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## Scaling Theory of the Critical Region for Systems with Long-Range Forces\*

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A scaling theory of the critical region is developed for systems with a pair potential  $v(\vec{r})$  that falls off like a power of  $r$ , the distance between particles, when  $r$  is large. The development, which leads to the same relations among critical exponents that weak-scaling theory predicts in the case of short-range forces, is associated with an appropriate generalization of Kadanoff's cell-site equations.

It is not clear that Kadanoff's derivation<sup>1,2</sup> of his cell-function-site-function scaling-theory relations is applicable to systems with long-range potentials that fall off as some power of the distance  $r$  between particles when  $r \rightarrow \infty$ . This adds an extra degree of difficulty to the task of evaluating his approach when it is used to predict the critical-exponent relations in systems with long-range potentials. The difficulty is vexing for two reasons. First, real fluids are thought to have just such potentials. Second, models with such potentials are among the very few systems for which interesting results have been obtained by means *other*<sup>3-5</sup> than scaling-theory or series-extrapolation techniques. It is therefore desirable to have scaling-theory results appropriate to such systems at hand for comparison, especially since the series-extrapolation results for long-range potentials are as yet so meager.

In this paper we develop a scaling theory of the critical region for systems with pair potentials of the form

$$v(\vec{r}) \sim -A/r^{d+\sigma} \quad \text{as } r \rightarrow \infty. \quad (1)$$

Here  $A > 0$ ,  $d$  is dimensionality, and  $\sigma > 0$ . The resulting theory has the same critical-exponent relations as the weak-scaling theory that we have already developed for short-range forces.<sup>6-8</sup> In fact, it is the same theory, with the same extra critical exponent  $\theta \leq 1$  that characterizes our earlier modification of scaling-theory results. The cell-site

scaling equations that we associate with our theory prove to be a natural generalization of Kadanoff's equations and, moreover, are as appropriate to short-range as to long-range potentials. They appear to be identical to the cell-site equations recently proposed by Snider<sup>9</sup> when the  $s$  of Eq. (14) is identified with  $d$ .

In the case of short-range  $v(\vec{r})$ , we found it unnecessary to follow Kadanoff in order to develop the weak-scaling relations that we have discussed elsewhere.<sup>6-8</sup> We obtained them instead by using Widom's approach<sup>10</sup> of combining an assumption of thermodynamic homogeneity with the argument that to an appreciable extent density fluctuations manifest themselves in the form of microdomains of conjugate phase. The sole difference between our development and that of Widom lies in our estimate of the order of magnitude of the characteristic size of these microdomains. Widom puts it at  $\xi^d$ , where  $\xi = \kappa^{-1}$  is the fundamental correlation length in the problem (i. e., the largest among the various lengths that can legitimately lay claim to the name of correlation length), while we judge it to be  $\xi^{\theta d}$  in general, with  $\theta \leq 1$ , and with  $\theta$  a non-increasing function of  $d$ . We have given elsewhere<sup>7,8</sup> the rationale for combining the results of this assumption with those scaling relations that do not explicitly involve  $d$ , namely, those that follow from thermodynamic homogeneity plus those that follow from the relation

$$K_T = \xi^{2-\eta} \quad (2)$$

Here  $K_T$  is the isothermal compressibility (susceptibility, in magnetic language) and  $\eta$  can be defined by the assumption

$$F_c(\vec{r}) \sim 1/\gamma^{d-2+\eta}, \quad \gamma \rightarrow \infty \quad (3)$$

where  $F(\vec{r})$  can be taken to be either the density-density correlation function [the  $\hat{F}(\vec{r})$  of our previous papers] or the spin-spin correlation function  $\langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle$ , and the subscript  $c$  refers to the critical value.

