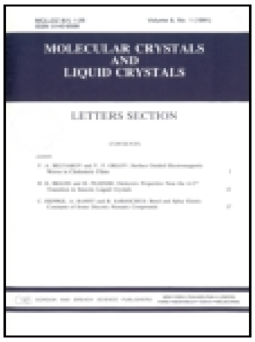

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Thermodynamic Scaling of Miesowicz Viscosity Coefficients via Molecular Dynamics Simulation

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Thermodynamic scaling of Miesowicz viscosity coefficients was investigated via molecular dynamics simulation using the Gay–Berne potential. The Miesowicz viscosity coefficients, which were calculated using an established theoretical expression under different pressures, were rescaled onto a master curve with the scaling parameter γ_η. The parameter was found to be identical to the thermodynamic parameter Γ and scaling parameters reported for other dynamic properties, such as the relaxation time for flip-flop motion, the rotational diffusion constant, and the Leslie rotational viscosity coefficients.

1. Introduction

Recently, investigations of thermodynamic scaling in which a master curve is obtained with one adjustable exponent parameter γ for various dynamic properties, such as viscosity and relaxation time, under different thermodynamic conditions (pressure, volume, and temperature) in glass-forming liquids have attracted attention. [1–6] These dynamic properties may be expressed solely as a function of TV^γ, where T and V are the temperature and volume, respectively. The exponent γ is material-dependent, and remarkably, is typically a unique value for each of materials. Experimentally, in some phases of liquid crystals, the master curves for the scaling of the low-frequency relaxation time and viscosity have also almost the same values for the exponent parameter. [7–13] Although the steepness of the repulsive force for soft core and Lennard–Jones potentials is sensitive to the exponent parameter in glass-forming liquids,[14] its influence on scaling and the associated exponent parameters in systems with orientational order has not yet been clarified. In addition, it has been reported that the thermodynamic parameter Γ is nearly identical to the exponent parameter for thermodynamic scaling in liquid crystals. [11, 13]

We recently studied the relationship between the scaling parameter γ and thermodynamic parameter Γ via molecular dynamics (MD) simulation with a simple anisotropic potential as a model for a highly ordered small cluster using the Lennard–Jones potential with an anisotropic attractive interaction term that was based on a Maier–Saupe type potential.[15] The simple cluster model clearly reproduced the master curve under different

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thermodynamic conditions. Furthermore, it was found that the values of these two parameters were essentially the same. A molecular model based on the Gay–Berne potential also confirmed this equivalent relationship and reproduced the master curve. [16] In addition, other dynamic properties related to the relaxation time, such as the rotational diffusion constant and the Leslie rotational viscosity coefficients, were also scaled using the molecular model. [16]

To gain more insight into the physical implications and origin of thermodynamic scaling, we explored other dynamic properties for which thermodynamic scaling can be applied using MD simulation with the Gay–Berne model. Herein we report that the Miesowicz viscosity coefficients can also be adapted to thermodynamic scaling.

2. Method

Molecular dynamics simulation was performed using a model mesogen with an ellipsoidal shape, namely the GB pair potential model. The system was simulated under isothermal–isobaric conditions (*NPT*) corresponding to the conditions used in many experiments. The details of the simulation have been described previously. [17] We used a cube-shaped simulation box. In the GB pair potential, [18] molecules i and j interact according to

$$U_{ij}^{GB}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j) = 4\varepsilon\left(\hat{\mathbf{r}}_{ij}, \mathbf{u}_i, \mathbf{u}_j\right)\left(d_{ij}^{-12} - d_{ij}^{-6}\right), \tag{1}$$

where

$$d_{ij} = \frac{r_{ij} - \sigma\left(\hat{\mathbf{r}}_{ij}, \mathbf{u}_i, \mathbf{u}_j\right) + \sigma_0}{\sigma_0}. \tag{2}$$

Here σ_0 is the cross-sectional diameter, r_{ij} is the distance between the centers of mass of molecules i and j, and $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is a unit vector along the intermolecular separation vector $\mathbf{r}_{ij}$. The molecular shape parameter, σ, and the energy parameter, ε, depend on the unit vectors $\mathbf{u}_i$ and $\mathbf{u}_j$, and also on $\hat{\mathbf{r}}_{ij}$, as shown in equations 3–6.

