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Shear-Induced Phase Changes in Mixtures[1]

K. D. Romig, Jr.,[2] and H. J. M. Hanley[2,3]

A thermodynamic theory to account for the behavior of liquid mixtures exposed to a shear is developed. One consequence of the theory is that shear-induced phase changes are predicted. The theory is based on a thermodynamics that includes specifically the shear rate in the formalism and is applied to mixtures by a straightforward modification of the corresponding states, conformal-solution approach. The approach is general but is used here for a mixture of Lennard–Jones particles with a Lennard–Jones equation of state as a reference fluid. The results are discussed in the context of the Scott and Van Konynenberg phase classification. It is shown that the influence of a shear does affect substantially the type of the phase behavior. Results from the model mixture are equated loosely with those from real polymeric liquids.

KEY WORDS: conformal-solution theory; corresponding states; Lennard–Jones fluids; mixtures; nonequilibrium molecular dynamics; nonlinear thermodynamics; shear-induced phase changes.

1. INTRODUCTION

Shear-induced phase changes in polymer solutions have been reported, although they were not necessarily recognized as such. There has been no clear-cut explanation for the effect but often the implication is that changes occur only because of the complex nature of the mixture. Thirty years ago, however, an investigation of shear-dependent phase behavior was undertaken by Silberberg and Kuhn [1]. They observed shear-dependent liquid–liquid critical-point depressions of as much as 10 K for shear rates to 200 s^{-1} in polystyrene–ethyl cellulose–benzene solutions. They modeled the

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[2] Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309, U.S.A.

[3] Thermophysics Division, National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

phenomenon as a surface effect but suggested that their results required the modification of thermodynamic criteria for phase behavior to include shear, hence implying that the effect of shear on phase equilibria should be fundamentally the same for any system.

Further observations of shear-dependent phase changes in polymer mixtures have been made by Ver Strate and Philipoff [2] and by Wolf and Kramer [3]. Shear-dependent melting effects have also been seen in liquid crystals by Hermans [4] and in colloidal suspensions by Ackerson and Clark [5].

The modern explanation for a shear-induced phase change in a fluid is relatively straightforward [6]. If the fluid can store energy in any way, i.e., by a rearrangement of molecular structure or by a rearrangement of particle distribution, then the thermodynamic stability of the fluid—and hence the phase behavior—must be affected. Furthermore, on the evidence of computer simulation [7] and the behavior of polymer solutions and colloidal suspensions [8], we would expect to observe nonlinear behavior, of which shear-induced phase changes are examples, if a product $\tau\gamma \geqslant 10^{-2}$. Here τ is a relaxation time and γ is the shear rate. This condition appears to be independent of the system. One can thus study a relatively simple model under conditions for which $\tau\gamma \geqslant 10^{-2}$ and scale the results to represent a complex system that normally would not be readily amenable to analysis. This is the approach taken in this paper. We give a consistent thermodynamic description of a sheared fluid based on nonequilibrium molecular dynamics (NEMD) studies of a model Lennard-Jones liquid. The results are applied to model binary mixtures via a modified conformal-solution one-fluid approach. We then argue that the subsequent conclusions are relevant to a real system, such as a polymer liquid mixture.

2. THERMODYNAMICS

The basis of this work is the NEMD study of Hanley and Evans [9], who showed that the energy of a sheared fluid is a state function of the shear rate at constant volume V (or density ρ) and temperature T (all quantities quoted are dimensionless):

$$E = E(V, T, \gamma) \tag{1}$$

Such a result led to a heuristic thermodynamics with

$$dE = T\,dS - p\,dV + \zeta\,d\gamma \tag{2}$$

where S is the entropy and ζ, $\zeta = \zeta(V, T, \gamma)$, a potential given by

$$\zeta = \int_{v}^{\infty} \frac{\partial p}{\partial \gamma}(V', T, \gamma)\,dV' + \zeta_{\infty}(T, \gamma) \tag{3}$$

where $\zeta_\infty(T, \zeta)$ is the ideal-gas contribution and p is the pressure; $p = p(V, T, \gamma)$.

