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# Experimental and theoretical studies of the equation of state of liquid 2-butyne from 248 to 293 K and pressures up to 104 MPa

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$$U_i^{\text{int}} = \sum_{\substack{j=1 \\ j \neq i}}^N (u_{ij}^{\text{LJ}}(r_{ij}) + u_{ij}^{\text{EL}}(r_{ij})) + \sum_w (u_{iw}) + u_{ip}^{\text{LJ}}(r_{ip}) + u_{ip}^{\text{int}}(r_i) \quad (\text{A24})$$

where

$$u_{ip}^{\text{int}}(r_i) = \sum_{m=1}^{15} [u_{im}^{\text{LJ}}(|\mathbf{r}_i - \mathbf{r}_m|) + u_{im}^{\text{EL}}(|\mathbf{r}_i - \mathbf{r}_m|)] \quad (\text{A25})$$

The sum in eq A25 is over the 15 fixed negative ions on the polyion segment inside the cell.  $|\mathbf{r}_i - \mathbf{r}_m|$  is the center-to-center distance of separation between counterion  $i$  and fixed polyion charge  $m$ . Notice that we now have two types of Lennard-Jones terms in (A24) and (A25):  $u_{ip}^{\text{LJ}}(r_{ip})$  and  $u_{im}^{\text{LJ}}(|\mathbf{r}_i - \mathbf{r}_m|)$ . The first, eq A6, prevents counterions from penetrating too far into the body of the polyion cylinder, and the second prevents them from getting too close to the negative charges on the polyion. The Lennard-

Jones and electrostatic terms in eq A15 are of the form given in eqs A4 and A5, with the dielectric constant in eq A5 taken as unity.

Similarly eqs A19 and A20, for the internal contribution to the water-polyion potential for these calculations, were replaced by

$$u_{wp}^{\text{LJ}} = 4\epsilon_{wp}^{\text{LJ}} \left[ \left( \frac{\sigma_{wp}^{\text{LJ}}}{r_{wp}} \right)^{12} - \left( \frac{\sigma_{wp}^{\text{LJ}}}{r_{wp}} \right)^6 \right] + \sum_{m=1}^{15} u_{wm}^{\text{LJ}}(|\mathbf{r}_w - \mathbf{r}_m|) \quad (\text{A26})$$

and

$$u_{wp}^{\text{EL,int}} = \sum_{m=1}^{15} \sum_{\alpha=1}^3 \frac{q_w^\alpha q_m}{|\mathbf{r}_w^\alpha - \mathbf{r}_m|} \quad (\text{A27})$$

respectively.

## Experimental and Theoretical Studies of the Equation of State of Liquid 2-Butyne from 248 to 293 K and Pressures up to 104 MPa

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The expansion method has been used to measure the density of liquid 2-butyne, from 248 to 293 K and pressures up to 104 MPa. The solid-liquid coexistence curve up to 100 MPa has also been determined. The experimental results have been fitted to the Strohbridge equation of state, which has been used to estimate several properties of compressed liquid. The abilities of other semitheoretical and theoretical equations of state to predict the density and thermodynamic properties have been examined and discussed.

### Introduction

Accurate *PVT* data of simple liquids over a wide range of densities are known to be suitable for testing semitheoretical and theoretical equations of state and very useful for improving intermolecular potential functions.<sup>1-3</sup>

In the last years, equations of state based on statistical mechanics have been proposed in order to attempt a molecular understanding of the properties of a fluid. Some of the more interesting equations of state can be obtained from perturbation theory, and we will concentrate our attention on a semitheoretical one, the Deiters<sup>4,5</sup> equation of state, which has been used to predict thermodynamic properties of 2-butyne over the whole density range, including liquid and vapor phases up to the critical point. Another theoretical equation of state, developed by Haar and Kohler,<sup>6</sup> has been tested in terms of our experimental density results and has been used to estimate thermodynamic properties at low densities, such as second virial coefficients, from high-pressure results.

In this work we present the experimental study of the equation of state of liquid 2-butyne at pressures from saturation to about 104 MPa and temperatures from 248 to 293 K. This substance is very interesting from the theoretical point of view because of its high degree of linearity and rigidity that allows one to compare

it with theoretical calculations. In addition, this work brings new and accurate experimental data at high liquid densities, up to the melting line, which are very scarce in the literature.

The results consist of 111 *PpT* points measured along seven isotherms, which covers a relatively wide region not previously studied; it is important to remark that the 2-butyne remains liquid only from 241 to 300 K at atmospheric pressure. The experimental densities have been correlated in terms of the Strohbridge<sup>7</sup> equation of state, which has been used to calculate the isothermal compressibility and thermal expansion coefficient at regular intervals of pressure and temperature. The experimental study has been completed with the measurement of the solid-liquid coexistence curve for pressures below 100 MPa which has been used, together with vapor pressure and critical data, to construct the phase diagram and estimate the triple point of this substance. The second virial coefficient as a function of temperature has been calculated from calorimetric and vapor pressure data, and the results have been compared with those predicted by semitheoretical and empirical expressions as well as those derived from the theoretical equations of state indicated above. Special attention has been given to the behavior of this property at low temperatures.

### Experimental Section

The results reported here have been obtained with an expansion technique. A detailed description of the method and apparatus used in this work has been published.<sup>1,8</sup>

Temperatures have been measured with an accuracy of 0.01 K, using a Leeds and Northrup calibrated platinum resistance thermometer, and were referred to the international temperature

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TABLE I: Experimental Values of Density ( $\rho$ ) of Liquid 2-Butyne for Pressures ( $P$ ) and Temperatures ( $T$ )

