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Communication: The Rosenfeld-Tarazona expression for liquids' specific heat: A numerical investigation of eighteen systems

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We investigate the accuracy of the expression of Rosenfeld and Tarazona (RT) for the excess isochoric heat capacity, $C_V^{\text{ex}} \propto T^{-2/5}$, for 18 model liquids. Previous investigations have reported no unifying features of breakdown for the RT expression. Here, liquids with different stoichiometric composition, molecular topology, chemical interactions, degree of undercooling, and environment are investigated. The RT expression is a better approximation for liquids with strong correlations between equilibrium fluctuations of virial and potential energy, i.e., "Roskilde-simple" liquids [T. S. Ingebrigtsen, T. B. Schröder, and J. C. Dyre, Phys. Rev. X **2**, 011011 (2012)]. This observation holds even for molecular liquids under severe nanoscale confinement which does not follow from the original RT bulk hard-sphere fluid perturbation theory arguments. The density dependence of the specific heat is predicted from the isomorph theory for Roskilde-simple liquids, which in combination with the RT expression provides a complete description of the specific heat's density and temperature dependence. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4827865>]

Fundamental theories for the temperature and pressure (or density) dependence of thermodynamic quantities have gained renewed attention in the last decade. These theories can serve as a valuable input to equations of state,^{1,2} but also as input to scaling strategies which relate key dimensionless transport coefficients to thermodynamic quantities, such as the excess (or "residual") entropy³ (with respect to an ideal gas) or the excess isochoric heat capacity.⁴ Predicting dynamical quantities from first principles is a challenging task. One such theory is mode-coupling theory⁵ which relates the dynamic density correlations of a fluid to its static structure. Alternative theories which relate dynamics to thermodynamics such as that of Adam and Gibbs⁶ and Rosenfeld's excess entropy scaling,³ consider the dynamics also in the highly supercooled liquid regime.^{7,8} Excess entropy scaling strategies, as proposed by Rosenfeld, have proven successful in predicting the dynamics of not only single-component atomic fluids,³ but also binary mixtures,^{7,8} ionic substances,^{9,10} small molecules,^{11,12} and polymers.¹³ In fact, excess entropy scaling strategies have been used as reliable predictors even for the perplexing dynamics of nanoconfined liquids^{4,14} which exhibit stratification and position-dependent relaxation processes.

To fully harness the power of predicting dynamics from thermodynamics, however, it is imperative to develop reliable theories for the temperature and pressure (or density) dependence of thermodynamic quantities. Rosenfeld and Tarazona¹⁵ (RT) argued for a mathematically simple expression for the temperature and density dependence of the potential energy U for fluids. Their arguments are based on thermodynamic perturbation theory, using a functional for hard-

spheres in combination with an expansion of the free energy around the $\eta = 1$ packing fraction. The arguments are not easy to follow, but their expressions have found widespread application.^{1,2,11,15–24}

From the potential energy one gains access to thermodynamic quantities such as the excess isochoric heat capacity $C_V^{\text{ex}} = (\partial U / \partial T)_V$ and the excess entropy S_{ex} via $C_V^{\text{ex}} = T(\partial S_{\text{ex}} / \partial T)_V$. Both of these quantities enter the aforementioned strategies. For a long time only few studies focused on the heat capacity.²⁵ Recently, however, the heat capacity of liquids has begun to receive more attention.²⁶ The RT expressions for the potential energy and excess isochoric heat capacity read

$$U(\rho, T) = \alpha(\rho)T^{3/5} + \beta(\rho), \quad (1)$$

$$C_V^{\text{ex}}(\rho, T) = 3/5\alpha(\rho)T^{-2/5}, \quad (2)$$

where $\alpha(\rho)$ and $\beta(\rho)$ are extensive functions of density ρ that relate to the specific system.¹⁵