The computer simulations show for many different model systems over a wide range in shear rate that the state functions follow a three-halfs power law in γ, for example,

$$E = E_{\mathrm{eq}}(V, T) + \gamma^{3/2} E_\gamma(V, T) \tag{4}$$

and

$$p = p_{\mathrm{eq}}(V, T) + \gamma^{3/2} p_\gamma(V, T) \tag{5}$$

Hanley and Evans were able to correlate E_γ and p_γ from the simulation energy and pressure data using the relationship

$$(\partial E_\gamma/\partial \rho)_{T,\gamma} = p_\gamma - T(\partial p_\gamma/\partial T)_{\rho,T} \tag{6}$$

They reported an empirical expression for a compressibility factor C_γ given by

$$C_\gamma = p_\gamma \gamma^{3/2}/\rho T \tag{7}$$

The expression and its constants are given in Ref. 9 and are not repeated here. Given the equilibrium compressibility factor of a Lennard–Jones fluid [10], one has an equation of state for a Lennard–Jones fluid under shear. This equation is used here as a reference equation.

Note that Eqs. (2) through (5) imply that the Helmholtz free energy A can be written as

$$A = A_{\mathrm{eq}} + \frac{2}{3}\gamma\zeta \tag{8}$$

where, using Eq. (7)

$$\frac{2}{3}\gamma\zeta = T\int_0^\rho C_\gamma \, d\rho'/\rho' \tag{9}$$

The thermodynamics described must predict shear-induced phase changes because the free energy contains a contribution from the shear, ζ. The meaning of this term has been discussed by Evans et al. [6]. It is a measure of the cost in free energy required to go from one steady state to another at a different shear rate. This cost reflects the rearrangements in the fluid structure needed to allow for a change in the shear rate. This rearrangement of a simple fluid should be compared and contrasted with a more obvious intramolecular rearrangement such as a polymer unraveling. It is this kind of comparison that opens up the possibility to scale shear-induced phenomena via a relaxation time, although the relaxing mechanism may be quite different from one fluid to another.

2.1. Conformal-Solution Theory

Hanley and Evans [9] demonstrated that the transition of a Lennard–Jones gas to the liquid is suppressed by a shear and one would suspect that the shear-induced phase transitions of a mixture would be especially interesting and varied. As remarked, our objective is to examine this problem; but it cannot be done directly via simulation at this time. We therefore use the results for the pure fluid and apply them to a binary mixture following the conformal-solution, one-fluid approach [11].

In classical corresponding states the properties of a fluid, *i*, can be mapped onto the properties of a reference fluid, o, by scaling with the ratios

$$h_{i0} = (V_i^{\mathrm{c}} | V_0^{\mathrm{c}}) = (\sigma_i/\sigma_0)^3 \tag{10}$$

$$f_{i0} = (T_i^{\mathrm{c}}/T_0^{\mathrm{c}}) = (\varepsilon_i/\varepsilon_0) \tag{11}$$

where the superscript c indicates the critical value and σ and ε are the potential size and energy parameters, respectively. The conformal-solution one-fluid concept is that a mixture at a given mole fraction, x, is equivalent to a pseudo pure fluid, and that the pseudo fluid can also be scaled with a reference fluid by the ratios (10) and (11) with the critical parameters defined by mixing rules, for example, the van der Waals mixing rules:

$$h_{x0} = \sum_i \sum_j x_i x_j h_{ij} \tag{12}$$

$$f_{x0} = \sum_i \sum_j x_i x_j h_{ij} f_{ij} / h_{x0} \tag{13}$$

where the combining rules are given by

$$h_{ij} = (1/8)[h_{i0}^{1/3} + h_{j0}^{1/3}]^3 \tag{14}$$

and

$$f_{ij} = (f_{i0} f_{j0})^{1/2} \tag{15}$$

The properties of the mixture can then be equated: for example,

$$p(V, T, \gamma) = (f_{x0}/h_{x0})[p_{\mathrm{eq},0}(V/h_{x0}, T/f_{x0}) + (\gamma/g_{x0})^{3/2} p_{\gamma,0}(V/h_{x0}, T/f_{x0})] \tag{16}$$

$$A(V, T, \gamma) = f_{x0}\left[A_{\mathrm{eq},0}(V/h_{x0}, T/f_{x0}) + \frac{2}{3}(\gamma/g_{x0})\,\zeta_0(V/h_{x0}, T/f_{x0}, \gamma/g_{x0})\right] + NT\left[\sum_i x_i \ln x_i - \ln h_{x0}\right] \tag{17}$$