$P$ , MPa	$\rho$ , mol·dm <sup>-3</sup>	$P$ , MPa	$\rho$ , mol·dm <sup>-3</sup>
$T = 293.19$ K			
103.81	13.841	40.35	13.255
97.24	13.788	31.49	13.162
91.39	13.737	19.68	13.031
76.57	13.605	15.21	12.980
71.55	13.562	10.91	12.930
65.85	13.509	7.64	12.891
60.00	13.452	4.37	12.851
51.81	13.372	1.95	12.821
45.94	13.313	0.29	12.799
$T = 283.18$ K			
102.00	13.982	31.78	13.348
95.77	13.940	24.12	13.266
89.58	13.887	20.81	13.230
82.24	13.822	18.19	13.201
76.25	13.777	14.16	13.156
68.85	13.705	10.76	13.117
61.55	13.641	8.08	13.087
49.21	13.523	5.04	13.049
45.07	13.478	2.42	13.018
40.33	13.433	0.21	12.991
35.28	13.384		
$T = 273.01$ K			
101.94	14.139	30.50	13.515
95.03	14.094	26.62	13.475
88.83	14.047	23.24	13.440
81.51	13.982	19.91	13.397
74.04	13.918	16.81	13.368
67.85	13.871	13.06	13.328
60.93	13.808	10.09	13.298
54.71	13.748	7.14	13.265
47.57	13.681	3.77	13.223
40.14	13.610	2.13	13.205
34.96	13.559	0.26	13.183
$T = 263.09$ K			
81.25	14.131	32.35	13.708
75.49	14.096	26.31	13.645
69.66	14.048	21.78	13.600
63.99	13.997	12.91	13.501
54.26	13.911	8.84	13.459
49.30	13.864	4.85	13.415
44.16	13.819	2.32	13.390
38.82	13.769	0.34	13.366
$T = 257.83$ K			
64.24	14.098	24.69	13.724
60.81	14.068	20.45	13.680
55.84	14.023	13.40	13.608
51.04	13.979	9.42	13.565
43.53	13.909	6.08	13.529
38.78	13.864	1.86	13.483
34.18	13.820	0.24	13.463
28.56	13.764		
$T = 253.07$ K			
43.17	13.990	13.52	13.696
37.65	13.937	9.53	13.650
32.20	13.885	6.48	13.616
27.89	13.841	3.62	13.588
23.71	13.800	0.31	13.549
19.13	13.752		
$T = 247.59$ K			
23.97	13.908	8.59	13.742
19.96	13.865	5.74	13.710
16.54	13.828	2.71	13.674
13.18	13.792	0.30	13.648

scale: ITS-90.<sup>9</sup> Temperatures in the pressure cell bath and expansion cell bath were controlled to within  $\pm 0.01$  K. High pressures were measured with a Sensotec TJE1108-20 pressure transducer (calibrated against a Desgranges et Huot Model 5403

TABLE II: Coefficients ( $A_i$ ) and Their Estimated Error and Gas Constant ( $R$ ) for Eq 1

$i$	$A_i$
1	$(-2.055_4 \pm 0.007) \times 10^{-2} \text{ dm}^3 \cdot \text{mol}^{-1}$
2	$(-1.754_8 \pm 0.006) \times 10^{-2} \text{ MPa} \cdot \text{dm}^6 \cdot \text{mol}^{-2}$
3	$(-9.66_{67} \pm 0.03) \times 10^{-5} \text{ MPa} \cdot \text{dm}^6 \cdot \text{K} \cdot \text{mol}^{-2}$
4	$(-4.78_{14} \pm 0.02) \times 10^{-7} \text{ MPa} \cdot \text{dm}^6 \cdot \text{K}^2 \cdot \text{mol}^{-2}$
5	$(-1.000_5 \pm 0.003) \times 10^{-11} \text{ MPa} \cdot \text{dm}^6 \cdot \text{K}^4 \cdot \text{mol}^{-2}$
6	$(-1.394_4 \pm 0.005) \times 10^{-1} \text{ dm}^6 \cdot \text{mol}^{-2}$
7	$(-1.787_1 \pm 0.006) \times 10^{-1} \text{ MPa} \cdot \text{dm}^9 \cdot \text{mol}^{-3}$
8	$(1.340_9 \pm 0.005) \times 10^{-4} \text{ MPa} \cdot \text{dm}^{12} \cdot \text{K}^{-1} \cdot \text{mol}^{-4}$
9	$(-3.93_{83} \pm 0.01) \times 10^{-9} \text{ MPa} \cdot \text{dm}^9 \cdot \text{K}^2 \cdot \text{mol}^{-3}$
10	$(-1.541_9 \pm 0.005) \times 10^{-11} \text{ MPa} \cdot \text{dm}^9 \cdot \text{K}^3 \cdot \text{mol}^{-3}$
11	$(-6.04_{09} \pm 0.02) \times 10^{-14} \text{ MPa} \cdot \text{dm}^9 \cdot \text{K}^4 \cdot \text{mol}^{-3}$
12	$(-6.59_{78} \pm 0.02) \times 10^{-7} \text{ MPa} \cdot \text{dm}^{15} \cdot \text{K}^2 \cdot \text{mol}^{-5}$
13	$(-2.609_7 \pm 0.009) \times 10^{-9} \text{ MPa} \cdot \text{dm}^{15} \cdot \text{K}^3 \cdot \text{mol}^{-5}$
14	$(-1.031_9 \pm 0.004) \times 10^{-11} \text{ MPa} \cdot \text{dm}^{15} \cdot \text{K}^4 \cdot \text{mol}^{-5}$
15	$(2.2_{852} \pm 0.2) \times 10^{-6} \text{ MPa} \cdot \text{dm}^{18} \cdot \text{mol}^{-6}$
16	$-0.046 \pm 0.001 \text{ dm}^6 \cdot \text{mol}^{-2}$
$R = 0.00831434 \text{ MPa} \cdot \text{dm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	
standard deviation = 1.10 MPa	
standard deviation = 0.012 mol·dm <sup>-3</sup>	

dead weight gauge) with an accuracy of about 0.02%. The lower pressures in the expansion system were measured with a calibrated Druck PDCR110/W low-pressure transducer with an absolute accuracy of 0.06%.

The reference density,  $\rho(288.15 \text{ K}) = 12.896 \pm 0.002 \text{ mol} \cdot \text{dm}^{-3}$ , was measured with a Anton Paar DMA 601 vibrating tube densimeter, and the isobaric heat capacity  $C_p$  of the liquid at atmospheric pressure was measured from 255 to 290 K with a Mettler TA4000 calorimeter. The accuracy of the heat capacity measurements is about 1.0%.