$$\sigma\left(\hat{\mathbf{r}}_{ij}, u_i, \mathbf{u}_j\right) = \sigma_0\left[1 - \frac{\chi}{2}\left\{\frac{\left(\mathbf{u}_i\cdot\hat{\mathbf{r}}_{ij} + \mathbf{u}_j\cdot\hat{\mathbf{r}}_{ij}\right)^2}{1+\chi\left(\mathbf{u}_i\cdot\mathbf{u}_j\right)} + \frac{(\mathbf{u}_i\cdot\hat{\mathbf{r}}_{ij} - \mathbf{u}_j\cdot\hat{\mathbf{r}}_{ij})^2}{1-\chi(\mathbf{u}_i\cdot\mathbf{u}_j)}\right\}\right]^{-1/2}, \tag{3}$$

with $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$, and

$$\varepsilon(\hat{\mathbf{r}}_{ij}, \mathbf{u}_i, \mathbf{u}_j) = \varepsilon_0[\varepsilon_1(\mathbf{u}_i, \mathbf{u}_j)]^{\nu}[\varepsilon_2(\hat{\mathbf{r}}_{ij}, \mathbf{u}_i, \mathbf{u}_j)]^{\mu}, \tag{4}$$

where the exponents μ and ν are adjustable,

$$\varepsilon_1(\mathbf{u}_i, \mathbf{u}_j) = [1 - \chi^2(\mathbf{u}_i\cdot\mathbf{u}_j)^2]^{-1/2}, \tag{5}$$

and

$$\varepsilon(\hat{\mathbf{r}}_{ij}, \mathbf{u}_i, \mathbf{u}_j) = 1 - \frac{\chi'}{2}\left\{\frac{(\mathbf{u}_i\cdot\hat{\mathbf{r}}_{ij} + \mathbf{u}_j\cdot\hat{\mathbf{r}}_{ij})^2}{1+\chi'(\mathbf{u}_i\cdot\mathbf{u}_j)} + \frac{(\mathbf{u}_i\cdot\hat{\mathbf{r}}_{ij} - \mathbf{u}_j\cdot\hat{\mathbf{r}}_{ij})^2}{1-\chi'(\mathbf{u}_i\cdot\mathbf{u}_j)}\right\}, \tag{6}$$

with $\chi' = (\kappa'^{1/\mu} - 1)\big/(\kappa\prime^{1/\mu} + 1)$,where $\kappa = \sigma_{ee}/\sigma_{ss}$ is the aspect ratio of the molecule (with σ_{ee} being the molecular length along the major axis and $\sigma_{ss} = \sigma_0$) and $\kappa' = \varepsilon_{ss}/\varepsilon_{ee}$, where ε_{ss} and ε_{ee} are the depths of the minima of the potentials of a pair of molecules aligned in side-by-side and end-to-end configurations, respectively. ε_0 and σ_0 are the units of energy and length, respectively. All quantities were scaled using these units.

The generic GB(4.4,20.0,1,1) was used because basic features of the model have previously been described in detail. [19,20] The reduced time step, $\Delta t^*(\equiv \Delta t(\varepsilon_0/m\sigma_0{}^2)^{1/2}$, where m is the mass of the particle), was taken to be 0.001. In real units, $1.0t^*$ corresponds to 4.0 ps. The reduced moment of inertia, $I_\perp{}^*(\equiv I_\perp/m\sigma_0{}^2)$, of the particles was set at 1.0. The reduced pressure, $P^*(\equiv P\sigma_0{}^3/\varepsilon_0)$, was set at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, 14.0, 15.0, and 20.0 in different simulations. We performed the simulations at a reduced temperature, $T^*(\equiv k_BT/\varepsilon_0)$, of 1.1–10.0. T^* was set at 1.1–3.0 for a P^* of 3.0, at 1.1–3.55 for a P^* of 4.0, at 1.6–3.95 for a P^* of 5.0, at 1.6–4.4 for a P^* of 6.0, at 2.0–5.0 for a P^* of 7.0, at 2.3–5.1 for a P^* of 8.0, at 2.3–5.6 for a P^* of 9.0, at 2.3–6.5 for a P^* of 10.0, at 2.3–6.8 for a P^* of 11.0, at 2.4–7.3 for a P^* of 12.0, at 2.6–7.7 for a P^* of 13.0, at 3.3–7.8 for a P^* of 14.0, at 3.6–8.5 for a P^* of 15.0, and at 5.2–10.0 for a P^* of 20.0. The isotropic and nematic phases were stable at each pressure within these temperature ranges. The cut-off distance, $r_c{}^*(\equiv r_c/\sigma_0)$, for the potential energy calculation was set at 7.2, and a Verlet neighbor list was used to improve the efficiency of the simulation. The second-rank orientational order parameter, $<P_2>$, was determined from the Q tensor, [21]