We see that Eqs. (16) and (17) are modifications of very well-known equations but the shear rate is now included. The shear rate has to be scaled and we choose, based on a mixing rule for the viscosity,

$$g_{x0} = \left(\sum_i \sum_j x_i x_j f_{ij}^{1/2} m_{ij}^{-1/2} h_{ij}^{-2/3}\right) h_{x0}^{1/3} \tag{18}$$

with

$$m_{ij} = 2m_{i0}m_{j0}/(m_{i0} + m_{j0}) \tag{19a}$$

where

$$m_{i0} = M_i/M_0 \tag{19b}$$

M_i and M_0 are the molecular msses of substance i and of the reference substance, resectively.

2.2. The Phase Diagram

We assume that a condition for two or more phases to be coexistent under shear is that the chemical potential μ_i of each species i be equal in each phase. We can then use

$$\mu_i = (\partial A/\partial n_i)_{V,T,\gamma} \tag{20}$$

where n_i is the number of moles of i. For a binary mixture [11]

$$\mu_1 = \hat{A} - x_2(\partial \hat{A}/\partial x_2)_{\hat{V},T,\gamma} + p\hat{V} \tag{21a}$$

$$\mu_2 = \hat{A} - x_1(\partial \hat{A}/\partial x_1)_{\hat{V},T,\gamma} + p\hat{V} \tag{21b}$$

where x_i is the mole fraction and the circumflex refers to a quantity per mole.

In summary, we wish to calculate the properties of a mixture whose species are characterized by the parameters σ_i, ε_i, and M_i at mole fraction x_i at volume $\hat{V}$ and temperature T under a shear rate of γ. We have the scaling ratios Eqs. (10)–(15) and (18) and (19). The properties follow from Eqs. (16) and (17), and the phase behavior follows from Eqs. (21a) and

(21b). The reference equation is the Lennard–Jones of Ref. 10 with the shear term of Hanley and Evans [9]. Expressions for the reference pressure and energy follow from Eqs. (5) and (7) to (9). The computational details are discussed in Ref. 11.

We carried out phase-behavior calculations both at equilibrium ($\gamma = 0$) and at various shear rates for several binary model mixtures. Such mixtures are defined by setting the potential, size, and mass parameters ($\varepsilon_2, \sigma_2, M_2$) of the more volatile component to 1.000. Thus the more volatile component is always taken as the reference substance. The potential and size parameters of the less volatile component (ε_1, σ_1) are defined as stated multiples of 1.000. The less volatile component's mass parameter (M_1) is taken as proportional to the cube of that component's size parameter. Results are then reported for mixtures as functions of $\Delta\varepsilon = \varepsilon_1 - \varepsilon_2$ and $\Delta\sigma = \sigma_1 - \sigma_2$.