The second virial coefficient  $B$  in the vapor phase of 2-butyne at 298.15 K was calculated from the  $PVT$  data and the heats of vaporization given in ref 10, giving  $B(298.15 \text{ K}) = -0.87 \pm 0.02 \text{ dm}^3 \cdot \text{mol}^{-1}$ .

The absolute accuracy of the densities reported here is estimated to be  $8 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ . This value is worse than others reported by this laboratory in previous studies<sup>8,11</sup> because the cell used has a volume of approximately 4.2 cm<sup>3</sup>, so designed to be used with relatively small quantities of sample.

The 2-butyne used in this work was Fluka purum, dehydrated with molecular sieves. The final purity is estimated to be 99.5 mol % or better.

## Results and Discussion

**$PVT$  and Mechanical Properties.** The 111 experimental  $P\rho T$  points are recorded in Table I. These results have been fitted to the Strohbridge<sup>7</sup> equation of state, which can be written in the following form:

$$p = RT\rho + (A_1RT + A_2 + A_3/T + A_4/T^2 + A_5/T^4)\rho^2 + (A_6RT + A_7)\rho^3 + A_8T\rho^4 + (A_9/T^2 + A_{10}/T^3 + A_{11}/T^4)\exp[A_{16}\rho^2]\rho^3 + (A_{12}/T^2 + A_{13}/T^3 + A_{14}/T^4)\exp[A_{16}\rho^2]\rho^5 + A_{15}\rho^6 \quad (1)$$

The parameters of eq 1 have been obtained using a method based on the maximum likelihood principle, widely described in the literature.<sup>12,13</sup> In order to better reproduce the low-temperature densities, we have assigned a statistical weight inversely proportional to the temperature. Otherwise, the lack of experimental points over the entire range of pressures, due to the formation of the solid, would introduce errors in the numerical computation of the coefficients, making the calculated properties unreliable.<sup>13,14</sup>

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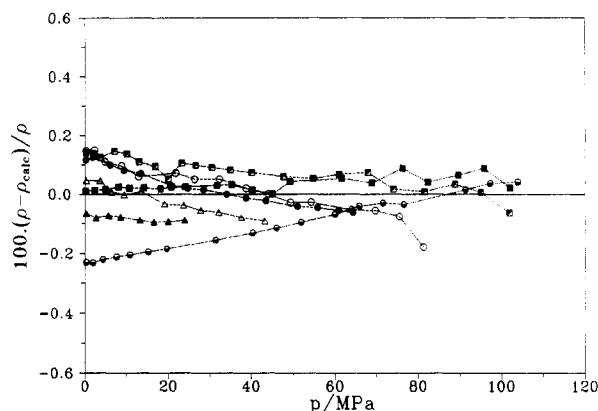


Figure 1. Density residuals of the isotherms in Table I.  $\rho$  is the experimental density and  $\rho_{\text{calc}}$  its value calculated from eq 1:  $\Delta$ , 247.59;  $\triangle$ , 253.07;  $\bullet$ , 257.83;  $\circ$ , 263.09;  $\blacksquare$ , 273.01;  $\blacksquare$ , 283.18;  $\circ$ , 293.19 K.

TABLE III: Orthobaric Density of Liquid 2-Butyne

T/K	$\rho/\text{mol-dm}^{-3}$				
	eq 1	ref 15	ref 10	ref 18	ref 19
298.15	12.722	12.74	12.675		
293.15	12.828	12.83	12.775 <sup>a</sup>	12.768	12.78
288.15	12.907	12.92			
278.15	13.073	13.10			
273.15	13.160	13.19			
268.15	13.249	13.28			
258.15	13.439	13.46			
248.15	13.643	13.64			

<sup>a</sup>See also ref 20.

TABLE IV: Isothermal Compressibility ( $\kappa_T/\text{GPa}^{-1}$ ) of Liquid 2-Butyne Calculated from Eq 1 at Round Values of Pressure (P) and Temperature (T)<sup>a</sup>

P/MPa	T/K					
	245.15	255.15	265.15	275.15	285.15	295.15
0.1	0.861	0.883	0.905	0.925	0.944	0.961
10.0	0.811	0.831	0.850	0.868	0.884	0.900
20.0		0.785	0.802	0.818	0.833	0.846
30.0		0.745	0.760	0.774	0.787	0.799
40.0		0.708	0.722	0.735	0.747	0.758
50.0		0.676	0.688	0.700	0.711	0.721
60.0			0.658	0.668	0.678	0.687
70.0			0.630	0.640	0.649	0.657
80.0			0.605	0.614	0.622	0.630
90.0				0.590	0.598	0.605
100.0				0.569	0.576	0.582

The coefficients  $A_1$ – $A_{15}$ , obtained from the fitting procedure, are recorded in Table II, as well as their estimated uncertainties. We have included more digits than statistically significant in order to avoid roundoff errors. The coefficient  $A_{16}$  has been fixed to  $-(\rho_c)^{-2}$ ; however, in the range of temperatures where eq 1 holds, it is not too important. Using these constants, eq 1 is valid only in the  $P\rho T$  range covered by the experiment. The maximum deviation observed between experimental values and those calculated from the fit is found to be 0.2% in density. Absolute average deviation is 0.08% in density. Figure 1 shows the differences between experimental and calculated densities for the different isotherms.

The densities at orthobaric conditions calculated from eq 1 have been compared with those given by Parker and Jonas.<sup>15</sup> Both sets of data are in close agreement and are recorded in Table III with other data available in literature.<sup>16–19</sup>

TABLE V: Selected Values of the Thermal Expansion Coefficient ( $10^3\alpha_p/\text{K}^{-1}$ ) for Liquid 2-Butyne

P/MPa	T/K					
	245.15	255.15	265.15	275.15	285.15	295.15
0.1	1.35	1.37	1.39	1.41	1.43	1.45
10.0	1.33	1.35	1.37	1.38	1.40	1.42
20.0		1.32	1.34	1.36	1.38	1.40
30.0		1.29	1.31	1.33	1.34	1.36
40.0		1.27	1.28	1.30	1.32	1.33
50.0		1.24	1.25	1.27	1.28	1.30
60.0			1.22	1.24	1.25	1.27
70.0			1.18	1.20	1.21	1.23
80.0			1.15	1.16	1.18	1.19
90.0				1.15	1.17	1.18
100.0				1.12	1.13	1.15

