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# Lattice gas with random-site energies and theory of novel amorphous metal hydride phase

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A lattice gas with random-site energies is investigated as a model for hydrogen in amorphous metals. The author's recent theory for calculating the chemical potential in a system with many competing interactions is modified to include the random-site energies. Results are qualitatively different from those recently presented by Griessen using simple mean-field (MF) theory. Whereas MF theory predicts no phase separation above a critical value of the site energy width $\Delta$, the present model gives a finite critical temperature $T_c \alpha 1/\Delta$ for large $\Delta$. It also predicts the critical concentration to decrease proportionally to $1/\Delta^2$ and yields a closed-loop, retrograde-solubility phase diagram. Thus, analogous to binary liquids with orientation-dependent interactions, there is a maximum concentration above which no phase separation occurs. For interactions and spread in site energy expected for Pd-based amorphous hydrides, the critical temperature is predicted to be approximately 200—250 K, which may be detectable by heat-capacity or spectroscopic techniques even if it is too low for pressure-versus-composition studies.

## I. INTRODUCTION

Hydrogen in crystalline metals is a system which produces a variety of phase transitions and complex hydride phase diagrams.[1] These have been described with some success by lattice-gas models with pairwise hydrogen-hydrogen interactions.[2] Hydrogen in amorphous metals, however, generally does not exhibit phase changes,[3] even in systems for which a crystalline alloy of the same composition does. Griessen[4] (referred to as RG) has shown that the lack of critical behavior can be explained by a lattice gas with random-site energies, as expected for the amorphous metal. His simple mean-field (MF) treatment predicts no phase transition above a critical value of $\Delta/J_0$ ($\Delta$ is the width of site energy distribution, $J_0$ is the mean-field interaction strength). The MF result is analogous to the Stoner theory of itinerant ferromagnetism with the spread in site energies here playing a similar role to the kinetic energy in a Stoner magnet.

Although RG has successfully explained the basic qualitative feature, there can be quantitative questions (and it turns out qualitative differences) because of his use of the MF approximation. Indeed Hill[5] showed some years ago in studies of adsorption on a heterogeneous surface that although MF predicts no phase transition above a critical $\Delta/J_0$, the improved quasichemical approximation does predict phase separation at sufficiently low temperature for any finite $\Delta/J_0$. MF is known to have severe limitations for lattice gas models as applied to hydrides. It always gives a critical concentration $c_0=\frac{1}{2}$ unless there are concentration-dependent energies which we ignore here ($c_0$ is the number of hydrogen atoms per available interstitial site which is usually less than the hydrogen to metal concentration ratio $x$), whereas in experiment and in more refined theory $c_0$ can be significantly less than $\frac{1}{2}$. MF theory also generally overestimates the critical temperature $T_c$. Both of these shortcomings can be traced to the strong (comparable to $k_B T_c$) interactions of alternating sign which characterize the elastic interactions used in lattice models.[6] I have recently employed a technique[7] (Ref. 7 referred to as I) which gives more reliable results while maintaining much of the analytic simplicity of MF. In particular $c_0$ and $T_c$ were found in I to agree with Monte Carlo calculations to within better than 10% for the same interactions used to model $PdH_x$ and $NbH_x$.

The methods of I are extended here to the case of random site energies. Detailed calculations are performed using the $PdH_x$ interaction parameters, and analytic expressions are obtained valid for large $\Delta$ and to second order in the interaction strength (MF is valid to first order only). In contrast to RG, I find $T_c \propto \Delta^{-1}$ for large $\Delta$ rather than being zero above a critical $\Delta$. This nonvanishing of $T_c$ is consistent with the quasichemical result[5] derived for nearest-neighbor interactions. Further, the critical concentration $c_0$, which is always $\frac{1}{2}$, independent of $\Delta$, in MF, is shown to decrease as $\Delta^{-2}$.

The calculated phase diagrams are closed loops (retrograde solubility) for large $\Delta$ so that there is a finite concentration, of the order of $c_0$, above which phase separation does not take place no matter how low the temperature; and the mixed-phase region is reentrant versus temperature. Such diagrams are well known[8–12] for binary liquid mixtures and have been successfully described by lattice models.[10–12] The diagrams here are novel, however, in that they are for a one-component system and have the lower critical point at zero temperature and concentration (see Fig. 5) rather than at finite values.