For the case of  $v(\vec{r})$  given by (1), it is instructive to begin by following the same line of thought that we have previously pursued for short-range potentials. *A priori*, there is no less reason for believing that thermodynamic homogeneity will be satisfied when  $v(\vec{r})$  is given by (1) than when  $v(\vec{r})$  is of short range, and all available evidence indicates that such homogeneity can be expected for long-range as well as short-range  $v(\vec{r})$ . In particular we have in mind the exact results<sup>3</sup> for the spherical model (SM) when (1) is satisfied, as well as all known van der Waals-like results<sup>11</sup> for systems that have a potential of the form

$$v(\vec{r}) = v_0(\vec{r}) + \lim_{\gamma \rightarrow 0} \gamma^d f(\gamma \vec{r}),$$

where  $f(\vec{r})$  is well behaved and  $\leq 0$ , and  $v_0(\vec{r})$  is short ranged. Likewise, within experimental uncertainty, the behavior of real fluids also appears to be consistent with thermodynamic homogeneity.<sup>2</sup>

The arguments concerning the manifestation of density fluctuation that lead to  $\theta \leq 1$  rather than  $\theta = 1$  also seem as sensible when  $v(\vec{r})$  is given by (1) as when  $v(\vec{r})$  is of short range. In fact, the heuristic argument given in Ref. 6 in support of the conclusion that  $\theta$  is a nonincreasing function of  $d$  with  $\theta < 1$  for large enough  $d$  can equally well be used to conclude that  $\theta$  is a nondecreasing function of  $\sigma$  for fixed  $d$  with  $\theta < 1$  for small enough  $\sigma$ . From the more detailed plausibility argument of Ref. 8, we further anticipate that  $\theta$  is no larger than its Ornstein-Zernike (OZ) value<sup>12,13</sup> (i. e., its spherical-model value<sup>3,13</sup>) for a given  $d$ , which is found to be [through Eq. (10) below]

$$\theta_{\text{OZ}} = \begin{cases} 1 & \text{for } \sigma_m/d > \frac{1}{2} \\ \sigma_m/(d - \sigma_m) & \text{for } \sigma_m/d < \frac{1}{2} \end{cases} \quad (4)$$

Here

$$\sigma_m = \min[\sigma, 2] \quad (5)$$

for  $v(\vec{r})$  satisfying (1), and  $\sigma_m = 2$  for short-ranged  $v(\vec{r})$  for which no  $\sigma$  exists. [Such  $v(\vec{r})$  can always be thought of as being defined by (1) with  $\sigma = \infty$  for the purposes of this paper.]

So far, we have simply assumed that an appro-

priate  $\xi$  exists in the case of  $v(\vec{r})$  given by (1); there remains the problem of precisely defining this  $\xi$ .

When (1) is satisfied,  $\lim[\ln F(\vec{r})]/r$  as  $r \rightarrow \infty$ , which is often used to define  $-\xi^{-1}$  in the short-range case, can be expected to be zero, and when  $\sigma < 2$ , the quantity  $[\int r^2 F(\vec{r}) d\vec{r} / \int F(\vec{r}) d\vec{r}]^{1/2}$ , which also provides a popular definition of  $\xi$ , cannot be expected to exist. However, suitable definitions *do* exist; for example,

$$\xi_1^{2-\eta} = \int F(\vec{r}) d\vec{r} \quad (6)$$

can be used, as can<sup>14</sup>

$$\xi_2^2 = \left[ \int |r|^{2p} F(\vec{r}) d\vec{r} / \int F(\vec{r}) d\vec{r} \right]^{1/p}, \quad (7)$$

with  $\sigma > 2p > 0$ . As long as the dominant contribution to the right-hand sides of (6) and (7) can be assumed to come from an  $F(\vec{r})$  of the form

$$F(\vec{r}) \sim f(r/\xi)/\gamma^{d-2+\eta}, \quad (8)$$

where

$$f(0) = \text{const} \neq 0,$$

then  $\xi_2$  will be independent of  $p$  over its permissible range, and we shall have  $\xi_1 = \xi_2 = \xi$ . Alternatively, we could consider  $\bar{F}(\vec{k})$ , the Fourier transform of  $F(\vec{r})$ . If there exists a  $\kappa$  such that  $\bar{F}(\vec{k})$  is homogeneous in  $k$  and  $\kappa$  for  $k \rightarrow 0$ ,  $\kappa \rightarrow 0$ , then (6) and (7) can again be expected to yield  $\xi_1 = \xi_2 = \xi$ . Even if additional correlation lengths of the form  $\Lambda = \xi^\theta$ ,  $\theta < 1$ , are present in the structure of  $F(\vec{r})$ , as we believe,<sup>7,8</sup> we would not expect them to show up in the dominant contribution to the  $p$ th moment of  $F(\vec{r})$ ,  $p < \sigma$ . Thus if  $\nu$ ,  $\gamma$ ,  $\epsilon$ , and  $\delta - 1$  are defined as usual by the relations  $\kappa \sim t^\nu$ ,  $K_T^{-1} \sim t^\gamma$  for  $m = 0$  and  $\kappa \sim m^\epsilon$ ,  $K_T^{-1} \sim m^{\delta-1}$  for  $t = 0$  [where  $t = (T - T_c)/T_c$  and  $m = (|\rho - \rho_c|/\rho_c)$ ], we still expect

