

tions, and definitions used in Ref. 2 have been employed here.

The limits on the summations in Eqs. (2) and (3) are $k_{\min} \leq k \leq k_{\max}$, $L_{\min} \leq L \leq L_{\max}$, $\lambda_{\min} \leq \lambda \leq \lambda_{\max}$, and $\bar{l}_{\min} \leq \bar{l} \leq \bar{l}_{\max}$, where

$$\begin{aligned} k_{\max} &= l_a + l_a', \\ k_{\min} &= \max\{ |l_a - l_a'|, \\ &\quad |m_a - m_a'| + \text{OE}(l_a + m_a + l_a' + m_a') \}, \\ L_{\min} &= \max\{ |\bar{l} - k|, |\lambda - l_a''|, \\ &\quad |m_b - m_a''| + \text{OE}(\lambda + m_b + l_a'' + m_a'') \}, \\ L_{\max} &= \min\{ \bar{l} + k, \lambda + l_a'' \}, \\ \lambda_{\min} &= \max\{ |k - l_a''| - \bar{l}, \\ &\quad |m_b| + \text{OE}(m_b + k + l_a'' + \bar{l}), \bar{l} - k - l_a'' \}, \\ \lambda_{\max} &= \min\{ \bar{l} + k + l_a'', l_b - \text{OE}(l_b + k + l_a'' + \bar{l}) \}, \\ \bar{l}_{\min} &= \max\{ |m_b| - k - l_a'', |k - l_a''| - l_b, \\ &\quad \delta(l_b, |m_b|) \text{OE}(l_b + k + l_a''), \\ &\quad |m_b - m_a''| - k + \delta(l_b, |m_b|) \text{OE}(l_a'' + m_a'') \}, \\ \bar{l}_{\max} &= l_b + l_a'' + k, \end{aligned} \quad (6)$$

with the odd-even function $\text{OE}(X)$ defined by

$$\begin{aligned} \text{OE}(X) &= 0 & \text{if } X \text{ even} \\ &= 1 & \text{if } X \text{ odd.} \end{aligned} \quad (7)$$

The indices L , k , and λ range in steps of two while the index \bar{l} ranges in steps of $1 + \delta(l_b, |m_b|)$.

Finally we remark that the integration in Eq. (2) is carried out numerically using techniques discussed in Ref. 3.

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Comments

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Comment on "Anomalous Specific Heat and Viscosity of Binary van der Waals Mixtures"*

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Several years ago Deutch and Zwanzig¹ (D-Z) extended van Kampen's treatment² of the weak, long-range force van der Waals model to binary mixtures. Attention was focused on the anomalous behavior of the specific heat and viscosity near the consolute critical line for three-dimensional systems. The analysis proceeded by computing the excess contribution to the free energy of quadratic concentration fluctuations at uniform density; the heat capacity at constant volume and concentration $C_{v,f}$ was found to diverge along the determined critical consolute line in a manner identical to that found earlier by Fixman.³ Recently, on the basis of certain general thermodynamic assumptions, Wheeler and Griffiths⁴ have shown that for a binary mixture a divergence in $C_{v,f}$ along a critical line is not to be expected. Previously, Rice⁵ pointed out that a locus of infinite heat capacity in a compressible system should be unstable and result in a lower order transition. The contradiction between the model and the results of Wheeler and Griffiths was first pointed out by Throop.⁶

In this Comment we wish to report the effects on the model and on the behavior of $C_{v,f}$ of including quadratic density fluctuations. We find that with the inclusion of density fluctuations this model exhibits both consolute and vapor-liquid transitions. In the notation of D-Z the excess free energy ΔA is

$$\begin{aligned} \exp(-\beta\Delta A) &= \sum'_{\{\delta x_i\}} \sum'_{\{\delta y_i\}} \exp \left\{ \frac{1}{2} \left[\left(\frac{\partial^2 \Phi}{\partial x_i \partial x_j} \right)^0 \delta x_i \delta x_j \right. \right. \\ &\quad \left. \left. + 2 \left(\frac{\partial^2 \Phi}{\partial x_i \partial y_j} \right)^0 \delta x_i \delta y_j + \left(\frac{\partial^2 \Phi}{\partial y_i \partial y_j} \right)^0 \delta y_i \delta y_j \right] \right\}, \end{aligned} \quad (1)$$

where only quadratic terms in the deviation from uniform number δx_i and composition δy_i in cell i have been retained. The right-hand side of Eq. (1) may be diagonalized by Fourier transformation yielding