Several numerical investigations have tested the applicability of the RT expressions for various model liquids. These liquids span from simple atomic model fluids to liquids showing a wide range of structural, dynamical, and thermodynamical anomalies in their phase diagram. More specifically, the RT expressions have been investigated for single-component atomic fluids,^{15–17} binary mixtures,^{2,18,19} ionic substances,^{1,20} hydrogen-bonding liquids,^{11,21,22} small molecules,²³ and sheared liquids.²⁴ These investigations showed that the RT expressions give a good approximation for a range of systems, but are less accurate when applied to systems known not to have strong virial/potential energy correlations,²⁷ such as the Dzugutov liquid and Gaussian core model, as well as for SiO₂ and BeF₂ in their anomalous

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regions. For SPC/E water different results for the applicability of RT have been reported.^{11,21,22}

The purpose of this paper is to investigate the conditions under which RT applies by simulating 18 different model systems possessing different stoichiometric composition, molecular topology, chemical interactions, degree of undercooling, and environment. We use GPU-optimized *NVT* molecular dynamics computer simulations (<http://rmd.org>; in total over 40 000 GPU hours) to calculate the potential energy and excess isochoric heat capacity along a single isochore for each of these 18 model systems (for the single-component Lennard-Jones (SCLJ) liquid we also vary the density). Here and henceforth quantities are reported in dimensionless units, e.g., by setting $\sigma = 1$, $\epsilon = 1$, etc. The heat capacity is calculated via Einstein's fluctuation formula $C_V^{\text{ex}} = \langle(\Delta U)^2\rangle/k_B T^2$. Table I presents the 18 investigated model systems, which range from simple atomic fluids to molecules under severe nanoscale confinement. The densities represent typical liquid-state densities.

Figure 1 shows the excess isochoric heat capacity at constant density as a function of temperature for selected systems of Table I. The inset shows NIST equation of state data for

TABLE I. The 18 model systems investigated. D_U and $D_{C_V^{\text{ex}}}$ are the coefficient of determination (Eq. (3)) for the potential energy and excess isochoric heat capacity, respectively, for the isochore of density ρ . The virial/potential energy correlation coefficient R is given for the lowest temperature state point T_{\min} . The abbreviations used are: Kob-Andersen binary Lennard-Jones mixture (KABLJ); inverse power-law fluid with exponent n (IPL n); LJ polymer chain of length n (LJC n); Lewis-Wahnström *o*-terphenyl (OTP); single-component Buckingham liquid (SCB); single-component LJ liquid (SCLJ); Wahnström binary LJ mixture (WABLJ). The “Nanoconfined dumbbell” is confined to a (smooth) slit-pore of width $H = 8.13$, corresponding to roughly 16 molecular lengths.

System	ρ	T_{\min}	D_U	$D_{C_V^{\text{ex}}}$	R
Core-soft water ²⁸	0.40	0.138	0.974	0.473	0.10
Dumbbell ²⁹	0.93	0.380	>0.999	0.999	0.96
Nanoconfined dumbbell ⁴	0.93	0.600	>0.999	0.998	0.91
Dzugutov ³⁰	0.80	0.540	0.997	0.786	0.71
Girifalco ³¹	0.40	0.840	0.999	−0.664	0.91
KABLJ ³²	1.20	0.420	>0.999	0.984	0.93
IPL 6	0.85	0.104	>0.999	0.997	1.00
IPL 12	0.85	0.195	>0.999	>0.999	1.00
IPL 18	0.85	0.271	>0.999	0.988	1.00
LJC 10 ³³	1.00	0.450	>0.999	0.998	0.86
LJC 4	1.00	0.510	>0.999	0.991	0.90
Molten salt ³⁴	0.37	0.018	>0.999	0.952	0.15
OTP ³⁵	0.33	0.640	>0.999	0.995	0.91
Repulsive LJ ³⁶	1.00	0.360	>0.999	0.995	1.00
SCB ³⁷	1.00	0.960	>0.999	0.991	0.99
SCLJ	0.85	0.700	>0.999	0.974	0.96
SCLJ	0.82	0.660	>0.999	0.962	0.94
SCLJ	0.77	0.740	>0.999	0.940	0.90
SCLJ	0.70	0.860	>0.999	0.954	0.82
SCLJ	0.66	0.910	>0.999	0.959	0.75
SCLJ	0.61	0.980	>0.999	0.859	0.64
SCLJ	0.59	0.990	>0.999	0.729	0.56
SCLJ	0.55	1.050	>0.999	0.644	0.51
SPC/E water ³⁸	1.00	3.800	0.987	0.558	0.07
WABLJ ³⁹	1.30	0.670	>0.999	0.911	0.98