TABLE VI: Experimental Results of the Solid–Liquid Coexistence Curve for 2-Butyne

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
267.32	100.0	250.14	34.3	243.65	10.3
262.97	83.9	247.58	24.7	241.91	4.4
258.14	65.4	244.69	14.5	241.25	1.2
253.07	45.8				

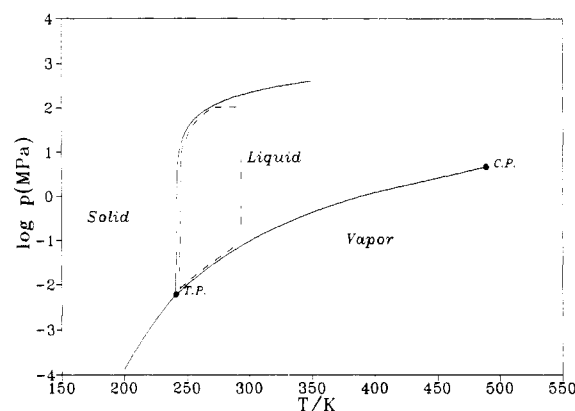


Figure 2. Phase diagram for 2-butyne constructed from eqs 2, 3a, b, and 4. The triple point is denoted as T.P. and the critical point as C.P. The dashed line encloses the region covered in this work.

The isothermal compressibility ( $\kappa_T$ ) of compressed liquid 2-butyne has been calculated as function of pressure and temperature from eq 1. Selected values of  $\kappa_T$  are recorded in Table IV.

Equation 1 alone, with the parameters of Table II, is not recommended for calculation of the thermal expansion coefficient ( $\alpha_p$ ). This property has been calculated from eq 1 together with the slopes of some isobars obtained from individual fittings of the isotherms to low-order polynomials. Selected values of  $\alpha_p$  are shown in Table V.

**Solid–Liquid Coexistence Curve.** The solid–liquid coexistence curve has been measured at 10 points up to 100 MPa. Each point is obtained as follows: the temperature is fixed to an arbitrary value, and small quantities of liquid are introduced into the cell with the compressor. The pressure increases slightly, and when it is stabilized, a new introduction is performed. During the coexistence of the two phases, the pressure remains nearly constant, and once the cell is filled with solid, the pressure increases rapidly in the next introductions. The process is then repeated downward. The points recorded in Table VI are the average of the coexistence pressures, with the estimated uncertainty about 0.3 MPa.

These results have been fitted to the Simon–Glatzel equation

$$P/\text{MPa} = -636.3 + 0.28754(T/\text{K})^{1.4044} \quad (2)$$

The standard deviation in the pressure is 0.4 MPa. The normal melting point calculated from eq 2 is  $240.9 \pm 0.1$  K. This value

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**TABLE VII: Heat Capacity at Constant Pressure ( $C_p$ ) at Selected Values of Temperature for Liquid 2-Butyne and Comparison with Those from Ref 17**

$T/K$	$C_p/J\cdot mol^{-1}\cdot K^{-1}$		$T/K$	$C_p/J\cdot mol^{-1}\cdot K^{-1}$	
	ref 17 <sup>a</sup>	this work <sup>b</sup>		ref 17 <sup>a</sup>	this work <sup>b</sup>
295.15	124.8		265.15	121.1	120.3
290.15	124.1	124.5	260.15	120.5	119.4
285.15	123.6	123.6	255.15	119.9	118.4
280.15	122.9	122.8	250.15	119.2	
275.15	122.3	122.0	245.15	118.6	
270.15	121.7	121.1			

<sup>a</sup> Accuracy 0.2%. <sup>b</sup> Accuracy 1.0%.

is in excellent agreement with those available from literature: 240.89,<sup>10</sup> 240.93,<sup>17</sup> 240.82,<sup>18</sup> 240.9,<sup>19</sup> and 240.89 K.<sup>20</sup>

**Phase Diagram.** The phase diagram has been constructed from eq 2, vapor pressures, and critical constants. Figure 2 shows a  $(\log P)$ - $T$  plot of the diagram as well as the liquid region covered in this work.

The vapor pressures along the liquid-vapor coexistence curve are given by<sup>10,21</sup>

$$\log(P_v/\text{MPa}) = 3.2036 - 1104.72/((T/K) - 36.96) \quad (3a)$$

$$\log(P_v/\text{MPa}) = 3.4728 - 1354.8/((T/K) + 4.65) \quad (3b)$$

Equation 3a is valid from the melting point to 365 K while eq 3b is valid from 365 K to the critical point.

The vapor pressures of the solid-vapor coexistence curve, between 200 and 240 K, have been taken from refs 17, 20, and 21 and correlated in terms of the Antoine vapor pressure equation

$$\log(P_v/\text{MPa}) = 4.4392 - 1357.09/((T/K) - 36.96) \quad (4)$$

Accurate values of the critical constants for 2-butyne are not available in the literature<sup>22</sup> (see Table XI), and we have found experimental results only for the critical temperature, while critical pressures and volumes are calculated or estimated values in all cases. The most reliable values, found in ref 22, are as follows:  $T_c = 488.7$  K,  $P_c = 5.07$  MPa, and  $V_c = 0.2145$  dm<sup>3</sup>·mol<sup>-1</sup>.

The triple point has been calculated from eqs 2, 3a, and 4 and has the values  $T_T = 240.94 \pm 0.05$  K and  $P_T = 6.1 \pm 0.1$  kPa.

**Enthalpies of Vaporization.** The enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ), as a function of temperature, has been calculated by solving the equation

$$d(\Delta H_{\text{vap}})/dT = \Delta C_p + \Delta H_{\text{vap}}(1/T - (\partial(\ln \Delta V)/\partial T)_p) \quad (5)$$

where  $\Delta C_p = C_p(\text{vapor}) - C_p(\text{liquid})$  and  $\Delta V = V_m(\text{vapor}) - V_m(\text{liquid})$ .

The results are compared to the experimental value  $\Delta H_{\text{vap}}(291 \text{ K}) = 26.945$  kJ·mol<sup>-1</sup>.<sup>17</sup>

The isobaric heat capacities of the vapor ( $C_p(\text{vapor})$ ) and the liquid ( $C_p(\text{liquid})$ ), used in the calculations, have been taken from refs 10, 23, and 17, respectively.