The theory of I is extended in Sec. II to include random-site energies. Numerical results for a fictitious amorphous $PdH_x$, that is hydrogen-hydrogen interactions the same as in crystalline $PdH_x$, are presented in Sec. III. Analytic expressions are given in Sec. IV for the large-$\Delta$, weak-interaction limit. These display the features found in the detailed $PdH_x$ calculation. The results are discussed in Sec. V, with emphasis on the physics of the unusual phase diagrams and on the possibility of observing phase separation in random metal hydrides.

## II. THEORY

The lattice gas Hamiltonian is the same as used in I except for the addition of random-site energies:

$$H=\tfrac{1}{2}\sum_{i,j}J_{ij}P_{ij}-\sum_{i}\epsilon_i P_i \ , \tag{1}$$

where $P_i$ is the site occupation number ($P_i=1$ or 0), $J_{ij}$ is the interaction, and $\epsilon_i$ is the random-site energy. Following I, the expectation value of $P_i$, defined as $c_i$, is calculated from the grand-canonical partition function,

$$\mathfrak{z}=\mathrm{Tr}\left[\exp\left[-\beta H+\beta\mu\sum_{j}P_j\right]\right] , \tag{2}$$

$$c_i=\mathfrak{z}^{-1}\mathrm{Tr}\left[P_i\exp\left[-\beta H+\beta\mu\sum_{j}P_j\right]\right] , \tag{3}$$

where $\beta=1/k_BT$ and $\mu$ is the chemical potential determined from the self-consistency condition

$$\sum_{i=1}^{N_I}c_i=N_Ic=N_Mx \ , \tag{4}$$

where $N_I$ and $N_M$ are the number of interstitial and metal atom sites, respectively, and $c$ and $x$ are the concentrations of hydrogen per interstitial site and hydrogen per metal atom, respectively. We had $c_i=c$ in I since all sites were equivalent, but here $c_i$ varies from site to site. The two approximations employed in I are also used here. The first, neglect of correlations $\langle P_iP_j\rangle=c_ic_j$ for $i\neq j$, allows $c_i$ to be written as

$$c_i=V_ie^{\beta\mu}/(V_ie^{\beta\mu}+1) \tag{5}$$

[see Eq. (6) of I], with

$$V_i=e^{-\beta\epsilon_i}\prod_{j}(1+U_{ij}c_{j,i}) \ , \tag{6}$$

where

$$U_{ij}=e^{-\beta J_{ij}}-1 \ , \tag{7}$$

and $c_{j,i}=\langle P_j\rangle_i$ is the expectation value of $P_j$ in an ensemble in which site $i$ is absent or, equivalently, in which $P_i$ is constrained to be zero. The second relates the restricted average to the complete ensemble average by

$$c_{j,i}/(1-c_{j,i})=(1+U_{ij}c_{i,j})^{-1}c_j/(1-c_j) \ . \tag{8}$$

The reader is referred to Eqs. (7)—(16) of I and the surrounding discussion for the meaning of these approximations and the derivation of Eq. (8). An important difference between Eq. (8) here and Eq. (16) of I is that in I it was legitimate to replace $c_{i,j}$ by $c_{j,i}$ since sites $i$ and $j$ were equivalent. With $c_{i,j}=c_{j,i}$ on the right-hand side (rhs) of Eq. (8), one has a single equation for $c_{j,i}$ whose solution is Eq. (17) of I. This simplification cannot be made for inequivalent sites. Use of Eq. (6) allows the determination of $V_i$ in terms of the site-occupation probabilities and $\mu$ is then given from Eq. (5) by

$$\beta\mu=\ln[c_i/(1-c_i)]+\beta\epsilon_i-\sum_{j}\ln(1+U_{ij}c_{j,i}) \ , \tag{9}$$

which is the same as Eq. (18) of I except for addition of the site energy $\epsilon_i$.

The chemical potential $\mu$ is of course the same at each site so that the complete rhs of Eq. (9) is not variable; but the separate terms on the rhs do change from site to site. We therefore take an average over the random distribution of site energies, indicated by curly brackets { }, on both sides of Eq. (9) to obtain

$$\beta\mu=\{\ln[c_i/(1-c_i)]\}-\sum_{j}\{\ln(1+U_{ij}c_{j,i})\} \ , \tag{10}$$

where we have selected the arbitrary zero of energy to be such that $\{\epsilon_i\}=0$ (as noted in I, a nonzero $\{\epsilon_i\}$ can simply be lumped into a redefined $\mu\to\mu-\{\epsilon_i\}$).