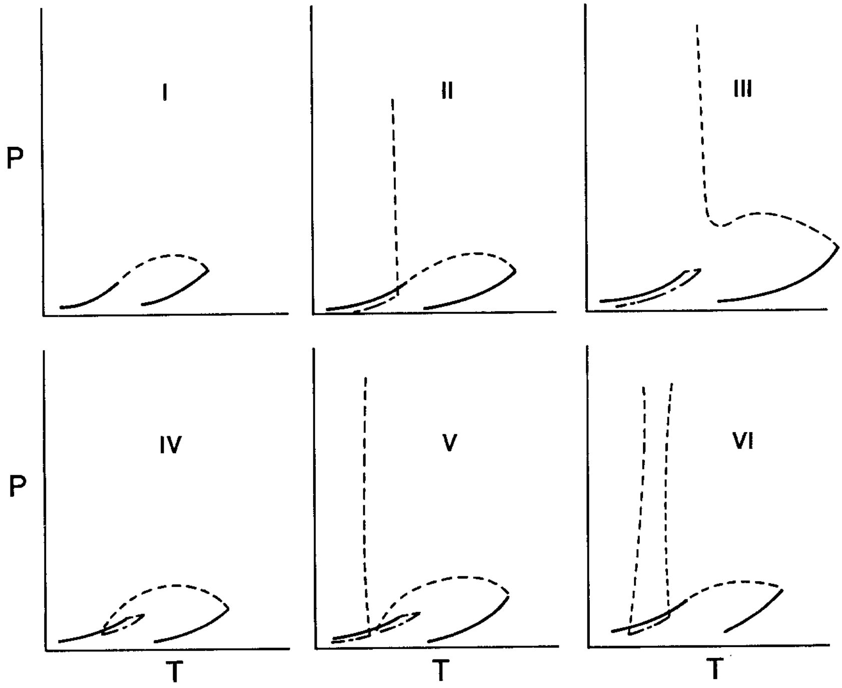

Fig. 1. Schematic pressure–temperature projection of vapor pressure curves (——), critical loci (----), and LLV loci (— — —) for the six types (I–VI) of binary fluid mixture phase behavior [13].

3. RESULTS

It is convenient to represent the phase behavior of a binary mixture under shear with respect to the classification of van Konynenberg and Scott [13]. Figure 1 gives pressure–temperature projections of typical critical loci and vapor pressure curves for the six phase diagrams of the classification.

Figure 2 shows the predicted change in the phase diagram as a function of γ and $\Delta\varepsilon$ for a typical series of binary mixtures, with $\Delta\sigma$ arbitrarily chosen as 0.070. Let us consider for illustration a mixture with $\Delta\varepsilon = 1.56$. The dashed horizontal line shows that the quite complicated equilibrium phase behavior (Type III) of this mixture is predicted to change drastically to a much simpler type (Type I) under the influence of a sufficient shear. The effect is shown more vividly in Figure 3, which is an isobar of that mixture's phase diagram at $p = 0.356$ both at equilibrium and at $\gamma = 3.10$. We see that not only has the liquid–liquid phase separation

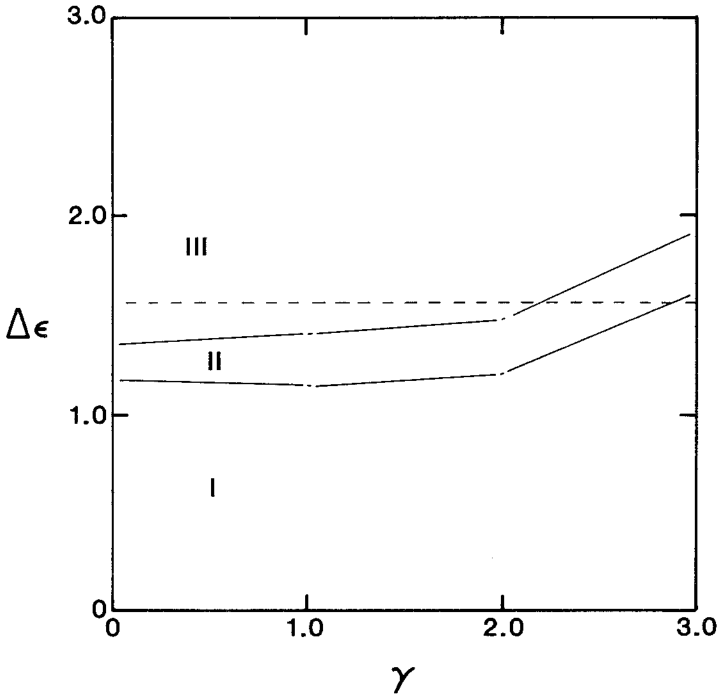

Fig. 2. Regions of phase diagram types as functions of intermolecular potential difference ($\Delta\varepsilon$) and shear rate (γ) in a Lennard–Jones binary mixture for which $\Delta\sigma = 0.07$. The dashed horizontal line at $\Delta\varepsilon = 1.56$ shows how the phase diagram can change with shear.