We have measured the  $C_p$  of the liquid, at atmospheric pressure, along three series from 255 to 290 K. The average results are presented in Table VII together with those from ref 17. Although the results agree well within the combined uncertainties, the data of Yost et al.<sup>17</sup> have been used in the calculations because of their better quality. The discrepancies between the calculated enthalpies of vaporization are not relevant.

The molar volumes of the liquid ( $V_m(\text{liquid})$ ) have been calculated from eq 1, while the molar volumes of the vapor ( $V_m(\text{vapor})$ ) can be determined from the second virial coefficient  $B$ . The available experimental results for  $B$  cover only temperatures between 291 and 302 K,<sup>10,17,24</sup> and in the absence of other data,

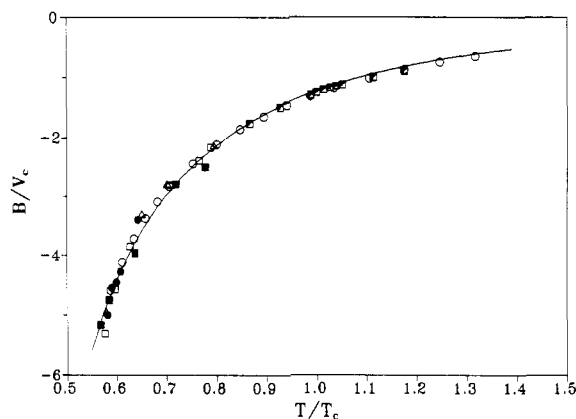
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**Figure 3.** Reduced second virial coefficients for several substances: ●, 1-butyne; ○, *n*-butane; ■, 2-butene (trans); □, 2-butene (cis); ▲, propyne; △, 1-butene. Eq 6 is represented by the continuous line.

**TABLE VIII: Enthalpy of Vaporization for 2-Butyne as a Function of Temperature**

$T/K$	$\Delta H_{\text{vap}}/\text{kJ}\cdot\text{mol}^{-1}$		$T/K$	$\Delta H_{\text{vap}}/\text{kJ}\cdot\text{mol}^{-1}$	
	this work <sup>a</sup>	ref 10		this work <sup>a</sup>	ref 10
298.15	26.560	26.585	268.15	28.100	28.104
288.15	27.091	27.091	258.15	28.606	28.614
278.15	27.598	27.598	248.15	29.125	29.121

<sup>a</sup> Uncertainty 0.010 kJ·mol<sup>-1</sup>.**TABLE IX: Second Virial Coefficient for 2-Butyne**

$T/K$	$B(T)/\text{dm}^3\cdot\text{mol}^{-1}$		
	this work	ref 10	ref 17
301.80	$-0.853 \pm 0.008$	$-0.827 \pm 0.012$	
300.12	$-0.865 \pm 0.008$	$-0.835 \pm 0.015$	
298.15	$-0.879 \pm 0.008$	$-0.867 \pm 0.020$	
293.15	$-0.912 \pm 0.010$		
291.00	$-0.927 \pm 0.015$		$-0.92 \pm 0.03$
288.15	$-0.940 \pm 0.020$		
283.15	$-0.962 \pm 0.035$		
278.15	$-0.974 \pm 0.060$		

we have estimated the behavior of  $B$  at low temperatures with the assumption that 2-butyne conforms to the principle of corresponding states. The dependence of  $B$  on temperature can be expressed as  $B/V_c = \phi(T/T_c)$ , where  $V_c$  and  $T_c$  are the critical volume and temperature and  $\phi$  denotes the same function for all substances conforming to the principle. This correlation has been introduced before by other authors.<sup>25,26</sup>

In order to obtain  $\phi$ , we have correlated the second virial coefficients of several substances similar to 2-butyne for which data at low temperatures are available. These substances are 1-butyne, *n*-butane, 1-butene, 2-butene (trans and cis), and propyne. The experimental second virial coefficients have been taken from Dymond and Smith<sup>24</sup> and the critical constants from ref 22. The results for the reduced second virial coefficient  $B/V_c$  vs the reduced temperature  $T/T_c$  are shown in Figure 3, and the function  $\phi$  can be written in the form

$$B/V_c = 0.336 - 0.81203(T_c/T) - 0.737816(T_c/T)^3 \quad (6)$$

The enthalpies of vaporization ( $\Delta H_{\text{vap}}$ ), calculated from eq 5, are shown in Table VIII together with those given in ref 10. The agreement between the two sets of data is very good.

**Second Virial Coefficients.** The Clausius-Clapeyron equation has been used to obtain the second virial coefficient as a function of temperature

$$B(T) = \left( \frac{\Delta H_{\text{vap}}}{T(dP/dT)_{\text{sat}}} \right) - RT/P_v + V_m(\text{liquid}) \quad (7)$$

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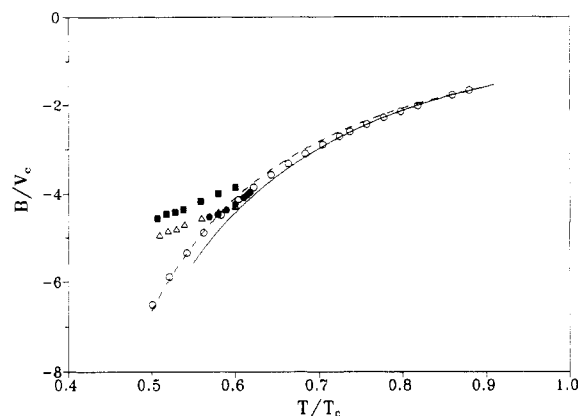


Figure 4. Reduced second virial coefficient as a function of temperature for 2-butyne: ●, this work (calculated from experimental data); —, eq 6; —, eq 8; ○, eq 9 with the fitted parameters of Table X; ■, eq 15 with the parameters of Table XIII; △, eq 17 with the parameters of Table XIV.

where  $\Delta H_{\text{vap}}$  are those calculated in the previous section,  $P_v$  and  $(dP/dT)_{\text{sat}}$  were calculated from eq 3a, and the molar volumes of the liquid ( $V_m(\text{liquid})$ ) have been obtained from eq 1.

