

Determination of the parameters of the Migdal equation of state

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Experimental P - ρ - T data near the CO_2 critical point are obtained. The critical exponents β , γ , and δ are determined. The data obtained are approximated by the Migdal equation of state, and a comparison is made with other equations of state.

Migdal^[1] has proposed a phenomenological equation of state for single-component systems near the Curie point and near the critical point of vaporization. We have attempted to verify the accuracy of this equation in the description of the critical point of CO_2 , using experimental P - ρ - T data obtained from measurements with a variable-volume piezometer (see Fig. 1). The piezometer consisted of a horizontal stainless-steel cylinder 1 with inside diameter 15 mm. There were two glass windows 2 in the piezometer to permit observation of the phase boundary. The piezometer volume could be varied from 14 to 20 cm^3 by moving the teflon-sealed steel plunger 3. The piezometer temperature was maintained constant to within 0.0002°K in a 70-liter water thermostat. The temperature was measured with a platinum resistance thermometer. The absence of gradients in the piezometer was recorded by copper-constantan thermocouples.

To accelerate the establishment of equilibrium, the carbon dioxide was stirred with a magnetic agitator. The pressure was measured by a specially graduated MP-60 piston manometer 5 with a mercury seal 6. The mass of the gas was determined by weighing the special steel vials that were used to fill the piezometer. The volume change was determined from the number of turns of the micrometric screw that moved the plunger. The errors in the measurement of the changes in the pressure, temperature, and density were respectively

$$\delta P = 0.0025 \text{ bar}, \quad \delta T = 0.0002 \text{ K}, \quad \delta \rho = 1.3 \times 10^{-4} \text{ mmole/cm}^3.$$

The CO_2 was purified by the usual methods (see, e.g.,^[2]).

The boundary curve was determined from the vanishing of the phase boundary (see Table I), and the critical density from the motion of the phase boundary with changes in temperature. The critical density was taken to be that at which the meniscus ceased to move as $T \rightarrow T_{\text{cr}}$. This density corresponded to the highest temperature (within the error limit of $2 \times 10^{-4}^\circ\text{K}$) at which phase separation was observed; it differs from the value obtained from the rectilinear-diameter rule by 0.03 mmole/cm^3 . For an approximate fit to the data we took the values $\rho_{\text{cr}} = 10.63636 \text{ mmole/cm}^3$ and $T_{\text{cr}} = 304.1524^\circ\text{K}$. The reproducibility of T_{c} for different fillings of the piezometer was within several thousandths of a degree Kelvin. With the chosen values for T_{cr} and ρ_{cr} , determined by the least-squares method (see, e.g.,^[3]), the boundary curve can be approximated, with mean square error 0.029 mmole/cm^3 , by the function

$$|\rho - \rho_{\text{cr}}| = B|\tau|^\beta, \quad (1)$$

where $B = 17.4 \pm 1.3$ and $\beta = 0.324 \pm 0.009$.

Our experimental data for the boundary curve were obtained in the immediate vicinity of the critical point,

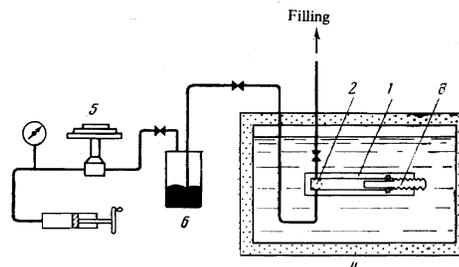


FIG. 1. Experimental apparatus: 1—piezometer, 2—glass windows, 3—plunger, 4—water thermostat, 5—piston manometer, 6—mercury seal.

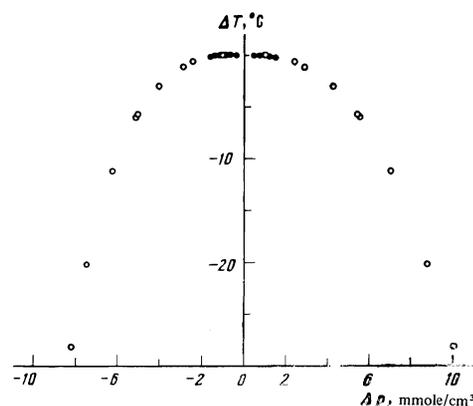


FIG. 2. Boundary curve of CO_2 : ● = our data, ○ = data of Michels et al.^[4]

$\tau \leq 5 \times 10^{-4}$, and despite the stirring it was necessary to evaluate the influence of the gravitational effect on β in our experiments. For this reason we carried out a joint analysis of our data and the data of Michels et al.^[4], which were obtained at some distance from the critical point (see Fig. 2) and thus are less subject to the gravitational effect. This analysis showed that $\beta = 0.348 \pm 0.015$, which agrees within the limits of error with the value of β obtained in our own experiments. This fact indicates not only the compatibility of our measurements with those of^[4], but also the effectiveness of our stirring arrangement in eliminating the gravitational effect.