$$Q^n_{\alpha\beta} = N^{-1}\sum_i \left(3u^i_\alpha u^i_\beta - \delta_{\alpha\beta}\right)/2, \tag{7}$$

where $u^i{}_\alpha$ is a component ($\alpha = x$, y, or z) of the unit vector that describes the orientation of the symmetry axis for molecule i, and N is the number of molecules. The second-rank orientational order parameter, P_2, was defined as the maximum eigenvalue obtained by diagonalizing the Q tensor; the eigenvector then being identified as the director. The time steps from 1.0×10^6 to 5.0×10^6 were typically used to allow equilibration and then 1.0×10^5 or 5.0×10^5 time steps were used to investigate the static and dynamic properties. In particular, the configuration data used 5.0×10^5 steps for calculating the first-rank orientational time correlation function mentioned below. A system of 4000 GB molecules was used.

In general, molecular reorientation can be expressed using the Wigner rotation matrix,[22]

$$\phi^{\mathrm{LL'}}_{\mathrm{mn}}(\mathrm{t}) \equiv < \mathrm{D}^{\mathrm{L}}_{\mathrm{mn}}(\Omega_0)\mathrm{D}^{\mathrm{L'}*}_{\mathrm{mn}}(\Omega_{\mathrm{t}}) >, \tag{8}$$

where Ω is the angle of the molecular orientation with respect to the director. The reorientation of linear molecules is described by a time correlation function defined as [23]

$$c_l(t) = \langle P_l\left(\mathbf{u}_i(t)\cdot\mathbf{u}_i(0)\right)\rangle, \tag{9}$$

where $\mathbf{u}_i$ is a unit vector parallel to the axis of molecule i and $P_l()$ is a Legendre polynomial. The relaxation time is interpreted as an integral correlation function, i.e.,

$$\tau_l = \int_0^\infty c_l(t)\mathrm{d}t. \tag{10}$$

One of the first-rank orientational correlation functions ($L = L' = 1$) for the flip–flop motion of mesogenic molecules with a longitudinal electric dipole is related to the dielectric relaxation experiment [24] and IR spectra. [25] The analogous second-rank time correlation function ($L = L' = 2$) is associated with the half-width of the Lorentzian Raman spectrum [26] and the nuclear spin relaxation rate. [27]

The relevant correlation function for the first-rank is

$$c_{||}^{(1)}(t) = < P_1(\cos\beta_0) P_1(\cos\beta_t) >, \tag{11}$$

where β is the angle between the molecule and the director. The following formula was used to calculate the correlation function, considering fluctuations in the director,

$$\mathrm{c}_{||}^{(1)}(\mathrm{t}) = < (\mathbf{u}_\mathrm{i}(0) \cdot \mathbf{n}(0))(\mathbf{u}_\mathrm{i}(\mathrm{t}) \times \mathbf{n}(\mathrm{t})) >, \tag{12}$$

where $\mathbf{n}(t)$ is the director at time t. Configuration data at each of 500.0 time steps for 1000.0 t^* (1.0×10^6 time steps) were used to obtain the relaxation decay for flip–flop rotation to calculate Leslie and Miesowicz viscosity coefficients. Several data sets with different initial configurations were used to analyze the rotational dynamics. It was possible to obtain a good fit for all of the functions with a single exponential form, i.e.,

$$\mathrm{c}_{||}^{(1)}(t) = \mathrm{c}_{||}^{(1)}(0)\exp(-t^*/\tau_{||}^*), \tag{13}$$

where the initial value of $c_{||}^{(1)}(0)$ at t^* of 0 is $1/2 + 2/3P_2$, and $\tau_{||}^*$ is the relaxation time for flip–flop rotations.