Because the experimental uncertainty of the vapor pressure is about 0.08 kPa, the calculation of  $B(T)$  is only significant for vapor pressures higher than 40 kPa. The uncertainty increases dramatically for lower pressures:  $\approx 25\%$  at 25 kPa ( $T = 268$  K) and  $\approx 70\%$  at 15 kPa ( $T = 258$  K). This situation allows us to calculate the second virial coefficients in the relatively narrow temperature range from 278 to 302 K. The results are recorded in Table IX and plotted in Figure 4 together with those calculated from eq 6 and those predicted by McGlashan et al.<sup>26,27</sup> with their empirical correlation, valid for saturated hydrocarbons and  $\alpha$ -olefins, given by the equation

$$B/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (8)$$

where  $n$  is approximately the number of carbon atoms,  $V_c$  is the critical volume, and  $T_c$  is the critical temperature of the liquid. The dashed line drawn in Figure 4 represents the reduced second virial coefficients ( $B/V_c$ ) from eq 8 with  $n = 4$ .

**Deiters Equation of State.** This semitheoretical equation of state was derived by Deiters<sup>4</sup> for a set of spheres interacting through a square-well potential of depth  $-\epsilon$ . The final expression for the pressure is

$$P = \frac{RT}{V_m} \left( 1 + c_0 \frac{4\eta - 2\eta^2}{(1-\eta)^3} \right) - \frac{abR\tilde{T}_{\text{eff}}}{V_m^2} (\exp(\tilde{T}_{\text{eff}}^{-1}) - 1) I_1(\eta) \quad (9)$$

The equation has three adjustable parameters: the characteristic temperature ( $a$ ), the covolume ( $b$ ), and the correction factor for the number of density dependent degrees of freedom ( $c$ ), which can also be interpreted as a shape parameter ( $c = 1$  for spherically shaped molecules).

The three characteristic parameters are related to other physical quantities by

$$a = \epsilon/k_B \quad (10a)$$

$$b = N_A \sigma^3 / \sqrt{2} \quad (10b)$$

$$\tilde{T}_{\text{eff}} = (cT/a + \lambda b/V_m)/\gamma \quad (10c)$$

$$\eta = (\pi/6)\rho\sigma^3 N_A \quad (10d)$$

$\eta$  is the packing fraction;  $c_0 = 0.6887$  is a universal constant which accounts for the deviation of the real pair potential from the rigid-core model, although the repulsive part of the Carnahan–

TABLE X: Parameters for Deiters Equation of State and Standard Deviations of the Pressure and the Density from the Experimental Values Recorded in Table I

$a/K$	$b/\text{dm}^3\cdot\text{mol}^{-1}$	$c$	$\sigma/\text{MPa}$	$\sigma/\text{mol}\cdot\text{dm}^{-3}$
Calculated				
$530 \pm 20^a$	$0.0479 \pm 0.0008^a$	$1.20 \pm 0.01^a$	24.5	0.261
$591 \pm 18^b$	$0.0466 \pm 0.0005^b$	$1.25 \pm 0.01^b$	25.9	0.282
Fitted				
$615 \pm 2$	$0.04800 \pm 6 \times 10^{-5}$	$1.263 \pm 0.002$	2.0	0.019

<sup>a</sup> From critical constants given in ref 19. <sup>b</sup> From critical constants given in ref 22.

TABLE XI: Critical Constants for 2-Butyne

$T_c/K$	$V_c/\text{dm}^3\cdot\text{mol}^{-1}$	$P_c/\text{MPa}$
Literature		
$488.6^a$	$0.221^a$	$5.09^a$
$488.7^{b,c}$	$0.215^{b,d}$	$5.07^{b,d}$
$488.7^{b,c}$	$0.2143^d$	$4.78^d$
$488.7^{b,c}$	$0.2147^d$	$4.72^d$
Calculated <sup>e</sup>		
$487 \pm 4$	$0.221 \pm 0.001$	$4.9 \pm 0.1$

<sup>a</sup> Reference 19. <sup>b</sup> Recommended values in ref 22. <sup>c</sup> Experimental values from ref 22. <sup>d</sup> Calculated in ref 22. <sup>e</sup> Calculated from the fitted values of  $a$ ,  $b$ , and  $c$  of Table X, according to ref 5.

TABLE XII: Parameters for the Square-Well Potential According to the Parameters of Table X (See Text)

$(\epsilon/k_B)/K$	$\sigma/\text{nm}$	$w$
Calculated		
530	0.534	1.369
591	0.529	1.339
Fitted		
615	0.534	1.331

Starling<sup>28</sup> equation has been retained as a good approximation for the hard-body repulsion;  $I_1(\eta)$  and  $\gamma$  are complex functions of  $\eta$  and  $c$  derived from statistical mechanics; finally,  $\lambda = -0.06911c$  is a parameter that introduces three-body effects into the equation of state.

An explicit dependence of the characteristic parameters on the critical constants may be found by solving the set of equations that results from the application of the two conditions of the critical point,  $(\partial P/\partial V_m)_T = 0$  and  $(\partial^2 P/\partial V_m^2)_T = 0$ , to the complete equation of state and obeying the equation of state to reproduce the critical pressure  $P_c$  for a given substance.<sup>5</sup> The *calculated* parameters obtained in this way are unique and temperature independent for a given set of critical constants.

Rubio and co-workers<sup>2,29</sup> have obtained the parameters  $a$ ,  $b$ , and  $c$  by fitting their experimental  $P\rho T$  data to eq 9 and allowing the parameters to be temperature dependent.