The experimental values of the pressure and the corresponding density on different isotherms are shown in Tables II and III ($\Delta\rho = \rho - \rho_{\text{cr}}T = T - T_{\text{cr}}$, $P = P - P_{\text{cr}}$; $P_{\text{cr}} = 74.0408 \text{ bar}$).

In the following analysis the data of Tables II and III along each i -th isotherm were approximated by an equation of the Landau expansion type^[5], supplemented by the following terms of the expansion, which permit us to take into account the nonsymmetry of the isotherms above T_{c} :

$$P - P_{cr} = A_i + B_i(\rho - \rho_{cr}) + C_i(\rho - \rho_{cr})^2 + G_i(\rho - \rho_{cr})^3 + H_i(\rho - \rho_{cr})^4. \quad (2)$$

Table IV shows the values of the coefficients for each i -th isotherm, as obtained by the least-squares method, together with the mean square error δP of the approximation.

Taking from Table IV the value of $\chi^{-1} = (\partial P / \partial \rho)_T$ at $\rho - \rho_{cr} = 0$, we obtained the temperature dependence of the compressibility, which may be approximated with mean square error $\delta \chi^{-1} = 0.0021 \text{ mmole/cm}^3 \cdot \text{bar}$ by the function

$$\chi(\rho_{cr}, \tau) = \left(\frac{\partial \rho}{\partial P} \right)_\tau = \frac{1}{\rho_{cr}} \left(\frac{\partial \rho}{\partial \mu} \right)_\tau = C_+ \tau^{-\gamma}, \quad (3)$$

where $C_+ = 0.0082 \pm 0.0003$ and $\gamma = 1.226 \pm 0.007$.

To determine the reliability of our value for the index γ , we also calculated it from the data of Michels et al. [4] in a similar manner and obtained $\gamma = 1.23 \pm 0.07$, which agrees with our values within the limits of error. Figure 3 shows the points that were used to determine γ in our case and in [4].

The critical exponents of the specific heat and the critical isotherm, as specified by the relations $\alpha + 2\beta + \gamma = 2$ and $\beta\delta = \beta + \gamma$, are respectively $\alpha = 0.126 \pm 0.019$ and $\delta = 4.8 \pm 0.1$; the exponent ratio is $\beta/\gamma = 0.264 \pm 0.009$.

To determine independently the values of D and δ pertaining to the critical isotherm, following Roach [6], we used our data for the pressure on the isotherm lying closest to the critical isotherm. The values of $P_e - P_c - B(\rho - \rho_{cr})$ and the corresponding $\rho - \rho_{cr}$ were plotted on a logarithmic scale (here P_c is the pressure on the chosen i -th isotherm at $\rho = \rho_{cr}$, and P_e is the experimental pressure). We found $D = 3.1 \pm 0.1$ and $\delta = 4.3 \pm 0.1$. The value of δ obtained from the analysis of the

TABLE IV

$T - T_{cr}, \text{ K}$	A_i	B_i	C_i	G_i	H_i	$\delta P, \text{ bar}$
0.5149	0.876359	0.063261	0.003089	-0.009764	0.010520	0.0049
1.0026	1.701871	0.111998	0.022348	-0.001393	0.003591	0.0031
1.0116	1.731804	0.112228	0.023942	-0.002052	0.002580	0.0026
1.2977	2.212952	0.149575	0.027094	-0.005232	0.004728	0.0061
1.9976	3.409369	0.258146	0.030373	0.010364	0.003304	0.0018
2.1672	3.695396	0.280349	0.031638	0.019583	-0.006055	0.0016
2.6947	4.609493	0.371782	0.033987	0.017192	0.002771	0.0016
3.0022	5.144304	0.421290	0.035831	0.021216	0.003055	0.0028
3.969	5.820146	0.494629	0.032689	0.035732	-0.002082	0.0058
3.7741	6.470427	0.558895	0.038123	0.026475	0.003508	0.0020