We proceed to compute the necessary averages by noting that Eq. (5) may be written as

$$c_i=[1+\exp(-z_0-t_i)]^{-1} \ , \tag{11}$$

where

$$z_0\equiv\{\ln[c_i/(1-c_i)]\}=\{\ln V_i\}+\beta\mu \ , \tag{12}$$

and

$$t_i=\ln V_i-\{\ln V_i\} \ . \tag{13}$$

The quantity $z_0$ is then determined by the condition

$$\{c_i\}=c=\int dt\,\rho(t)[1+\exp(-z_0-t)]^{-1} \ , \tag{14}$$

where $\rho(t)$ is the probability distribution for the random function $t$. Solution of Eq. (14) gives $z_0(c)$ which can then be inserted in Eq. (10) to give $\mu(c)$ provided the second (interaction) term on the rhs of (10) can be expressed in terms of $c$.

Before dealing with the more complex treatment employed in I it is instructive to consider the MF solution as obtained by RG. MF is equivalent to taking $|U_{ij}|\ll 1$ and $c_{j,i}=c_j$ in Eq. (10) whereby it reduces to

$$\beta\mu_{\mathrm{MF}}=z_0+\beta J_0c \tag{15}$$

for the mean-field solution with $J_0=\sum_j J_{ij}$ for $|U_{ij}|\ll 1$, which implies $\beta|J_{ij}|\ll 1$. The fluctuation in $t_i$ is

$$\{t_i^2\}=\beta^2\{\epsilon_i^2\}+\sum_{j}[\{\ln^2(1+U_{ij}c_{j,i})\}-\{\ln(1+U_{ij}c_{j,i})\}^2] \tag{16}$$

if $\epsilon_i$ and $c_{j,i}$ are uncorrelated, which must be true since by its definition [see under Eq. (7)] $c_{j,i}$ cannot depend on properties of site $i$. A further simplification of MF is that terms of the order of $U_{ij}^2$ are ignored so that the interaction term does not contribute to $\{t_i^2\}$. Thus in MF the distribution of $t_i$ is the same as the distribution of $\beta\epsilon_i$ so that $\rho(t)$ in Eq. (14) may be replaced by whatever has been chosen for the distribution of site energies. Thus $z_0$ in (15) is a given function of $c$ and the site energy distribution, and $\mu(c)$ is thereby determined.

Improvement upon MF consists of using Eq. (8) and not making the small $U_{ij}$ approximation in Eq. (10), and also of using a "true" $\rho(t)$ whose width is enhanced by interactions according to (16) rather than $\rho_0(t)$, the distribution of site energies only.

A configurational average of Eq. (8) is obtained as follows. Assume by analogy with Eq. (11) that

$$c_{j,i}=[1+\exp(-z_{ji}-t_{ji})]^{-1}\ , \tag{17}$$

where $z_{ji}=\{c_{j,i}/(1-c_{j,i})\}$ and the random variable $t_{ji}$ has the same distribution as $t_j$ in Eq. (11) for $c_j$. [Examination of the expression for $c_{j,i}$ in Eqs. (11) and (12) of I leads to the conclusion that

$$\{t_j^2\}-\{t_{ji}^2\}=\{\ln^2(1+U_{ij}c_{i,j})\}-\{\ln(1+U_{ij}c_{i,j})\}^2\ ,$$

which is a negligible difference when there are many interaction terms $U_{ij}$ contributing to $\{t_i^2\}$ in Eq. (16), which is the case of interest.] The average of Eq. (8) then becomes

$$z_{j,i}=z_0-\{\ln(1+U_{ij}c_{j,i})\}\ , \tag{18a}$$

$$\{\ln(1+U_{ij}c_{j,i})\}=\int dt\,\rho(t)\ln[1+U_{ij}x(z_{ji}+t)]\ , \tag{18b}$$

with

$$x(u)=(1+e^{-u})^{-1}\ ,$$

which leads to an integral equation for $z_{ji}$. Note that we have taken $\{f(c_{i,j})\}=\{f(c_{j,i})\}$ for any function $f$ of the variable. This is correct for the average as long as $U_{ij}=U_{ji}$ although, as remarked under Eq. (8), it is not true before averaging.