In this work, we have used both methods in order to obtain the parameters. The *calculated* parameters, recorded in Table X, have been obtained only from critical data, as explained before, while the *fitted* parameters have been obtained from the fitting of our experimental  $P\rho T$  data to eq 9 and treatment of the three adjustable parameters as independent of temperature, as Deiters proposed in the original papers.<sup>4,5</sup> The temperature dependence of the parameters can be well characterized when the temperature range is at least 200 K and the isotherms are represented by a large number of experimental points. In this work, the temperature range covered by experimental data is about 50 K (subcritical isotherms between  $0.5T_c$  and  $0.6T_c$ ) and the low-temperature isotherms are represented by just a few points below the melting

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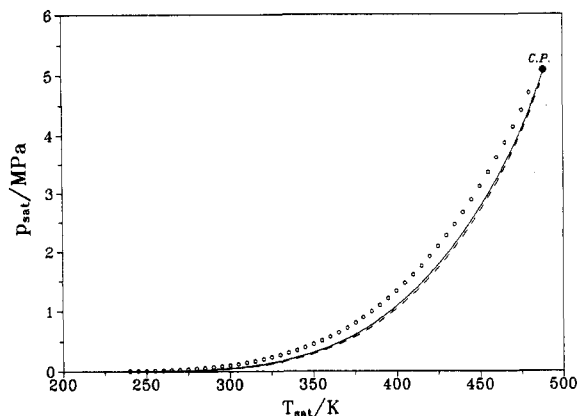


Figure 5. Experimental vapor pressures (O) for 2-butyne, given by parts a and b of eq 3 and predictions from eq 9: —, with the calculated parameters (see text) of Table X; --, with the fitted parameters of Table X. The critical point (●) is denoted as C.P.

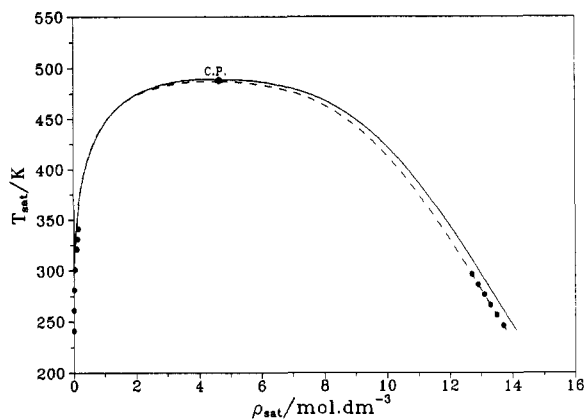


Figure 6. Saturation temperature as a function of density for 2-butyne predicted from eq 9: —, with the calculated parameters (see text) of Table X; --, with the fitted parameters of Table X. The full circles represent the experimental data taken from eq 1 (high densities) and ref 10 (low densities), and C.P. represents the critical point.

line. The variation in the parameters may thus be an artifact of the numerical procedure. These *fitted* parameters are recorded in Table X, together with the standard deviation of the fit.

Table XII records the square-well potential parameters derived from the characteristic constants  $a$ ,  $b$ , and  $c$ . From eq 10a,b,  $\epsilon$  and  $\sigma$  can be directly determined, while the width of the square-well ( $w$ ) is related with  $I_1(\eta)$  through the expression  $I_1(0) = (2\pi\sqrt{2/3})(w^3 - 1)$ .

Once we have determined the parameters, we can use the complete equation of state to calculate some properties of liquid and vapor phases as well as the phase equilibrium. The vapor-liquid phase equilibrium of a pure substance can be calculated by solving the system of equations that results from the requirement that the chemical potentials are equal in both coexisting phases and the molar densities have to be consistent with the complete equation of state.

Both set of parameters, *calculated* and *fitted*, have been used to predict vapor pressure ( $P_{\text{sat}}$ ), saturated liquid and vapor densities ( $\rho_{l,\text{sat}}$  and  $\rho_{v,\text{sat}}$ ), and the second virial coefficient ( $B$ ) as functions of temperature.

We have used only the *calculated* parameters obtained from the critical constants recommended in ref 22 (see Table XI) because we have no additional information about the accuracy of the critical constants given by the other sources.

Figure 5 shows the predicted vapor pressure curves together with the experimental curves given by parts a and b of eq 3<sup>10</sup> up to the critical point.

Saturated temperatures are plotted in Figure 6 against the liquid and vapor densities for both set of parameters.

The comparison of the calculated second virial coefficients ( $B(T)$ ) (for temperatures below the critical point) with several

TABLE XIII: Parameters for the Haar-Kohler Equation of State with the Repulsive Part of Carnahan-Starling Equation

$T/K$	$\sigma_{\text{eff}}/\text{nm}$	$B/\text{dm}^3\cdot\text{mol}^{-1}$
293.19	$0.4971 \pm 0.0002$	$-0.83 \pm 0.01$
283.18	$0.4969 \pm 0.0003$	$-0.86 \pm 0.01$
273.01	$0.4967 \pm 0.0003$	$-0.90 \pm 0.01$
263.09	$0.4965 \pm 0.0005$	$-0.94 \pm 0.02$
257.83	$0.4965 \pm 0.0008$	$-0.95 \pm 0.02$
253.07	$0.4963 \pm 0.0010$	$-0.96 \pm 0.03$
247.59	$0.4962 \pm 0.0015$	$-0.98 \pm 0.04$

predictions are also shown in Figure 4. The calculated second virial coefficients, represented by open circles, are those calculated from eq 9 with the *fitted* parameters recorded in Table X. The  $B(T)$  obtained from the *calculated* parameters are indistinguishable.

The predictions are very satisfactory even at very low temperatures where the extrapolations from other empirical or theoretical equations are very uncertain.

**Haar and Kohler Equation of State.** The purpose of the original paper<sup>6</sup> was to show how the free energy difference function ( $\Delta$ ), defined as

$$\Delta = (f^*/RT - B\rho)_{\text{real fluid}} - (f^*/RT - B\rho)_{\text{hard spheres}} \quad (11)$$

where  $f^*/RT$  is the configurational Hemholtz energy per mole,  $B$  is the second virial coefficient, and  $\rho$  is the molar density, can be used to correlate thermodynamic properties of simple fluids.

From eq 11 and using the integrated form of the Carnahan-Starling equation for  $(f^*/RT - B\rho)_{\text{hard spheres}}$ , the final form of the equation of state is

$$\frac{P}{\rho RT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} + \eta \left( \frac{\partial \Delta}{\partial \eta} - 4 + B^* \right) \quad (12)$$

with  $\eta$ , the packing fraction, given by

$$\eta = (\pi/6)\rho\sigma_{\text{eff}}^3 N_A \quad (13)$$

and

$$B^* = B[6/(\pi\sigma_{\text{eff}}^3 N_A)] \quad (14)$$

where  $\sigma_{\text{eff}}$  is the effective hard sphere diameter and  $B^*$  is the reduced second virial coefficient according to eq 13.