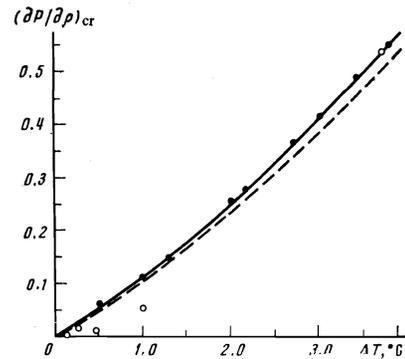


FIG. 3. Elasticity of CO_2 on the critical isochore: \bullet = our data, \circ = data of Michels et al. [4]. The solid and dashed lines were calculated from Eq. (3) for our data and the data of [4] respectively. One point ($(\partial P / \partial T)_{\rho_c} = 1.5322$, $\Delta T = 9.047^\circ\text{C}$) which entered into the determination of γ from the data of [4] is not included, as lying outside the limits of the figure.

isotherm differs from that found above from scaling theory. Also, the Griffiths inequality [7] $\alpha + \beta(\delta + 1) \geq 2$ is not satisfied, since in our case the left side of the inequality equals 1.84. According to Roach [6], a similar situation was observed in He^4 , where $\alpha + \beta(\delta + 1) = 1.89$. This may be a result of the inaccuracy of the method used here and in [6] to determine the exponent δ from an analysis of the data on a noncritical isotherm.

By expanding with the approximating functions (2) we calculated the parameters of the Migdal equation of state, which for the critical point of evaporation of a one-component system may be put in the form

$$P - P_c = (\rho - \rho_{cr})\chi^{-1} + \varphi_3(\rho - \rho_{cr})^3\chi^{-1+2\beta/\gamma} + \varphi_5(\rho - \rho_{cr})^5\chi^{-1+4\beta/\gamma}; \quad (4)$$

$$\chi(\rho_{cr}, \tau) = (\partial \rho / \partial P)_\tau = C_+ \tau^{-\gamma}.$$

Here P_c is the pressure on the critical isochore (P_c equal the values of A_i from Table IV), ρ_{cr} is the critical density, φ_3 and φ_5 are some phenomenological coefficients, and β and γ are the critical exponents. To determine the coefficients φ_3 and φ_5 and the ratio β/γ in Eq. (4) it is convenient to know the values of P and ρ on the isoclines (lines of equal slope) of the family of isotherms. Finding these values from Eq. (2), and thus knowing the pressure at some densities and compressibilities, we used the least-squares method to determine the parameters of Eq. (4), obtaining $\varphi_3 = -0.10174$, $\varphi_5 = 0.001219$, and $\beta/\gamma = 0.284$, with an approximation error $\delta P = 0.030 \text{ bar}$.

To determine the exponents β and γ themselves we used the Migdal relation, which arises from the requirement that the equation of state be analytic as $\tau \rightarrow 0$:

$$\frac{\varphi_5}{\varphi_3} = \frac{2(\beta + \gamma)(\beta + \gamma - 1)(2\beta + 2\gamma - 3)}{\gamma(4\beta + 4\gamma - 5)^2}. \quad (5)$$

Substituting here the values obtained for φ_3 , φ_5 , and β/γ ,

TABLE I. Boundary curve of CO_2

$T, \text{ K}$	$\rho, \text{ mmole/cm}^3$
303.9629	9.04485
304.0335	9.25909
304.0826	9.48376
304.1198	9.71957
304.1419	9.96745
304.1501	10.22830
304.1526	10.50312
304.1524	10.63636
304.1512	10.79317
304.1467	11.09970
304.1281	11.42407
304.0832	11.76804
303.9973	12.13332

TABLE II. Experimental P - ρ - T data near the critical point of CO_2 (first filling of the piezometer)