Use of (18a) in (10) gives

$$\beta\mu=z_0-\sum_j(z_0-z_{j,i})\ , \tag{19}$$

where $z_{ji}$ is a function $z_{ji}(z_0)$ from solution of Eqs. (18) and $z_0$ is a function $z_0(c)$ from solution of Eq. (14) in which $\rho(t)$ has been determined self-consistently via Eq. (16). Thus in principle we have obtained the desired solution $\mu(c)$, although it is not entirely satisfactory in terms of a simple closed form expression. To make the situation more tractable we consider, as did RG, a rectangular $\rho(t)$ which allows analytic solution of Eq. (14) and replace $c_{j,i}$ by $c_j$ in Eq. (16), which greatly simplifies calculation of the width of $\rho(t)$. Results based on this are presented in Sec. III, and Sec. IV presents an analytic expression valid for the rectangular distribution and to the order of $U_{ij}^2$ (next highest order in the interaction beyond MF).

## III. CALCULATION FOR RECTANGULAR DISTRIBUTION

For a rectangular

$$\rho(t)=\begin{cases}1/(2\beta\Delta)\ , & |t|\le\beta\Delta\ ,\\ 0\ ,\ |t|>\beta\Delta\ , & \end{cases} \tag{20}$$

the solution to Eq. (14) is

$$z_0=\beta\Delta+\ln[(1-e^{2\beta\Delta c})/e^{2\beta\Delta(1-c)}-1)]\ , \tag{21}$$

as given by RG. Another useful result is for the fluctuation $\sigma_c^2$,

$$\sigma_c^2\equiv\{c_i^2\}-c^2=c/(1-c)-e^{-z_0}[\sinh(\beta\Delta)/\beta\Delta]/[1+e^{-2z_0}+2e^{-z_0}\cosh(\beta\Delta)]\ . \tag{22}$$

Equation (16) may be written as

$$\Delta^2/3=\Delta_0^2/3+\sigma^2\ , \tag{23}$$

where $\Delta^2/3$ is the second moment of the site energy distribution and $\sigma^2$ is the enhancement due to interactions.

The tacit assumption has been made that the variable $t=\beta\epsilon-\ln V$ has a distribution whose mean-square width is given by the sum of the squares of the widths of the separate distributions, which implies Gaussian distributions. $\ln V$ is expected to have a Gaussian distribution because of the large number of terms (many interactions $U_{ij}$) which comprise it, and the given distribution of $\epsilon$ can reasonably be chosen as Gaussian. Thus the rectangular distribution is meant as a convenient approximation to a Gaussian of the same mean-square width whereby simple analytic expressions can be obtained.

A completely self-consistent treatment would require $\sigma^2$ to be determined by simultaneous solution of the system of Eqs. (21), (23), and (18) for each $c_{j,i}$. Considerable simplification is achieved by replacing $c_{j,i}$ with $c_j$ in Eq. (16) so that $\sigma^2$ becomes a function $\sigma^2(z_0,\Delta)$ whereby solution of the single set of two equations (21) and (23) gives $\Delta=\Delta(c)$ which is then used for the distribution $\rho(t)$ for each $c_{ji}$ in Eqs. (18). This is exact to order $U_{ij}^2$, which is sufficient to describe all the qualitative differences from MF and is unimportant in the interesting region of very large $\Delta$ as discussed in Sec. IV.

The required averages of $\ln(1+U_{ij}c_i)$ and $\ln^2(1+U_{ij}c_i)$ cannot be done analytically even for the rectangular distribution. It is not overly time consuming to perform the necessary integrals numerically. However, useful and sufficiently accurate approximations are

$$\{\ln(1+U_{ij}c_j)\}\approx(1-\epsilon)\ln(1+U_{ij}c)+\epsilon c\ln(1+U_{ij})\ , \tag{24}$$

$$\{\ln^2(1+U_{ij}c_j)\}-\{\ln(1+U_{ij}c_j)\}^2 \approx\sigma_c^2[(1-\epsilon^{1/2})\widetilde{U}_{ij}^2+\epsilon^{1/2}\ln^2(1+U_{ij})]\ , \tag{25}$$

where

$$\epsilon=\sigma_c^2/c(1-c)\quad(\epsilon\to0\text{ for }\Delta\to0\ ,\quad \epsilon\to1\text{ for }\Delta\to\infty)$$

and

$$\widetilde{U}_{ij}=U_{ij}/(1+U_{ij}c)\ .$$

Equation (24) is good to more than 1% and Eq. (25) is good to more than 10% for a wide range of values of interest.