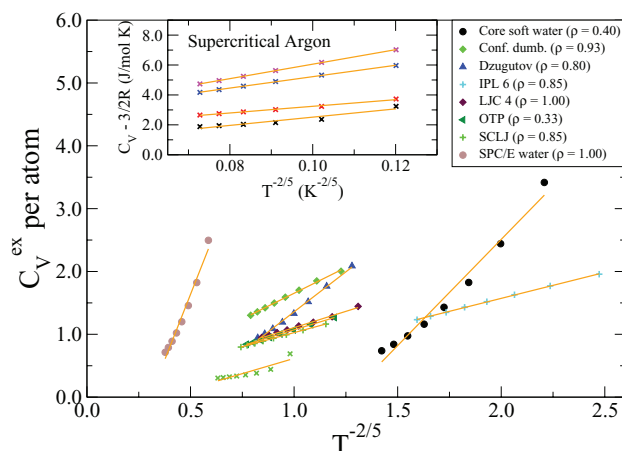


FIG. 1. Isochores studied for selected model systems of Table I. The inset shows NIST equation of state data for supercritical argon at $\rho = 20, 25, 32.6, 35$ mol/L and $200 \text{ K} \leq T \leq 700 \text{ K}$. The orange lines represent linear regression fits of the individual isochores, testing the correct RT power-law exponent dependence. The excess isochoric heat capacity $C_V^{\text{ex}} = \langle(\Delta U)^2\rangle/k_B T^2$ per atom is shown as a function of $T^{-2/5}$. For all liquids C_V^{ex} decreases with increasing temperature.

supercritical argon at $\rho = 20, 25, 32.6, 35$ mol/L and $200 \text{ K} \leq T \leq 700 \text{ K}$. The orange lines represent linear regression fits of the individual isochores, testing the correct RT power-law exponent dependence. In all cases, the excess isochoric heat capacity decreases with increasing temperature.

The data points of the main plot of Fig. 1 (and Table I) were generated by the following procedure.

1. First the system is cooled at constant density until one of the following happens: The system crystallizes or the pressure becomes negative or the relaxation time is of the order 10^5 time units. This happens at the temperature T_{\min} . The system is then equilibrated at $T = T_{\min}$; in the case of crystallization or negative pressure, the temperature is increased slightly (and this new temperature defines T_{\min}).
2. Next, the temperature is increased from T_{\min} up to $T_{\max} = 3T_{\min}$, probing state points along the isochore with a spacing of $\Delta T = 2/7 T_{\min}$. A total of eight equilibrium state points are hereby generated for each isochore.

Turning now to the RT expressions, we show in Figs. 2(a) and 2(b) the coefficient of determination⁴⁰ D for the potential energy and excess isochoric heat capacity as a function of $1 - R$ (see below) for all model systems. For a generic quantity X , the coefficient of determination D_X is defined by

$$D_X = 1 - \frac{\sum_{i=1}^N (X_i - f(X_i))^2}{\sum_{i=1}^N (X_i - \langle X \rangle)^2}, \quad (3)$$

where $f(X_i)$ is a function that provides the model values, and the average $\langle X \rangle$ is taken over a set of data points $\mathbf{X} = \{X_1, \dots, X_N\}$. In our case $f(X_i)$ is given by best fits to the data points in \mathbf{X} using, respectively, $U = A_0 T^{3/5} + A_1$, and $C_V^{\text{ex}} = 3/5 A_2 T^{-2/5}$, where A_0 , A_1 , and A_2 are constants. D_X measures the proportion of variability in a data set that is accounted for by the statistical model;⁴⁰ $D_X = 1$ implies perfect account of the variability.