$$(2 - \eta)\nu = \gamma, \quad (2 - \eta)\epsilon = \delta - 1. \quad (9)$$

Taken together with the result of our fluctuation argument,

$$2 = (d - 2 + \eta)\epsilon\theta, \quad (10)$$

and the relations that follow from thermodynamic homogeneity, such as (in standard notation)

$$\beta = \gamma/(\delta - 1), \quad \alpha = \alpha', \quad \gamma = \gamma', \quad (11)$$

$$2\beta + \gamma = 2 - \alpha_s \quad (\text{if } 2\beta + \gamma \neq 2),$$

we have a full set of weak-scaling relations among the most common exponents used in describing fluid in the bulk. One simple way to relate these to previously derived "strong" scaling laws is to introduce  $q$  by means of the relation

$$d - q = \theta d + (1 - \theta)(2 - \eta). \quad (12)$$

Then weak-scaling relations follow from the strong upon replacement of  $d$  by  $d - q$ , which can be seen from (12) to be an "effective dimension" that ap-

pears as a linear combination of the actual  $d$  and  $2 - \eta$ , looking like  $d$  for  $\theta \approx 1$  and like  $2 - \eta$  for small  $\theta$ .

Although we have succeeded in obtaining a set of relations among exponents, it would be reassuring to have an argument such that thermodynamic homogeneity and the asymptotic homogeneity of  $F(\vec{r}, \xi)$  in  $r$  and  $\xi$  come out of, rather than go into, our considerations. The Kadanoff cell-site approach<sup>1,2</sup> provides such an argument. For simplicity we use Kadanoff's magnetic language:  $h$  is field and  $m$  is now magnetization per site. Tildes refer to cell-system properties for cells of length  $L$ . Assuming

$$\begin{aligned}\tilde{h} &= L^x h, \\ \tilde{t} &= L^y t,\end{aligned}\quad (13)$$

we are led by the observation that the cell-system description and site-system description describe the same thermodynamics to the equation

$$G(\tilde{h}, \tilde{t}) = L^s G(h, t), \quad (14)$$

where in the Kadanoff picture  $s$  is identified with  $d$ , and  $G(h, t)$  is (the singular part of) the Gibbs free energy per site. The function  $\tilde{G}(\tilde{h}, \tilde{t}, L)$  discussed below, will denote the Gibbs free energy *per cell*, which is just  $L^d G(h, t)$ . Equation (14) immediately implies thermodynamic homogeneity in the sense of Widom, with

$$\begin{aligned}(x/s)(1 - x/s)^{-1} &= \delta, \\ s/y &= \gamma + 2\beta = \gamma + \beta(\delta + 1), \\ s/y &= 2 - \alpha_s \quad (\text{if } s/y \neq 2).\end{aligned}\quad (15)$$

We note the great generality of this argument for homogeneity. The restriction that  $\tilde{h}/h$  and  $\tilde{t}/t$  should be powers of  $L$ , rather than any smooth functions of  $L$ , is really unnecessary in order to arrive at homogeneity, as Cooper has pointed out.<sup>15</sup> Moreover, no reference whatsoever has been made to the range of the interaction. The only way we can imagine the range entering is via the  $s$  in (14), but in that equation the role of  $L^s$  is simply to define the volume of a cell, once we agree that  $\tilde{G}(\tilde{h}, \tilde{t}, L) = G(\tilde{h}, \tilde{t})$ .<sup>15</sup> However, even if we agree only to a weaker statement  $\tilde{G}(\tilde{h}, \tilde{t}, L) = L^p G(\tilde{h}, \tilde{t})$ , so that the  $s$  in (14) can turn out to be different from  $d$ , one would still have (11). Thus not only does the cell-site scaling argument strongly support thermodynamic homogeneity independent of potential range, but the homogeneity assumption is seen to be weaker and more fundamental than the cell-site assumptions that lead to it.