$\Delta \rho, \text{ mmole/cm}^3$	$\Delta P, \text{ bar}$		
	$\Delta T = 0.5149 \text{ K}$	1.2977 K	2.1672 K
-0.99316	0.8073	2.0329	3.3993
-0.76654	0.8269	2.0844	3.4753
-0.52902	0.8440	2.1432	3.5488
-0.27979	0.8637	2.1677	3.6175
-0.01783	0.8710	2.2021	3.6886
0.25760	0.8857	2.2496	3.7694
0.54769	0.9053	2.2938	3.8625
0.85366	0.9323	2.3575	3.9630
1.17685	0.9691	2.4433	4.0930
1.51874	1.0181	2.5512	--
1.88100	1.1162	2.7105	--
2.26570	1.2730	2.9605	--
2.67461	1.5770	3.3380	--

TABLE III. Experimental P - ρ - T data near the critical point of CO_2 (second filling of the piezometer)

$\Delta \rho, \text{ mmole/cm}^3$	$\Delta P, \text{ bar}$						
	$\Delta T = 1.0026 \text{ K}$	1.0116 K	1.9976 K	2.6947 K	3.0022 K	3.969 K	3.7741 K
-1.59151	1.4501	1.4773	2.9233	3.9423	4.4002	4.9786	5.5153
-1.37728	1.5043	1.5312	3.0066	4.0502	4.5227	5.1135	5.6648
-1.15260	1.5433	1.5704	3.0851	4.1572	4.6428	5.2409	5.8118
-0.91679	1.5849	1.6121	3.1586	4.2604	4.7507	5.3733	5.9540
-0.68892	1.6143	1.6538	3.2346	4.3585	4.8585	5.5032	6.0962
-0.40807	1.6536	1.6881	3.3032	4.4565	4.9713	5.6086	6.2408
-0.13324	1.6879	1.7126	3.3767	4.5620	5.0865	5.7557	6.3977
0.15680	1.7246	1.7481	3.4478	4.6674	5.2115	5.9027	6.5595
0.46333	1.7541	1.7871	3.5336	4.7875	5.3512	6.0645	6.7384
0.78770	1.8006	1.8362	3.6390	4.9321	5.5106	6.2410	6.9492
1.13168	1.8644	1.9023	3.7616	5.1086	5.7042	6.4714	7.1992
1.49695	1.9600	1.9942	3.9381	5.3292	5.9542	--	7.5081
1.88569	--	2.1450	--	5.6356	6.2949	--	7.9199

TABLE V

Parameter	Values obtained from the condition of best fit to the isoclines of the family of isotherms by the Migdal method ¹⁾			Values obtained without including the Migdal equation of state
	$9 \frac{\text{mmole}}{\text{cm}^3} < \rho < 13.3 \frac{\text{mmole}}{\text{cm}^3}$	$\rho_{\text{cr}} \sim \rho < 13.3 \frac{\text{mmole}}{\text{cm}^3}$	$\frac{\text{mmole}}{\text{cm}^3}$	
	2	3	4	5
α	0.09 ²⁾	—	—	0.126 ²⁾
β	0.346 ³⁾	—	—	0.324 ³⁾
γ	1.219	—	—	1.226 ⁴⁾
δ	4.5 ⁶⁾	—	—	4.3 ⁵⁾ ; 4.8 ⁶⁾
β/γ	0.284	—	—	0.264
φ_3	-0.10174	-0.1040	-0.02614	—
φ_5	0.001219	0.001044	0.000066	—
m_0	2.92	2.88	—	—
m_1	3.37	3.28	—	—
B	18.7	17.7	18.8	17.4 ³⁾
C_+	—	—	—	0.0082 ⁴⁾ ; 0.087 ⁷⁾
C_-	0.0019	0.0017	0.018	—
C_+/C_-	4.3	4.8	4.8	4.4 ⁷⁾
D	3.1	3.3	5.8	3.1 ⁵⁾
$C_+ B^{\gamma}/D^{\beta+\gamma}$	1.16	1.11	1.11	1.20
M_c	13.41	12.418	13.260	—
H_c	1633	1512	151.8	—

¹⁾Columns 2 and 3 show the parameters of the Migdal equation of state in coordinates $P-\rho-(\partial\rho/\partial P)_T$; column 4, in coordinates $\mu-\rho-(\partial\rho/\partial\mu)_T$.

In the calculation of the values of the constants in column 2, the independent parameters were taken to be β/γ , φ_3 , and φ_5 , chosen from the condition of best fit to the isoclines, and C_+ from column 5. In columns 3 and 4 the independent parameters were φ_3 , chosen from the condition of best fit, and β , γ , and C_+ from column 5. The remaining parameters in these columns were determined from the Migdal theory.