3. Results and Discussion

The adaptability of the Miesowicz viscosity coefficients to thermodynamic scaling was studied after confirming the reliability of the temperature and pressure dependence of the Leslie and Miesowicz coefficients by comparing real liquid crystals.

Temperature Dependence of the Leslie and Miesowicz Viscosity Coefficients

According to the microscopic theory expression of Kuzuu and Doi, [28] six viscosity parameters (Leslie coefficients), α_i, appearing in phenomenological theory are expressed with molecular parameters as

$$\alpha_i \propto \rho k_B T / D_\perp^r, \tag{14}$$

where ρ is the density, k_B is the Boltzmann constant, T is the absolute temperature, and $D_\perp^r$ is the rotational diffusion constant, which is the perpendicular component of the molecular long axis for rod-like molecules (references [16, 28]). The temperature dependence of the coefficients obtained from an MD simulation using the model molecules together with experimental data for 4-methoxybenzylidene-4’-*n*- butylaniline (MBBA) [29] is shown in Fig. 1. The model system was effective for qualitatively reproducing the temperature variation of the coefficients of the real system; quantitative agreement with real nematics is not expected in such a coarse-grained model. The pressure dependence of the Leslie rotational viscosity coefficients determined using the Gay–Berne model GB(4.4,20,1,1) is shown in Fig. 2. A similar trend was observed for all the coefficients. However, to our knowledge, there is no available experimental data for the pressure dependence of the Leslie viscosity coefficients, while the influence of pressure variation on the rotational viscosity coefficient γ_1 has been reported. [30] The slopes of the nearly straight lines and changes in the slightly curved lines for all the coefficients decreased as the pressure decreased. Because the α_3 values for the system were negative as is known for real nematics with long