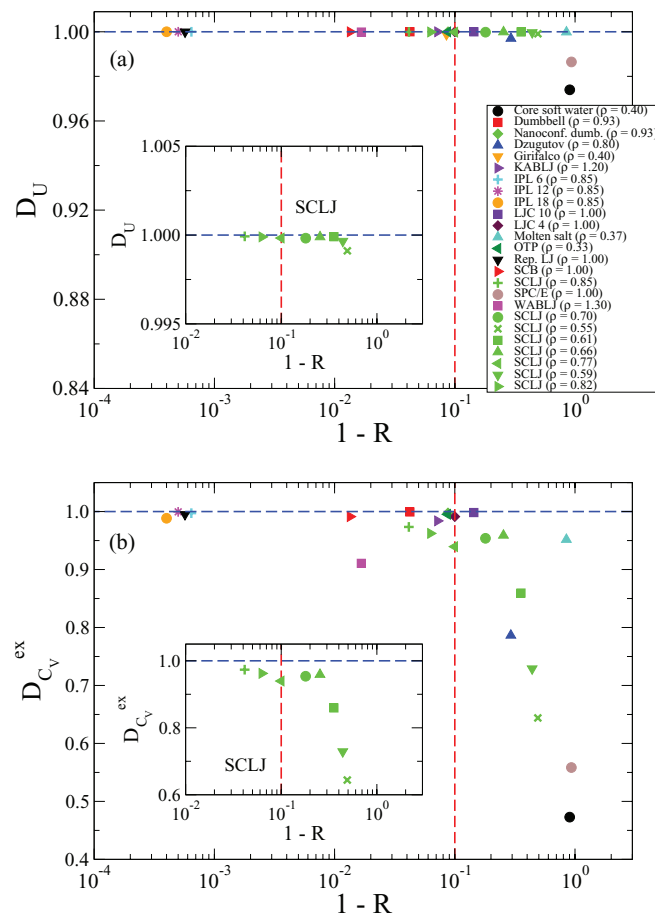


FIG. 2. The coefficient of determination D (Eq. (3)) for U and C_V^{ex} as a function of $1 - R$ for the 18 different model systems. The insets show D for the SCLJ liquid (see Table I). (a) D_U and (b) $D_{C_V^{ex}}$. The Girifalco system gives a negative value for $D_{C_V^{ex}}$ and has for clarity of presentation been left out (see Table I). For both the potential energy and the excess isochoric heat capacity, RT is seen to deteriorate as R decreases below 0.90 (to the right of the red line); in particular, see insets for the SCLJ liquid.

The virial/potential energy correlation coefficient R is defined²⁷ via

$$R = \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle} \sqrt{\langle (\Delta U)^2 \rangle}}, \quad (4)$$

and calculated from the canonical ensemble equilibrium fluctuations at T_{min} . The “Roskilde-simple” liquids⁴¹ are defined by $R \geq 0.90$. Only inverse power-law fluids are perfectly correlating ($R = 1$), but many models²⁷ as well as some experimental liquids⁴² have been shown to belong to the class of Roskilde-simple liquids. We believe this class includes most or all van der Waals and metallic liquids, whereas covalently, hydrogen-bonding or strongly ionic or dipolar liquids are generally not Roskilde simple.²⁷

We observe from Fig. 2(a) that for all liquids D_U gives a value close to 1, but RT provides a better approximation for liquids with R larger than 0.90 (to the left of the red line). A similar behavior is observed for $D_{C_V^{ex}}$ in Fig. 2(b) (note the change of scale). The insets of both figures show for the SCLJ liquid how RT deteriorates as R decreases below 0.90. We conclude that the RT expressions work better for systems that are Roskilde simple at the state points in question. We ob-

serve, however, also from Fig. 1 that for supercritical argon the excess isochoric heat capacity does not seem to go zero at very high temperatures which is in contrast to all simulated Roskilde liquids.