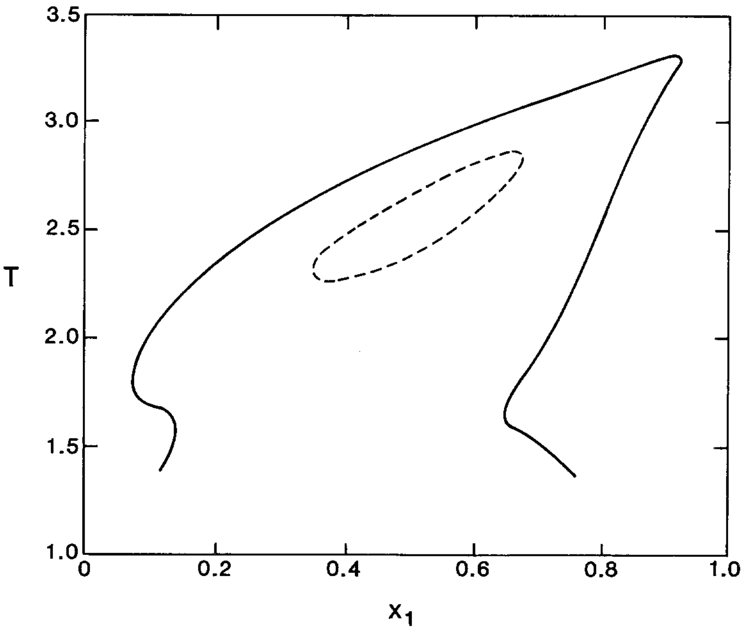

Fig. 3. Calculated phase diagram at $p = 0.356$ for the Lennard–Jones binary mixture $\Delta\varepsilon = 1.56$, $\Delta\sigma = 0.07$ at equilibrium (——) and at $\gamma = 3.10$ (----).

disappeared under shear, but the vapor–liquid phase separation has nearly disappeared as well.

Finally, let us make a very rough comparison between our results, based on a computer simulation, and a real system. We calculated the liquid–liquid phases at a pressure of 0.005, chosen to represent approximately an atmospheric pressure, for a Type II mixture of equal-sized particles ($\Delta\sigma = 0$) with $\Delta\varepsilon = 1.000$ at equilibrium and at $\gamma = 0.20$, respectively. The observed shear-dependent change of the consolute temperature is $\Delta T = 0.08$. As noted above, Silberberg and Kuhn [1] recorded changes in consolute temperature as high as 10 K for shear rates of the order of $10^2\ \mathrm{s}^{-1}$ for a polymer mixture. These authors suggested that their system had a relaxation time of 10^{-3} s. Now the relaxation time for the Lennard–Jones mixture is of the order of 10^{-1}. Thus, the $\tau\gamma$ products are of similar orders of magnitude for both systems. A scaling parameter for the temperature of a polymer system (e.g., critical temperature) would have a value of the order of 10^3 K. If this is multiplied by ΔT we find that $\Delta T_{\mathrm{unscaled}}$ is of the order 10 K. Although we recognize that this polymer behavior cannot be modeled directly by the simple two-body potentials used in this work and in spite of the very preliminary nature of the above comparison, the result lends support to the theory developed here and suggests strongly the connection between the phase behavior predictions for simple systems and the data for more complicated systems such as polymer mixtures.

4. CONCLUSIONS

We have discussed shear-dependent phase behavior of fluid mixtures in terms of the principle of corresponding states and a one-fluid thermodynamic model. We predict that a sufficient shear could affect significantly the fluid phase behavior of mixtures. Shear has been demonstrated to suppress liquid–liquid phase separation and to enlarge a mixture's homogeneous region. Finally, the predicted shear effect on the phase behavior of a model mixture has been shown to scale very approximately as the observed shear effect on the phase behavior of a polymer mixture. As a word of caution: when calculating the phase diagrams presented, we have assumed as a limiting case that the coexisting phases have the same shear rate; also, in principle the diagrams depend on the mixing rules proposed and, most importantly, on the particular choice of reference equation of state that was established for Couette flow.

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