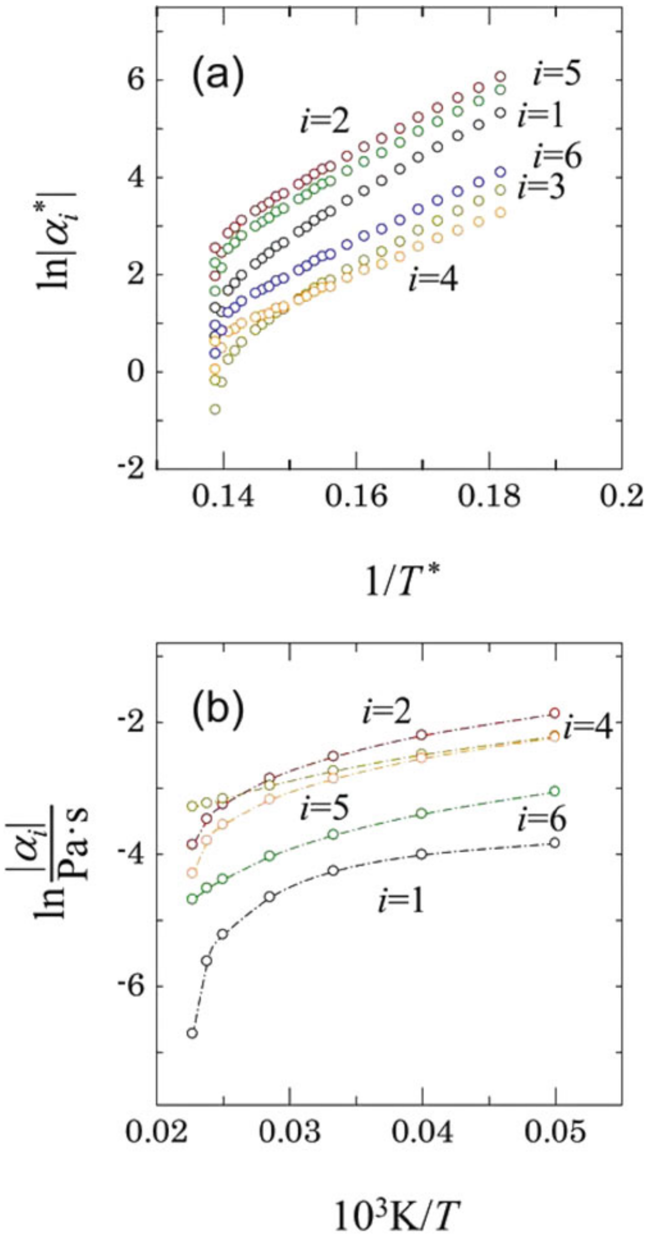

Figure 1. Leslie viscosity coefficients α_i (i = 1–6) as a function of temperature obtained using the Gay–Berne model GB(4.4,20,1,1) at a reduced pressure P^* of 15.0 and experimentally determined for MBBA. [29]

chains, the flow alignment angle θ_0 could not be defined. The temperature variation of three Miesowicz viscosity coefficients η_i ($i = 1$–3) for the system are presented along with typical experimental data for a eutectic mixture of 4'-n-pentylphenyl 4-methoxybenzoate and 4'-n-pentylphenyl 4-n-hexyloxybenzoate (EM) [31] in Fig. 3. Here, the Helfrich notation was