Having obtained $\Delta$ as a function $\Delta(c)$, the transcendental Eq. (18a) is solved for each $z_{ij}$ and the result put into Eq. (19) for the chemical potential. The procedure has been carried out for the set of interactions used in I to characterize $\mathrm{PdH}_x$. These, found in Table II of I, give $J_{ij}$ for the first 11 shells and range from $-123$

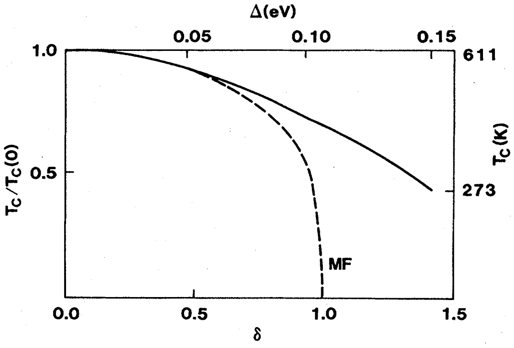

FIG. 1. Critical temperature $T_c$ vs site energy width $\Delta$ for $PdH_x$ interactions. Both normalized and actual values are shown. [$T_c(0)=611$ K is $T_c$ at $\Delta=0$; $\delta=\Delta_0/2T_c(0)$.] Solid curve, results of calculation described in Sec. III. Dashed curve, mean-field (MF) theory as given in Eq. (26)

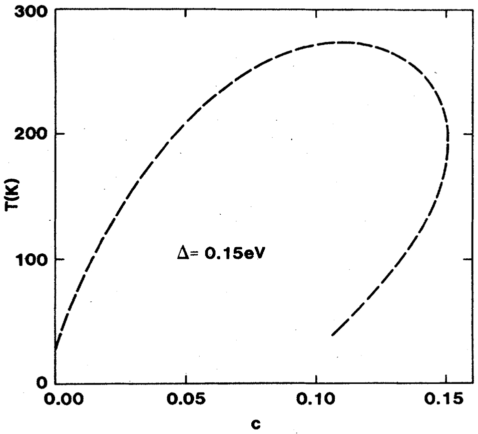

FIG. 3. Spinodal ($d\mu/dc=0$) boundary for same model as in Fig. 1 at $\Delta=0.15$ eV.

$\leq J_{ij}/k_B \leq 400$ K. The remaining long-range elastic interactions, as in I, add an MF term $-\alpha c$ to $\mu$. It takes about 0.05 sec on a Control Data Corporation model CDC Computer 7600 to compute $\mu$ at a given $c$ and $T$.

Results for the critical temperature $T_c$ and critical concentration $c_0$, defined as the points where $\partial^2\mu/\partial c^2 = \partial\mu/\partial c = 0$, are shown in Figs. 1 and 2 as a function of $\Delta_0$. Also shown is RG's result

$$T_c(\Delta)/T_c(0) = 2\delta/\ln[(1+\delta)/(1-\delta)] \;, \tag{26}$$

where he has $\delta=-2\Delta_0/a$ with $a$ the mean-field interaction such that $k_B T_c\,(\text{MF}) = -a/4$. A natural way to transcribe his result is to replace $T_c$ (MF) with $T_c(0)$, the calculated $T_c$ at $\Delta_0=0$, so that $\delta=\Delta_0/2T_c(0)$, which is used for the plot of Eq. (26). The calculated $T_c(\Delta)$ agrees with RG in this manner for $\delta<0.7$ but there is strong departure for larger $\delta$. Whereas RG has $T_c=0$ for $\delta \geq 1$, the $PdH_x$ model calculation shows $T_c$ is only reduced to about 0.64 of its initial value (from 610 to 390 K) at $\delta=1$ and there is no indication of a finite cutoff $\delta$ above which $T_c=0$. The spinodal boundaries ($d\mu/dc=0$), shown in Fig. 3, have the unusual property of giving a maximum $c$ above which there is no phase separation and a reentrant mixed phase. A typical $\mu$-versus-$c$ curve below $T_c$ is presented in Fig. 4.