Originally,¹⁵ RT was argued from thermodynamic perturbation theory using a bulk hard-sphere reference system and via simulation shown to describe inverse power-law systems to a high degree of accuracy. Later investigations showed that RT is a good approximation also for LJ liquids. These systems are all Roskilde simple, and a recently argued quasi-universality⁴³ for Roskilde simple single-component atomic systems implies this behavior. We have shown that the key determining factor for RT is not whether systems are atomic or molecular (see the results for the dumbbell model, OTP, and LJC in Fig. 2), but rather the degree of strong correlation between virial and potential energy. This was shown to be the case even for severely nanoconfined molecular systems which exhibit a completely different physics from bulk hard-sphere fluids⁴ and are thus *not* expected to satisfy the original RT arguments. The latter is, in particular, true also for the elongated non-spherical molecules studied here. The observed correlation between RT and Roskilde-simple liquids is thus not trivial.

As a further validation of the above viewpoint, we relate the function $\alpha(\rho)$ in the RT expression to $h(\rho)$ for Roskilde liquids. For such liquids, temperature separates³⁶ into a product of a function of excess entropy per particle and a function of density via $T = f(s_{ex})h(\rho)$. Roskilde liquids are characterized by having isomorphs to a good approximation.⁴⁴ Isomorphs are curves in the thermodynamic phase diagram along which structure and dynamics in reduced units, as well as some thermodynamic quantities are invariant. Along an isomorph both C_V^{ex} and $h(\rho)/T$ are invariant, and consequently one may write

$$C_V^{ex} = F \left(\frac{h(\rho)}{T} \right). \quad (5)$$

Since by the RT expression; $C_V^{ex} = 3/5 \alpha(\rho) T^{-2/5} = 3/5 (\alpha(\rho)^{5/2} / T)^{2/5}$, it follows that $h(\rho) = \alpha(\rho)^{5/2}$ or, equivalently,

$$\alpha(\rho) = h(\rho)^{2/5}. \quad (6)$$

For a LJ system, it was shown in Refs. 36 and 45 that $h(\rho)$ is given by

$$h(\rho) = (\gamma_0/2 - 1)\rho^4 + (2 - \gamma_0/2)\rho^2, \quad (7)$$

in which γ_0 is calculated from the virial/potential energy fluctuations at the state point $\rho = 1$ and $T = 1$ via $\gamma_0 = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$.

Equation (6) is tested in Fig. 3 for the KABLJ and the repulsive LJ system (for which, respectively, $\gamma_0 = 5.35$ and $\gamma_0 = 3.56$). The latter system is defined from $v(r) = (r^{-12} + r^{-6})/2$ and has R above 99.9% in its entire phase diagram; γ varies from 2 at low density to 4 at high density. We determine $\alpha(\rho)$ for different densities by fitting Eq. (1) as a function of temperature for each isochore and system. $h(\rho)$ is calculated analytically from Eq. (7). Figure 3 shows that $\alpha(\rho)$ as predicted by the isomorph theory to a very good approximation is given by $h(\rho)^{2/5}$. Equations (2) and (7) thus provide a

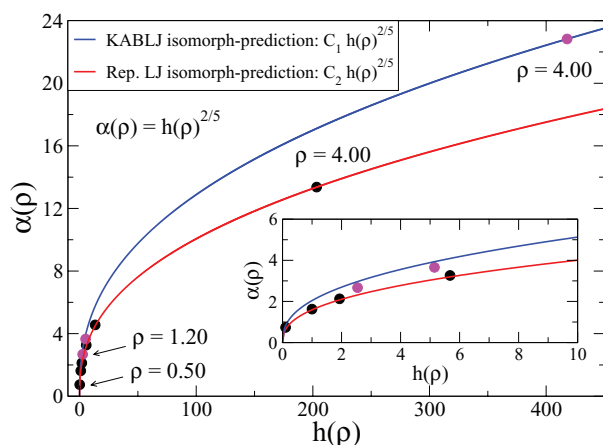


FIG. 3. $\alpha(\rho)$ in the RT expression plotted as a function of $h(\rho)$ of the isomorph theory (Eq. (7)) for the KABLJ and repulsive LJ system (see text). The red and blue curves are proportional to $h(\rho)^{2/5}$ with the proportionality constant determined from the highest density state point ($\rho = 4.00$) for each system.