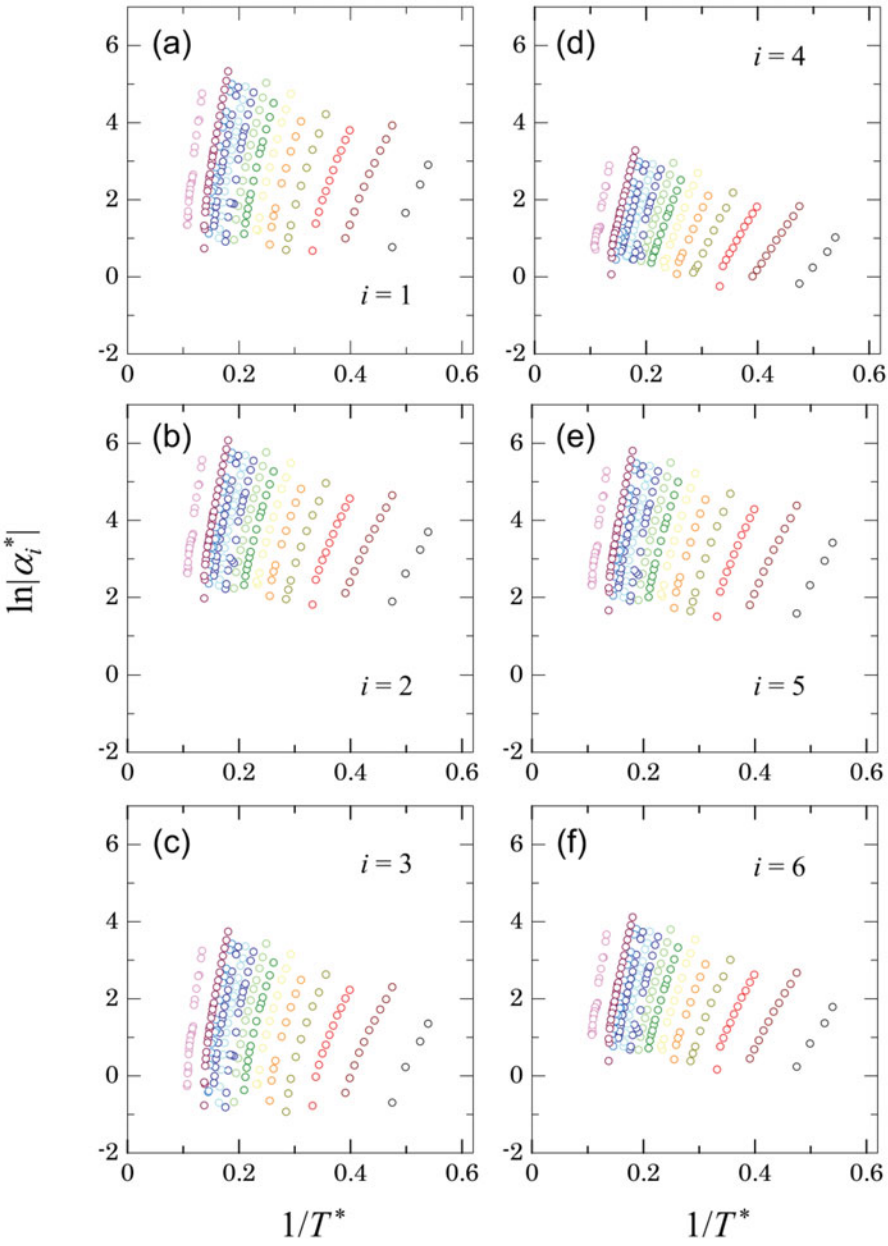

Figure 2. Leslie viscosity coefficients α_i ($i = 1$–6) as a function of temperature obtained using the Gay–Berne model GB(4.4,20,1,1) at reduced pressures P^*ranging from 3.0–20.0. From right to left; $P^* = 3.0$, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, 14.0, 15.0, and 20.0.

used as follows [32, 33]:

$$\eta_1 = 1/2(-\alpha_2+\alpha_4+\alpha_5), \tag{15}$$

$$\eta_2 = 1/2(\alpha_3+\alpha_4+\alpha_6), \tag{16}$$

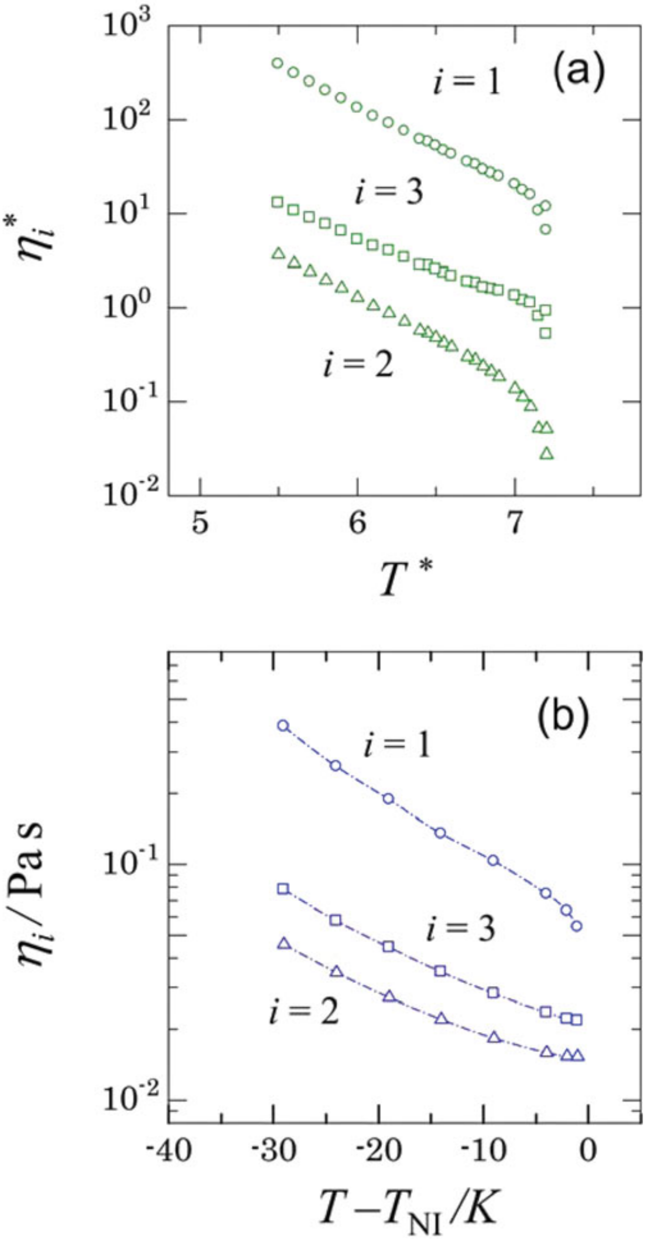

Figure 3. Temperature dependence of the Miesowicz coefficients η_{i} ($i = 1$–3) (a) obtained using the Gay–Berne model GB(4.4,20,1,1) at $P^* = 15.0$ and (b) experimentally determined for a eutectic mixture of 4'-*n*-pentylphenyl 4-methoxybenzoate and 4'-*n*-pentylphenyl 4-n-hexyloxybenzoate (EM). [31]

$$\eta_3 = 1/2\alpha_{4.} \tag{17}$$

Although the changes in temperature were not the same for the model and experimental systems, the Miesowicz coefficients increased exponentially as the temperature decreased,