²⁾Determined from the relation $\alpha + 2\beta + \gamma = 2$.

³⁾Determined from the boundary curve $|\rho - \rho_{\text{cr}}| = B|\tau|^{\beta}$.

⁴⁾Determined from the relation $(\partial\rho/\partial P)_T = C_+ \tau^{-\gamma}$.

⁵⁾Determined from the isotherm.

⁶⁾Determined from the relation $\delta\beta = \beta + \gamma$.

⁷⁾Determined from the relation $(\partial\rho/\partial\mu)_T = C_{\pm} \tau^{-\gamma}$.

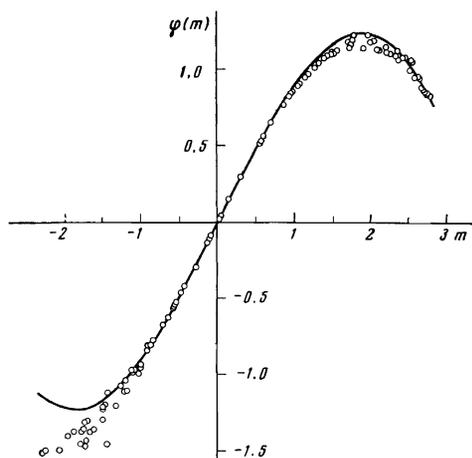


FIG. 4. The solid curve is function (6) with $\varphi_3 = -0.10174$, $\varphi_5 = 0.00129$. The experimental points are the function $\varphi(m) = (P - P_c)(\partial\rho/\partial P)^{\beta+\gamma}$, where $\beta/\gamma = 0.284$.

we found $\beta = 0.346$ and $\gamma = 1.219$. These values agree sufficiently well with those that we obtained above. As a further verification of the Migdal equation of state, we used it to calculate the coefficients C_+ , B , and D in the laws for the temperature behavior of the susceptibility and the density on the boundary curve and the critical isotherm, as well as their dimensionless ratios. The results of comparing these quantities with experiment are shown in Table V.

Figure 4 shows the function $\varphi(m)$, which plays the principal role in the Migdal theory:

$$\varphi(m) = m + \varphi_3 m^2 + \varphi_5 m^5, \quad m = (\rho - \rho_{\text{cr}}) (\partial\rho/\partial P)^{1/\gamma}. \quad (6)$$

The experimental points are also plotted here. The

systematic deviations of the points from the curve, in excess of our experimental error, are related to the nonsymmetry of the CO_2 isotherms with respect to the critical isochor; the Migdal theory in this approximation assumes the presence of such symmetry. To obtain better agreement between theory and experiment, as Migdal has suggested (private communication), we can introduce a term $\sim \tau m^3$ in the expansion (6) which would take into account the nonsymmetry of the isotherms and the boundary curve in the case of a critical point of vaporization. However, in practice this would greatly complicate the comparison of theory with experiment, we shall not attempt it here.

In approximating the experimental data with the Migdal equation there is some question about the correctness of choosing as the "field" the quantity $\Delta P = P(\rho, T) - P(\rho_{\text{cr}}, T)$, since from theoretical considerations the field quantity corresponds to $\Delta\mu = \mu(\rho, T) - \mu(\rho_{\text{cr}}, T)$. However, Fisher^[8] points out that the difference between $\Delta\mu$ and ΔP is small near the critical point, so that $\Delta H \sim \Delta\mu \sim \Delta P$. In order to verify this assumption we carried out an approximation that used $\Delta\mu$ together with ΔP as the field quantity. To obtain the isotherms in the $\mu-\rho$ plane we made use of the relation $d\mu = (1/\rho)dP$ and integrated each isotherm of Eq. (2) in the corresponding manner. The resulting $\mu-\rho$ isotherms were used, in the same way as the $P-\rho$ isotherms above, to calculate the parameters of the Migdal equation of state. However, in the determination of β and γ from the values of φ_3 , φ_5 , and β/γ it was found that Eq. (5) has no real roots. The apparent reason for this is the increased error in the determination of φ_3 , φ_5 , and β/γ related to the additional integration required to find the $\mu-\rho$ isotherms.