## IV. LARGE-$\Delta$, SMALL-$J_{ij}$ LIMIT

We obtain here a solution valid to second order in $U_{ij}=\exp(-\beta J_{ij})-1$ which displays analytically the features $T_c \propto \Delta^{-1}$, $c_0 \propto \Delta^{-2}$ in the large-$\Delta$ limit. The condition $|J_{ij}|/k_B T_c(0) < \frac{2}{3}$ is satisfied in the $PdH_x$ model, so an expansion in $U_{ij}$ is reasonable. MF corresponds to going only to first order in $J_{ij}$ and gives poor results for competing interactions because $(\sum_j J_{ij}^2)^{1/2} \sim \sum_j J_{ij}$ so that, as in spin-glasses, significant differences can result from going to $O(J_{ij}^2)$. For example, the $PdH_x$ model (Table II in I) has

$$\left[\sum_j J_{ij}^2\right]^{1/2} / k_B = 1.56\times 10^3 \text{ K}$$

and

$$\sum_j J_{ij}/k_B = -3.37\times 10^3 \text{ K}$$

while

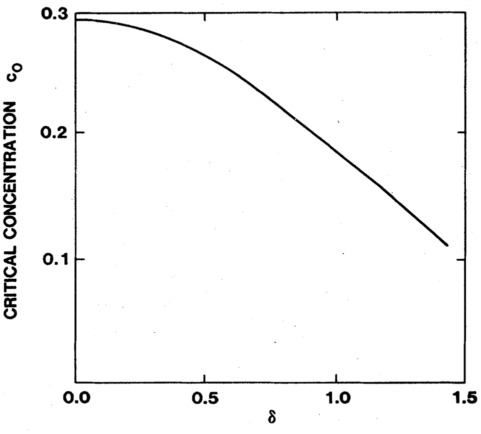

FIG. 2. Critical concentration $c_0$ vs normalized site energy width $\delta$ for same model as in Fig. 1.

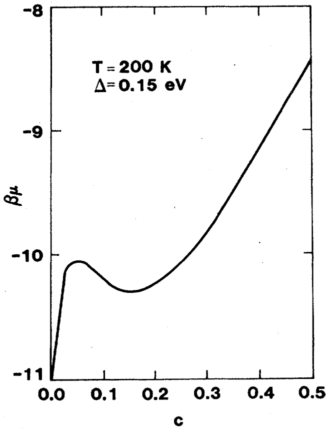

FIG. 4. Chemical potential $\mu$ vs concentration $c$ for same model as in Fig. 1 at $\Delta=0.15$ eV, $T=200$ K.

$$-\sum_j |J_{ij}|/k_B = -17.8\times 10^3\ \mathrm{K}$$

(the MF term $\alpha$ has been included in $\sum_j J_{ij}$ and $\sum_j |J_{ij}|$). Thus if all interactions were the same sign the $O(J_{ij}^2)$ term would be an order of magnitude smaller than the $O(J_{ij})$ term and one might expect MF to be reasonable, but with them alternating in sign the $O(J_{ij})$ term is reduced considerably with a concomitant worsening of MF.

Equation (9) shows that $c_{j,i}$ need be obtained only to $O(U_{ij})$ in order to have a solution for $\mu$ valid to $O(U_{ij}^2)$. Since $c_{j,i}$ is determined from $z_{ji}$ by Eq. (17), it follows that $z_{j,i}$ is only needed to $O(U_{ij})$ whereby the rhs of Eq. (18a) can be replaced by

$$\ln(1+U_{ij}c_{j,i}) = U_{ij}c_j + O(U_{ij}^2)\ ,$$

and thus Eq. (18a) becomes simply

$$z_{ji} = z_0 - U_{ij}c + O(U_{ij}^2)\ . \tag{27}$$

This enables one to compute the average of any function of $c_{j,i}$ in the same way as he would compute the average of the function of $c_j$ with $z_0$ replaced by $z_0 - U_{ij}c$.