complete description for the temperature and density dependence of the specific heat, i.e., $C_V^{\text{ex}} = (h(\rho)/T)^{2/5}$.

Scaling strategies which relate dynamics to thermodynamics have in the past proven useful to predict perplexing dynamical phenomena. We identified here the range of applicability for RT as the class of Roskilde liquids. By combining the RT expressions with the isomorph theory, we were able to provide also the full temperature and density dependence of the specific heat. Roskilde liquids include most or all van der Waals and metallic liquids. In contrast, water is a prime example of a non-Roskilde liquid with R close to zero near its density maximum. Water is thus not a good candidate for satisfying RT in large parts of its phase diagram as the simulation results presented here also show.

Beyond RT, Roskilde liquids also exhibit other types of simple behavior, for instance, they obey density scaling^{42,46} and isochronal superposition.⁴⁷ Taking density scaling as an example, this property has been studied for a wide range of experimental liquids. A potential estimate of whether an experimental liquid obeys RT is thus to use whether this liquid obeys also density scaling.

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¹F. J. Spera, D. Nevins, M. Ghiorso, and I. Cutler, *Geochim. Cosmochim. Acta* **73**, 6918 (2009).

²T. B. Schröder, N. Gnan, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, *J. Chem. Phys.* **134**, 164505 (2011).

³Y. Rosenfeld, *Phys. Rev. A* **15**, 2545 (1977).

⁴T. S. Ingebrigtsen, J. R. Errington, T. M. Truskett, and J. C. Dyre, “Predicting how nanoconfinement changes the relaxation time of a supercooled liquid,” *Phys. Rev. Lett.* (unpublished).

⁵W. Götze, *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory*, 1st ed. (Oxford University Press, New York, 2009).

⁶G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).

⁷J. Mittal, J. R. Errington, and T. M. Truskett, *J. Chem. Phys.* **125**, 076102 (2006).

⁸S. Sengupta, S. Karmakar, C. Dasgupta, and S. Sastry, *Phys. Rev. Lett.* **109**, 095705 (2012).

⁹M. Agarwal, M. Singh, B. S. Jabes, and C. Chakravarty, *J. Chem. Phys.* **134**, 014502 (2011).

¹⁰B. S. Jabes and C. Chakravarty, *J. Chem. Phys.* **136**, 144507 (2012).

¹¹R. Chopra, T. M. Truskett, and J. R. Errington, *J. Phys. Chem. B* **114**, 10558 (2010).

¹²E. H. Abramson and H. West-Foyle, *Phys. Rev. E* **77**, 041202 (2008).

¹³G. Galliero, C. Boned, and J. Fernández, *J. Chem. Phys.* **134**, 064505 (2011).

¹⁴J. Mittal, J. R. Errington, and T. M. Truskett, *Phys. Rev. Lett.* **96**, 177804 (2006).

¹⁵Y. Rosenfeld and P. Tarazona, *Mol. Phys.* **95**, 141 (1998).

¹⁶R. D. Leonardo, L. Angelani, G. Parisi, and G. Ruocco, *Phys. Rev. Lett.* **84**, 6054 (2000).

¹⁷H.-O. May and P. Matuschek, *Fluid Phase Equilib.* **313**, 156 (2012).

¹⁸B. Coluzzi, M. Mézard, G. Parisi, and P. Verrocchio, *J. Chem. Phys.* **111**, 9039 (1999).