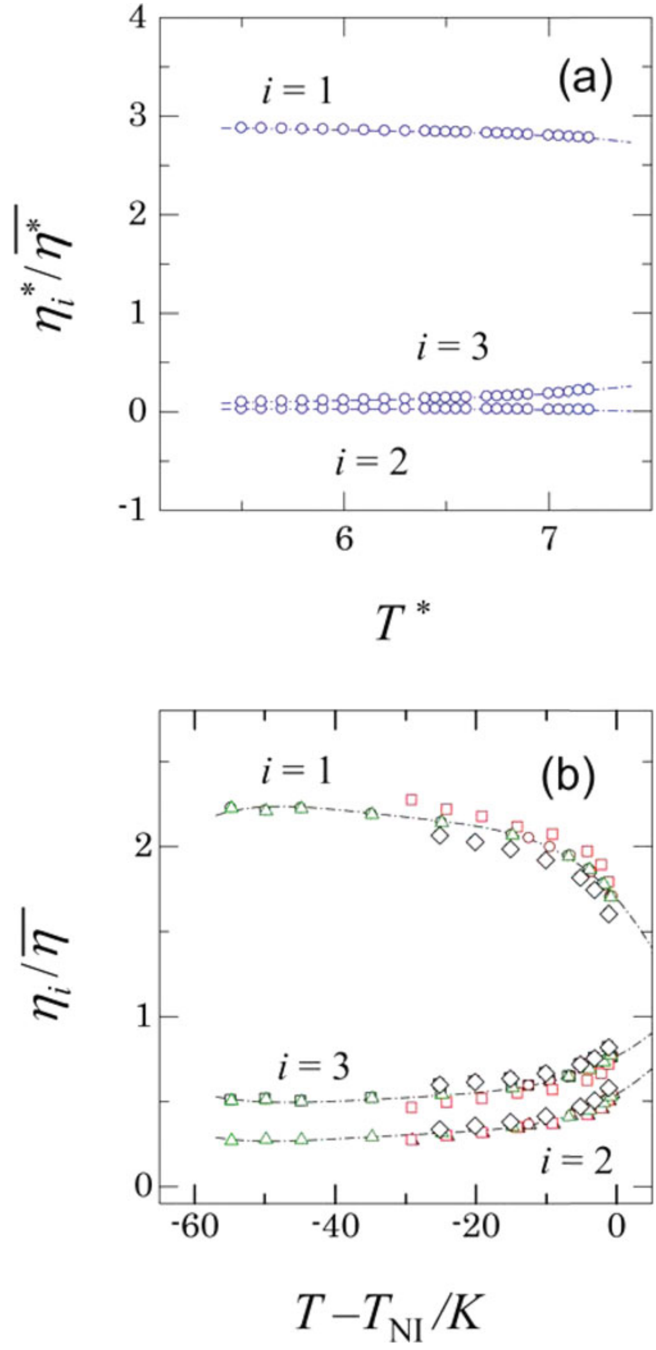

Figure 4. Reduced Miesowicz coefficients (a) obtained using the Gay–Berne model GB(4.4,20.0,1,1) at $P^* = 15.0$ and (b) experimentally determined for 4MBBA (diamonds), 4-*n*-pentyl-4'-cyanobiphenyl (5CB) (circles), a eutectic mixture of the two isomers of 4-methoxy-4'-*n*-butylazoxybenzene (N4) (triangles), and EM (squares). [31, 34]