To measure the agreement of the values of φ_3 and φ_5 with β and γ we set

$$\varphi_5 = \varphi_3^2 (\varphi_5/\varphi_3^2)^*, \quad (7)$$

where $(\varphi_5/\varphi_3^2)^* = 0.096576$ was calculated from Eq. (5) with $\beta = 0.324$ and $\gamma = 1.226$. In addition, taking $\beta/\gamma = 0.264$ and using Eq. (7), we found φ_3 , and accordingly φ_5 , by using Eq. (4) to approximate the dependence of μ on the density ($\rho_{\text{cr}} < \rho < 13.3 \text{ mmole/cm}^3$) and the compressibility. The same calculations were performed for the isotherms in the $P-\rho$ plane in the same range of ρ ; see Table V. It was found that the values of the coefficients B and M_c , whose dimensionality does not depend on the choice of $\Delta\mu$ or ΔP as the field, and also the dimensionless combinations of the coefficients C_+ , B , and D , agree within the limits of error (see Table V). Thus, within the region near the critical point which we studied we could, without introducing a large error, use $\Delta P = P(\rho, T) - P(\rho_{\text{cr}}, T)$ as the field quantity.

For comparison, we also approximated our data for $\rho_{\text{cr}} < \rho < 13.3 \text{ mmole/cm}^3$ with the Schofield^[9] equations

$$\rho - \rho_{\text{cr}} = r^{3+\gamma} a \theta (1 - \theta^2), \quad T - T_{\text{cr}} = r(1 - b^2 \theta^2), \quad \rho - \rho_{\text{cr}} = r^2 \theta g, \quad (8)$$

where $a = 1515$, $b^2 = 1.34$, and $g = 12.25$; the approximation error $\delta P = 0.02$ bar; and with the Landau equation^[5]

$$P - P_{\text{cr}} = A(T - T_{\text{cr}}) + B(T - T_{\text{cr}})(\rho - \rho_{\text{cr}}) + C(\rho - \rho_{\text{cr}})^2 + D(T - T_{\text{cr}})^2 + G(T - T_{\text{cr}})(\rho - \rho_{\text{cr}})^2 + H(\rho - \rho_{\text{cr}})^4, \quad (9)$$

where $A = 1.692386$, $B = 0.154404$, $C = 0.013188$, $D = 0.006109$, $G = 0.007907$, and $H = 0.004137$; the approximation error $\delta P = 0.031$ bar. As a comparison we may note that the approximation error for our data with

the Migdal equation in the given range of density is 0.02 mmole/cm^3 .

There is a vast amount of discussion in the literature about the validity of the Landau expansion (9). We wish to note here only that despite the increase (to six) in the number of the curve-fitting coefficients, Eq. (9) still gives a large approximation error and leads, as the critical point is approached, to an incorrect qualitative picture of the behavior of the thermodynamic derivatives.

The linear model of the Schofield equation of state and the Migdal equation of state in the second approximation give approximately the same approximation error with our data, and in this sense no preference can be given to either of these equations. This is also apparent from the fact that the constant b^2 in the expression $\tau = r(1 - b^2\theta^2)$, which has the same form in both the linear Schofield model and the parametric Migdal equation in the second approximation, nearly coincides (respective values 1.34 and 1.33). It should be stressed, however, that the expression for b^2 in the Schofield equation was chosen rather from the condition of the best approximation to the experimental data, so that b^2 represents a sort of curve-fitting constant, although it is universal for the systems investigated to within the accuracy of their critical indices. In the Migdal equation there is no such curve-fitting constant, and in this sense it is preferable, since it contains only four fitting parameters (β/γ , φ_3 , φ_5 , C_+) rather than five (β , γ , a , g , b^2) as in the linear model.

We attempted to analyze the Michels^[4] P- ρ -T data for CO₂ in the same manner. The isotherms of Michels were approximated by polynomials of type (2). We then used the Migdal equation to approximate the family of

isoclines of these isotherms. However, because the isotherms in^[4] are not known in such detail as ours and have a much greater scatter than ours, this process led to a clearly unreal value for the ratio $\beta/\gamma = 0.41$. Thus the results of Michels et al.^[4] do not contradict our data, but unfortunately they cannot be used to obtain the critical indices and the isoclinical coefficients by the Migdal method.

In conclusion we wish to thank A. A. Migdal for discussions of this work.

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