¹⁹N. Allsopp, G. Ruocco, and A. Fratallocchi, *J. Comput. Phys.* **231**, 3432 (2012).

²⁰I. Saika-Voivod, F. Sciortino, and P. H. Poole, *Phys. Rev. E* **63**, 011202 (2000).

²¹A. Scala, F. W. Starr, E. L. Nave, F. Sciortino, and H. E. Stanley, *Nature (London)* **406**, 166 (2000).

²²M. Agarwal, M. Singh, R. Sharma, M. P. Alam, and C. Chakravarty, *J. Phys. Chem. B* **114**, 6995 (2010).

²³S. Mossa, E. L. Nave, H. E. Stanley, C. Donati, F. Sciortino, and P. Tartaglia, *Phys. Rev. E* **65**, 041205 (2002).

²⁴L. Angelani, G. Ruocco, F. Sciortino, P. Tartaglia, and F. Zamponi, *Phys. Rev. E* **66**, 061505 (2002).

²⁵D. C. Wallace, P. H. Sides, and G. C. Danielson, *J. Appl. Phys.* **31**, 168 (1960).

²⁶D. Bolmatov, V. V. Brazhkin, and K. Trachenko, *Sci. Rep.* **2**, 421 (2012).

²⁷N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schröder, and J. C. Dyre, *J. Chem. Phys.* **129**, 184507 (2008).

²⁸A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, *J. Chem. Phys.* **124**, 084505 (2006).

²⁹T. B. Schröder, U. R. Pedersen, N. P. Bailey, S. Toxvaerd, and J. C. Dyre, *Phys. Rev. E* **80**, 041502 (2009).

³⁰M. Dzugutov, *Phys. Rev. A* **46**, R2984 (1992).

³¹L. A. Girifalco, *J. Phys. Chem.* **96**, 858 (1992).

³²W. Kob and H. C. Andersen, *Phys. Rev. E* **51**, 4626 (1995).

³³K. Kremer and G. S. Grest, *J. Chem. Phys.* **92**, 5057 (1990).

³⁴J. P. Hansen and I. R. McDonald, *Phys. Rev. A* **11**, 2111 (1975).

³⁵L. J. Lewis and G. Wahnström, *J. Non-Cryst. Solids* **172–174**, 69 (1994).

³⁶T. S. Ingebrigtsen, L. Böhling, T. B. Schröder, and J. C. Dyre, *J. Chem. Phys.* **136**, 061102 (2012).

³⁷R. A. Buckingham, *Proc. R. Soc. London, Ser. A* **168**, 264 (1938).

³⁸H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).

³⁹G. Wahnström, *Phys. Rev. A* **44**, 3752 (1991).

⁴⁰R. G. D. Steel and J. H. Torrie, *Principles and Procedures of Statistics* (McGraw-Hill, New York, 1960).

⁴¹T. S. Ingebrigtsen, T. B. Schröder, and J. C. Dyre, *Phys. Rev. X* **2**, 011011 (2012).

⁴²D. Gundermann, U. R. Pedersen, T. Hecksher, N. P. Bailey, B. Jakobsen, T. Christensen, N. B. Olsen, T. B. Schröder, D. Fragiadakis, R. Casalini, C. M. Roland, J. C. Dyre, and K. Niss, *Nat. Phys.* **7**, 816 (2011).

⁴³J. C. Dyre, *Phys. Rev. E* **87**, 022106 (2013).

⁴⁴N. Gnan, T. B. Schröder, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, *J. Chem. Phys.* **131**, 234504 (2009).

⁴⁵L. Böhling, T. S. Ingebrigtsen, A. Grzybowski, M. Paluch, J. C. Dyre, and T. B. Schröder, *New J. Phys.* **14**, 113035 (2012).

⁴⁶D. Coslovich and C. M. Roland, *J. Phys. Chem. B* **112**, 1329 (2008).

⁴⁷C. M. Roland, R. Casalini, and M. Paluch, *Chem. Phys. Lett.* **367**, 259 (2003).