$\sigma_{\text{eff}}$  can be calculated from the intermolecular potential or can be chosen in order to make  $\Delta$  or  $(\partial\Delta/\partial\eta)$  small.<sup>6</sup> The last choice results in a strong dependence of  $\sigma_{\text{eff}}$  with  $T$  but yields a very simple equation of state as function of  $\eta$  and  $B^*$

$$\frac{P}{\rho RT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} + \eta(B^* - 4) \quad (15)$$

Haar and Kohler<sup>6</sup> have used eq 15 to predict second virial coefficients of simple fluids (such as Ar, O<sub>2</sub>, N<sub>2</sub>, or CH<sub>4</sub>), from high-density results, with reasonably good results. Especially interesting are the low-temperature results (i.e.  $T < 0.6T_c$ ) where not only the experimental results but also the empirical correlations (i.e. our eq 6 or 8) and more elaborated theoretical predictions are subject to large errors.

We have fitted our high-pressure experimental results to this equation, and the values of  $\sigma_{\text{eff}}$  and  $B$  obtained from the nonlinear regression procedure are recorded in Table XIII for the different temperatures. The results for  $B$  are also plotted in Figure 4.

A considerable improvement in the results for the second virial coefficient can be obtained by using a model more realistic than the spherical model for the 2-butyne molecule.

The molecular anisotropy can be adequately introduced in terms of the Boublik-Nezbeda<sup>30</sup> equation of state for hard convex body

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TABLE XIV: Parameters for the Haar–Kohler Equation of State with the Repulsive Part of Boublik–Nezbeda Equation of State for Rodlike Molecules

$T/K$	$d_{\text{eff}}/\text{nm}$	$B/\text{dm}^3\cdot\text{mol}^{-1}$
293.19	$0.3466 \pm 0.0002$	$-0.92 \pm 0.01$
283.18	$0.3463 \pm 0.0002$	$-0.95 \pm 0.01$
273.01	$0.3460 \pm 0.0002$	$-0.98 \pm 0.01$
263.09	$0.3457 \pm 0.0003$	$-1.01 \pm 0.02$
257.83	$0.3455 \pm 0.0003$	$-1.03 \pm 0.02$
253.07	$0.3453 \pm 0.0006$	$-1.04 \pm 0.03$
247.59	$0.3451 \pm 0.0012$	$-1.06 \pm 0.04$

fluids following the same scheme used in the derivation of eq 15.

If we redefine  $\Delta$  as

$$\Delta = (f^*/RT - B\rho)_{\text{real fluid}} - (f^*/RT - B\rho)_{\text{hard convex body}} \quad (16)$$

the equation of state, for the special case of  $(\partial\Delta/\partial\eta) = 0$ , becomes

$$\frac{P}{\rho RT} = \frac{1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3}{(1 - y)^3} + \frac{y(B^* - (1 + 3\alpha))}{(1 - y)^3} \quad (17)$$

where  $\alpha$  is the nonsphericity parameter,  $y = \rho v^*$ , and  $B^* = B/v^*$ , with  $v^*$  the molar volume of the hard convex bodies.

We have treated the 2-butyne molecule as a rodlike molecule of length  $L$ . For this model,  $\alpha$  and  $v^*$  can be expressed as

$$\alpha = \frac{(2d_{\text{eff}} + L)(d_{\text{eff}} + L)}{d_{\text{eff}}(2d_{\text{eff}} + 3L)} \quad (18)$$

$$v^* = (\pi/12)d_{\text{eff}}^2(2d_{\text{eff}} + 3L)N_A \quad (19)$$

with  $(d_{\text{eff}}/2)$  being an effective, temperature-dependent thickness

of a hard outer layer parallel to the hard core,<sup>31</sup> which plays an analogous role to that of the effective hard sphere diameter ( $\sigma_{\text{eff}}$ ) of eq 15.

The length  $L = 0.414$  nm of the hard rod core has been obtained as the sum of the interatomic distances taken from the electron diffraction experiments of Pauling et al.<sup>32</sup>

The effective thickness ( $d_{\text{eff}}$ ) and second virial coefficients ( $B$ ) obtained from the correlation of the high-pressure results to eq 17 are recorded in Table XIV. The behavior of  $d_{\text{eff}}$  is similar to that of  $\sigma_{\text{eff}}$ , while the second virial coefficients are much closer to the experimental values, as can be seen in Figure 4.

Similar results can be obtained by leaving both  $\sigma_{\text{eff}}$  or  $d_{\text{eff}}$  as constants over the temperature range studied. This procedure is acceptable for data correlation as well as for the prediction of second virial coefficients, which are obtained within the combined uncertainties, but we think that the inclusion of the temperature dependence is quite interesting in connection with the great number of studies on effective diameters published elsewhere.<sup>33,34</sup>

Nevertheless, these results indicate that eq 15 or 17, although very simple, is suitable to be used in PVT data correlations, yielding a semiquantitative prediction for the second virial coefficient from very high density results.

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**Registry No.** 2-Butyne, 503-17-3.

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## Domain Energies of the Dipolar Lattice Gas

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We analyze the low-temperature behavior of the dipolar lattice gas in two dimensions. Analytic expressions for the energy of single circular, stripe, rippled stripe, and faceted domains for this system have been obtained in the continuum limit. We have also obtained energy expressions for regular arrays of these structures. These analytic results are compared to the results of direct lattice sums to show the applicability of these expressions in predicting equilibrium domain sizes at low temperatures. The energetics of stripe domain rippling are analyzed. Brief comparisons are also made to Monte Carlo simulation results on this system.

### 1. Introduction

Self-organization is known to occur in a variety of biological and chemical systems. The balance of forces entailed in self-organization results in a stunning variety of phases from monolayer domains to micelles to liquid crystalline arrays of large amphiphilic molecules. This topic is of great current interest from both an experimental and theoretical viewpoint.<sup>1–31</sup>

In this paper we address self-organization of domains in a two-dimensional dipolar monolayer at zero temperature. Magnetic

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