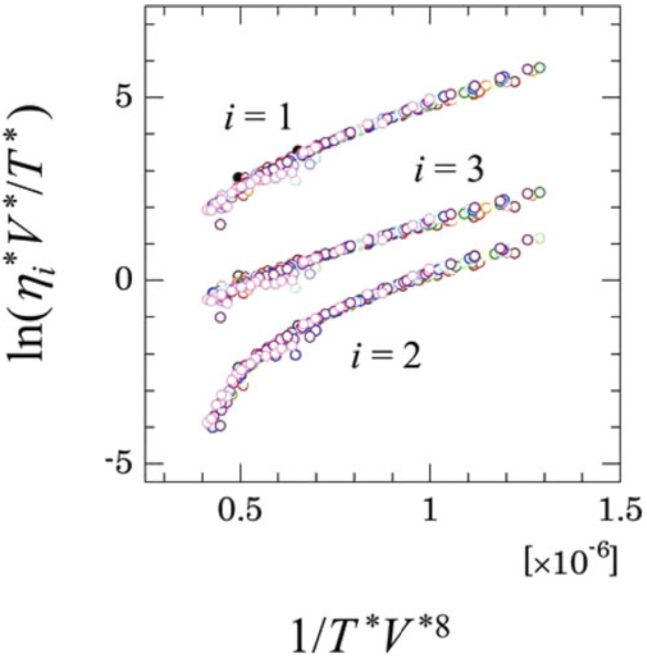

Figure 5. Thermodynamic scaling of the Miesowicz viscosities η_i ($i = 1$–3) obtained using the Gay–Berne model GB(4.4,20,1,1). The best fit value for the scaling exponent γ was 8.0.

and the behavior over the entire temperature range for the coarse-grained model system was similar to that for the real system. The calculated reduced Miesowicz coefficients (divided by the average values for the three coefficients: $\bar{\eta} = (\eta_1 + \eta_2 + \eta_3)/3$) as a function of temperature, along with selected experimental data,[31, 34] are shown in Fig. 4. As can be observed in the figure, the experimentally determined reduced coefficients for different nematics behaved similarly. It should be noted that the behavior near the nematic–isotropic transition temperature for the model system looks simpler than that of the real system because the temperature steps in the simulation were larger than those used to obtain the experimental data. However, the temperature variation was similar to that of the real systems. In particular, the relationship between the coefficients was well-reproduced for the model molecular system.

Thermodynamic Scaling of the Miesowicz Viscosity Coefficients

In experiments reported by Urban's group, low-frequency rotational relaxation times were scaled for several tens of substances. [11, 13] Model simulations of mesogenic systems have also been used to predict the results for not only the relaxation time but also the rotational diffusion constant and Leslie viscosity coefficients, as described above. Thus, we attempted to verify the thermodynamic scaling of the Miesowicz viscosity coefficients, which represent another important hydrodynamic property of liquid crystals. The plots for the coefficients multiplied by V/T for thermodynamic scaling with the best fit scaling exponent γ_η are shown in Fig. 5. The best fit scaling exponent γ_η was 8.0, which was exactly the same as that for the other rotational dynamic properties (relaxation time, diffusion constant, and Leslie viscosity coefficients).[16] Furthermore, the value was also coincident with the thermodynamic parameter Γ defined as follows:[35, 36]

$$\Gamma = -[\partial \log T/\partial \log V]_{\mathrm{P2}}, \tag{18}$$

where T, V, and P_2 are the absolute temperature, molar volume, and an order parameter of the second rank, respectively.

4. Conclusions

The temperature and pressure dependence of the viscosity coefficients were investigated and the adaptability of thermodynamic scaling for the Miesowicz viscosity coefficients were verified via MD simulation with the Gay–Berne mesogen model.

Temperature variations for the Leslie and Miesowicz viscosity coefficients were qualitatively reproduced for several real nematics, although there were some differences in the behavior near the nematic–isotropic transition point. The temperature dependence of the Leslie coefficients increased with increasing pressure. The plot of $1/TV^{\gamma_\eta}$ for the Miesowicz viscosity coefficients obtained via MD simulation with the model produced a master curve. Therefore, the coefficients scaled in a manner similar to that of the relaxation time for flip-flop motion, the rotational diffusion constant, and the Leslie viscosity coefficients. Notably, the best fit value for the scaling parameter γ_η was the same as that for these dynamic properties and was also identical to the value of the thermodynamic parameter Γ at which the second-rank orientational order parameter P_2 was constant.

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