Kadanoff also concludes that for the asymptotically dominant part of  $F$ , which one expects to depend upon  $\vec{r}$  only through  $|\vec{r}| = r$ , one has

$$F(r, h, t) = L^{2(x-d)} F(\tilde{r}, \tilde{h}, \tilde{t}), \quad (16)$$

where

$$\tilde{r} = r/L. \quad (17a)$$

Here we argue otherwise. It is clear to us that for low enough  $\sigma/d$ , it will be the value of  $\sigma/d$  rather than the scale of the cell length that will principally determine the asymptotic range of the cell-cell correlations, compared to that of the site-site correlations. Hence we consider the scale change

$$\tilde{r} = r/L^{d/z}, \quad (17b)$$

where we might expect  $d/z$  to be a function of  $\sigma$  and  $d$  only through  $\sigma/d$  for small enough  $\sigma/d$ , as long as  $\sigma$  itself is small enough compared to certain numbers in the problem [such as the 2 in Eq. (5)] that determine the  $\sigma$  at which  $\nu(\vec{r})$  can be treated as if it were truly short ranged. [We write the power of  $L$  in (17b) as a ratio involving  $d$  for subsequent notational convenience.]

Our weak-scaling postulate that microdomains of spin fluctuation are generated with a characteristic volume of order  $\Lambda^d \sim \xi^{\theta d}$  rather than  $\xi^d$  enters as follows: Letting  $s_i = \pm 1$  be the site spin and  $\tilde{s}_\alpha$  the corresponding cell variable, also with values  $\pm 1$ , we consider the function  $\mathcal{L}(L)$  defined by

$$\sum_{i \in \alpha} s_i = L^d \mathcal{L} \tilde{s}_\alpha, \quad (18)$$

where  $i \in \alpha$  means that the sum runs over sites in the cell  $\alpha$ . As long as  $0 \ll L/\Lambda \ll 1$  we would expect to be able to approximate  $\mathcal{L}^2$  by

$$\langle s \rangle_L^2 = \sum_{i \in \alpha} \sum_{j \in \alpha} \frac{\langle s_i s_j \rangle}{L^{2d}} \sim L^{-(d-2+\eta)}.$$

However, as soon as we wish to consider all  $L$  such that  $0 \ll L/\Lambda \ll 1$ , we must measure  $L$  on a scale on which  $\xi = \kappa^{-1}$  is the unit of length. On this scale our weak-scaling postulate tells us that  $\mathcal{L}$  will no longer be of the same order of magnitude as the  $\langle s \rangle_L$  defined above; it will have dropped quite precipitously because clusters of mostly up or mostly down spin that attain a diameter of  $\xi$  are so exceedingly rare. We write then

$$\mathcal{L}(L) \sim L^{-(d-2+\eta+f)/2}, \quad (19)$$

where we are introducing  $f \geq 0$  with  $f > 0$  when  $\theta < 1$ , and  $f = 0$  when  $\theta = 1$ . If we could easily guess how rare are clusters of diameter  $L$  for all  $L > \Lambda$  at given  $d$  and  $\eta$ , we could give  $f = f(\theta, \eta, d)$ . Instead we shall let  $f(\theta, \eta, d)$  come out of our scaling theory.<sup>16</sup> To do this we note that since  $m(h, t) = -\partial G(h, t)/\partial h$ , if  $\tilde{m}(\tilde{h}, \tilde{t})$  is defined as  $-\partial \tilde{G}(\tilde{h}, \tilde{t})/\partial \tilde{h}$ , then

$$m(h, t) = L^{x-d} \tilde{m}(\tilde{h}, \tilde{t}), \quad (20)$$

whereas our definition of  $\tilde{s}_\alpha$  implies

$$\langle \bar{s}_\alpha \rangle = \bar{m}(\bar{h}, \bar{t}), \tag{21}$$

and from this and (18) we conclude

$$m(h, t) = \mathcal{L} \bar{m}(\bar{h}, \bar{t}). \tag{22}$$

Taken together, (20) and (22) give  $\mathcal{L} \sim L^{x-d}$ , and comparison with (19) yields

$$x - d = -(d - 2 + \eta + f)/2.$$

From our weakened alternative to (16), given by (3) plus the equation

$$F(r, h, t) = L^{\text{power}} F(\bar{r}, \bar{h}, \bar{t}) \tag{23}$$

along with (17b), we can get the scaling properties of the dominant asymptotic contribution to  $F(\bar{r})$ . They imply

