M.; Grzybowski, A.; Adrjanowicz, K.; Grzybowski, K.; Kaminski, K.; Włodarczyk, P.; Pionteck, J. Study of Molecular Dynamics of Pharmaceutically Important Protic Ionic Liquid–Verapamil Hydrochloride. I. Test of Thermodynamic Saling. *J. Chem. Phys.* **2009**, *131*, 104505-1–104505-14.
- (29) Casalini, R.; Roland, C. M. Thermodynamical Scaling of the Glass Transition Dynamics. *Phys. Rev. E* **2004**, *69*, 062501-1–062501-3.
- (30) Bardik, V. Yu.; Shakun, K. S. Investigations of the Steepness of a Repulsive Potential in Accordance with the Equation of State and Light-Scattering Spectra. *Ukr. J. Phys.* **2005**, *50*, 404–406.
- (31) Bardic, V. Yu.; Malomuzh, N. P.; Sysoev, V. M. Functional Form of the Repulsive Potential in the High Pressure Region. *J. Mol. Liq.* **2005**, *120*, 27–30.
- (32) Hoover, W. G.; Ross, M. Statistical Theories of Melting. *Contemp. Phys.* **1971**, *12*, 339–356.
- (33) Papathanassiou, A. N. Density Scaling of the Diffusion Coefficient at Various Pressures in Viscous Liquids. *Phys. Rev. E* **2009**, *79*, 032501-1–032501-4.
- (34) Grzybowski, A.; Paluch, M.; Grzybowska, K.; Haracz, S. Relationships between Intermolecular Potential, Thermodynamics, and Dynamic Scaling in Viscous Systems. *Phys. Rev. E*, submitted for publication, 2010.