$$\beta\Delta A = \frac{1}{2} \sum_{k \neq 0} \ln[\lambda_+(k)\lambda_-(k)] + \text{const}, \quad (2)$$

where $\lambda_{\pm}(k)$ are the negatives of the eigenvalues of the

quadratic form appearing in Eq. (1). In the *simple* case where all the short-range repulsive interactions are identical and the long-range attractive interaction between the same species are equal ($W_{AA}=W_{BB}=W$) the quantities $\lambda_{\pm}(k)$ take the form

$$\lambda_{\pm}(k) = (2\rho)^{-1} \{ (2f)^{-1} + [2(1-f)]^{-1} + g(\rho) - \beta\rho\hat{W}(k) \} \pm \{ [-g(\rho) + \beta\rho\hat{W}_{AB}(k)]^2 + \frac{1}{4}[f^{-1} - (1-f)^{-1}]^2 \}^{1/2}. \quad (3)$$

Here $g(\rho)$ is related to the approximate form adopted for the intracell contribution of the repulsive cores to the partition function.^{1,2}

The limit of stability of the reference *homogeneous* system of free energy $A^0 = [-\Phi(x_i^0, y_i^0)/\beta]$ is found from the spinodal surface⁷ defined by $[-(\partial P/\partial v)_{T,f}(\partial\mu/\partial f)_{T,P}] = 0$, where μ is the difference in chemical potential of species A and B. In the model the limit of stability is found from the surface where the smallest eigenvalues $\lambda_{\pm}(0)$ cease to be positive; one arrives at the condition $[4\rho^4\lambda_+(0)\lambda_-(0)/\beta^2] = 0$ which may be shown to give the same spinodal surface as in the homogeneous reference system.

The divergence in the excess heat capacity $\Delta C_{v,f}$ persists, however, along both the consolute and vapor-liquid critical lines of the homogeneous system. If in the *simple* case we assume incompressibility along the consolute critical locus, our result reduces to that obtained by Fixman and D-Z.

The contradiction between the model and the results of Griffiths and Wheeler is not reconciled by including quadratic concentration and density fluctuations. The critical lines, however, have been located with respect to the *homogeneous* system A_0 and not with respect to

the over-all free energy $A_0 + \Delta A$. The assumption that the limit of stability is where $\lambda_{\pm}(0)$ ceases to be positive is not equivalent to the correct thermodynamic criterion that $A_0 + \Delta A$ be convex in the variables f and ρ . As pointed out by Mountain and Zwanzig⁸ this mislocation of the critical phase may be assessed by considering the *excess* contribution to the inverse isothermal compressibility $\Delta K_{T,f}^{-1}$. We find that $\Delta K_{T,f}^{-1}$ approaches minus infinity as T approaches T_c which is unphysical and identical to the condition obtained by Rice⁵ for explaining why a system will undergo a first-order phase transition before reaching the locus of infinite specific heat.

A correct analysis of the two-component model has not been accomplished; such an analysis may require inclusion of higher order fluctuations in analogy to the recent one-dimensional calculation of van Kampen.⁹ A proper analysis is important since it would likely lead to finite specific heats along the critical lines and provide a microscopic model for the intriguing Wheeler-Griffiths inequality.

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Dipole Moment of the First-Excited $\pi^* \leftarrow \pi$ State of Fluorobenzene

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Recently, a paper by Huang and Lombardi¹ appeared in this Journal, dealing with the determination of the dipole moment of fluorobenzene in its first $\pi^* \leftarrow \pi$ singlet state; from Stark effect measurements, they obtained

$$\mu(S_1^*) = (1.96 \pm 0.07) \text{ D.}$$

On the other hand, the most recent determination of the dipole moment of fluorobenzene in its ground state gave the value,

$$\mu(S_0) = (1.66 \pm 0.03) \text{ D,}$$

obtained from Stark effect measurements.² Hence it is found that, when going from the ground state to the

first-excited singlet, the dipole moment of fluorobenzene is increased by some (0.30 ± 0.10) D.

Last year, Dr. Chalvet and myself published³ the results of a theoretical study of the electronic properties for the 12 polyfluorobenzenes in their ground and excited singlet states. For fluorobenzene, the following π electronic densities on atoms were obtained, for the ground state and the first $\pi^* \leftarrow \pi$ excited singlet:

Atom	Ground state (S_0)	First $\pi^* \leftarrow \pi$ singlet (S_1^*)
C ₁	0.973	0.944
C ₂	1.030	1.036
C ₃	0.997	1.038
C ₄	1.016	0.976
F	1.957	1.934