$$F(r, h, t) = L^{-d(d-2+\eta)/s} F(r/L^{d/s}, hL^x, tL^y), \tag{24}$$

from which follows

$$d/zy = \nu, \quad d/xz = \epsilon/\delta. \tag{25}$$

Equation (24) also implies (8), another relation necessary to our weak-scaling theory, from which we have (9). From relations (15), (9), and (25), all other weak-scaling relations follow, with the combination  $sz/d$  appearing as  $d - q$ , according to (10) and (12),

$$sz/d = d - q = \theta d + (1 - \theta)(2 - \eta), \tag{26}$$

showing that  $sz/d$  is playing the role of the "effective dimension" noted below (12), and  $L^{d/s}$  the role of an "effective cell length." The  $\theta$  also appears in a comparison between the way  $F(\bar{r})$  and  $m$  scale. We have

$$\frac{F(r, h, t)}{F(\bar{r}, \bar{h}, \bar{t})} = \left( \frac{m(h, t)}{m(\bar{h}, \bar{t})} \right)^{2/\theta},$$

while in Kadanoff's theory the power on the right-hand side is 2.

We note that if we measure or calculate the usual exponents  $\delta, \eta$ , etc., for a system and find that  $q \neq 0$ , we have no way of telling whether it is  $s \neq d$  or  $z \neq d$  that is responsible. This is consistent with the absence of  $L$  in all our final results and is worth considering further. Suppose for cells of length  $L$  our weak-scaling equations (14), (24), (17b), etc., are satisfied with  $s = d$  and  $z \neq d$ . We can introduce new cells of length  $D = L^{d/s}$  and we have  $F(r, h, t) = D^{2-\eta-d} F(\bar{r}, \bar{h}, \bar{t})$  with  $\bar{r} = r/D$  (so that  $z = d$ ),  $h = hD^x$ ,  $t = tD^y$ , where  $x = \epsilon/\delta$  and  $y = 1/\nu$ . We shall also have  $G(\bar{h}, \bar{t}) = D^s G(h, t)$  with  $s$  equal to the old  $z$ . Thus the question of whether we choose to let  $s = d$  and  $z \neq d$  or  $s \neq d$  and  $z = d$  is a matter of language. Moreover, we see something else worth noting; within the framework of the cell picture, the original scaling formulation is artificially restrictive.

Since  $L$  is a construct in the first place,  $D$  equal to a power of  $L$  should do as well as  $L$  itself as a cell length, and *a priori* we see no reason to single out for special consideration the particular  $D$  that happens to be associated with  $s = d$ .

To our mind, the notable aspect of the above development is not that  $f > 0$  can force a breakdown of cell-site scaling, but that it can do it in such a graceful way that one is left with essentially the same simplicity of the cell-site transformations that makes scaling theory so attractive to begin with.

In the case of the spherical model, the  $x/d = \bar{x}$ ,  $y/d = \bar{y}$ , and  $sz/d = \bar{z}$  that are given in terms of the usual critical exponents by (25) and (26) and the  $\theta$  that is given by (10) can be immediately found, since the critical exponents are known exactly.<sup>3</sup> In terms of  $\sigma_m/d = \sigma^*$  one has, in addition to (4),

$$\bar{x} = \begin{cases} \frac{3}{4} & \text{for } \sigma^* < \frac{1}{2} \\ \frac{1}{2}(\sigma^* + 1) & \text{for } \sigma^* > \frac{1}{2}, \end{cases}$$

$$\bar{y} = \begin{cases} \frac{1}{2} & \text{for } \sigma^* < \frac{1}{2} \\ 1 - \sigma^* & \text{for } \sigma^* > \frac{1}{2}, \end{cases}$$

$$\bar{z} = \begin{cases} 2\sigma^* & \text{if } \sigma^* < \frac{1}{2} \\ 1 & \text{if } \sigma^* > \frac{1}{2}, \end{cases}$$

which imply that  $\delta, \gamma, \beta, \alpha, d\nu, d\epsilon$ , and  $(2 - \eta)/d$  are all functions of  $d$  and  $\sigma$  only through  $\sigma/d$  for  $\sigma < 2$  and also that  $\delta, \gamma, \beta\alpha, d\nu, d\epsilon$ , and  $\eta$  "stick" at their nearest-neighbor (nn) values when  $\sigma > \sigma_m$ . On the basis of their study of the linear Ising chain, Nagle and Bonner<sup>4</sup> (NB) have suggested that for the Ising model these same exponents might depend upon  $\sigma$  and  $d$  again only through  $\sigma/d$  as long as  $\sigma < \sigma_B(d)$ , sticking at their nn values for  $\sigma > \sigma_B(d)$ , where  $\sigma_B(d)$  is no longer 2 but depends (weakly) on  $d$ . It can readily be seen that the NB conjecture is equivalent to the assertion that  $\bar{x}, \bar{y}$ , and  $\bar{z}$  are functions of  $\sigma^*$ , but with  $\sigma^*$  now given by

$$\sigma^* = \min[\sigma/d, \sigma_B(d)/d].$$

A somewhat weaker version of this conjecture that appears very natural within the context of our scaling relations is that  $\bar{x}, \bar{y}$ , and  $\bar{z}$  stick at the values  $\sigma_{B,x}(d)$ ,  $\sigma_{B,y}(d)$ , and  $\sigma_{B,z}(d)$ , respectively, but with  $\sigma_{B,x} \neq \sigma_{B,y} \neq \sigma_{B,z}$  allowable. Regardless of the de-tailed form of  $\bar{x}, \bar{y}$ , and  $\bar{z}$ , it seems clear that their behavior for fixed  $d$  as  $\sigma \rightarrow \infty$  and their behavior for fixed  $\sigma$  as  $d \rightarrow \infty$  are closely related, and one would expect the same set of cell-site scaling laws to apply in both cases.

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<sup>16</sup>The content of footnote 40, Ref. 2, is that if one assumes (17a), one is forced to conclude that  $\mathcal{L} \sim \langle s \rangle_L$ , making it unnecessary to begin by postulating  $\mathcal{L} \sim \langle s \rangle_L$ . In strong scaling this demonstrates the redundancy of the postulate  $\mathcal{L} \sim \langle s \rangle_L$ . If one begins with the weak-scaling postulate that  $f > 0$ , as we do, it demonstrates instead the necessity of replacing (17a) by (17b).

## Activation Volumes of Carbon Diffusion in fcc Iron-Nickel Alloys\*

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The disaccommodation technique was used to determine the activation volume of carbon diffusion,  $\Delta V$ , in six fcc iron-nickel alloys. Measurements were made at temperatures ranging from 68 to 90 °C and pressures up to 6 kbar on samples having a nickel content between 31 and 63 at.%. A maximum activation volume of 3.9 cm<sup>3</sup>/mole was found at 34 at.% nickel. The compositional dependence of  $\Delta V$  is satisfactorily reproduced by a magnetic-energy continuum model in which it is assumed that the activation free energy of diffusion is essentially ferromagnetic in origin.

### I. INTRODUCTION

A thermally activated process is characterized by an activation free energy  $\Delta\phi$ . In the case of diffusion,  $\Delta\phi$  is the free energy difference between the energy minimum and the saddle point in configurational space<sup>1</sup> of the crystal in which diffusion is occurring. The pressure derivative of the activation free energy is the activation volume  $\Delta V$ . Physically, the activation volume of interstitial diffusion represents the change in volume of the crystal when a mole of interstitial atoms simultaneously moves from equilibrium sites to "activated sites."

In order to relate thermodynamic parameters of lattice defects such as the activation volume to the properties of the host crystal a continuum model may be used. In a continuum model the defect is viewed as a distortion of the continuum which displays the properties of the crystal being considered. For an estimate of the activation volume a strain-

energy continuum model<sup>2</sup> has been used, in which the free energy of activation is assumed to be essentially a strain energy. On the basis of this assumption, the activation volume of diffusion was found to be

$$\Delta V_s = 2\left(\gamma - \frac{1}{3}\right)\kappa \Delta\phi, \quad (1)$$

where  $\gamma$  is the Grüneisen parameter and  $\kappa$  is the compressibility of the host lattice. Within the limitations of a continuum model, the activation volumes calculated from Eq. (1) agree with the experimental data except for carbon and nitrogen in iron,<sup>2</sup> which were also the only ferromagnetic systems examined. This apparent discrepancy inspired the investigation of the pressure dependence of the interstitial diffusivity in the nickel-carbon, cobalt-carbon, and iron-silicon-carbon systems, where it was also found that the strain-energy model did not estimate satisfactorily the experimentally de-