To the desired accuracy, Eq. (10) thus becomes

$$\beta\mu = z_0 - \sum_j U_{ij}c(z_0 - U_{ij}c) + \tfrac{1}{2}\{c_i^2\}\sum_j U_{ij}^2\ , \tag{28}$$

where $c(z_0 - U_{ij}c)$ is the concentration determined from (14) with $z_0$ replaced by $z_0 - U_{ij}c$, and since it is only needed to $O(U_{ij})$,

$$c(z_0 - U_{ij}c) = c - U_{ij}c\frac{dc}{dz_0} = c - U_{ij}c\{c_i(1-c_i)\}\ , \tag{29}$$

the second equality following from differentiation of Eq. (14). Using Eq. (29) in Eq. (28) gives the form valid to $O(U_{ij}^2)$,

$$\beta\mu = z_0 - U_1c + \tfrac{1}{2}U_2[3c^2 - 2c^3 + \sigma_c^2(1-2c)]\ , \tag{30}$$

where $U_1 = \sum_j U_{ij}$, $U_2 = \sum_j U_{ij}^2$ and $\sigma_c^2$ is the fluctuation given by Eq. (22). We now take the limit $\beta\Delta \gg 1$ for $c < \frac{1}{2}$ so that $e^{2\beta\Delta(1-c)} \gg 1$ but do *not* assume $e^{2\beta\Delta c} \gg 1$, i.e., allow for $c \ll 1$. Equations (21) and (22) then reduce to

$$z_0 \approx -\beta\Delta(1-2c) + \ln(1-e^{2\beta\Delta c})\ , \tag{31}$$

$$\sigma_c^2 \approx c(1-c) - (1-e^{-2\beta\Delta c})/2\beta\Delta\ . \tag{32}$$

The above may be inserted into Eq. (30) to obtain an expression for $\mu$ which is still complicated because $\Delta$ is not the "bare" site energy width $\Delta_0$ but is enhanced by interactions as in Eqs. (16) and (23). In the same $O(U_{ij}^2)$ approximation these equations become

$$\Delta^2 = \Delta_0^2 + 3U_2[c(1-c) - (1-e^{-2\beta\Delta c})/2\beta\Delta] \tag{33}$$

upon use of Eq. (32). The correction can be neglected for sufficiently large $\Delta_0$, in which case the concentration dependence of $\Delta$ can be neglected in considering the necessary derivatives of $\mu$ for the critical point relations. With this simplification we have, for $c \ll 1$, $\beta\Delta \gg 1$ $(\Delta \approx \Delta_0)$,

$$d\beta\mu/dc = 0 = 2\beta\Delta/(1-e^{-2\beta\Delta c}) - U_1 + \tfrac{1}{2}U_2(1-e^{2\beta\Delta c})\ , \tag{34}$$

$$d^2\beta\mu/dc^2 = 0 = 4\beta\Delta - U_2(1-e^{-2\beta\Delta c})^2\ . \tag{35}$$

The critical concentration from Eq. (35) is

$$c_0 = -(k_BT_c/2\Delta)\ln[1 - 2(\Delta/k_BT_cU_2)^{1/2}]\ , \tag{36}$$

and the equation for $T_c$ becomes

$$2(U_2\Delta\beta_c)^{1/2} = U_1 \tag{37}$$

upon inserting (35) in (33) where $U_2$ and $U_1$ are functions of temperature to be evaluated at $T_c = 1/k_B\beta_c$. In the same spirit of keeping terms up to $O(\beta^2J^2)$,

$$U_1 = -\beta J_0 + \tfrac{1}{2}\beta^2J_e^2\ , \tag{38a}$$

$$U_2 = \beta^2J_e^2\ , \tag{38b}$$

where $J_0 = \sum_j J_{ij}$ is the mean-field interaction and $J_e^2 = \sum_j J_{ij}^2$. The solution to Eqs. (36) and (37) for $\Delta > |J_0|/2$ has

$$k_BT_c = (J_e^2\Delta/J_0)[1-(1-|J_0|/2\Delta)^{1/2}]^2\ . \tag{39}$$

For $|J_0| \ll \Delta$, $k_BT_c = J_e^2/16\Delta$ and $c_0 = J_e^2\ln 2/32\Delta^2$, so there is a transition for finite $\Delta$ even with zero mean field $(J_0 = 0)$.

As mentioned, the above critical-point expressions are valid only if $\Delta \approx \Delta_0$. We can examine the conditions for this by inserting the results obtained from Eqs. (36) and (39) into Eq. (33). For $\Delta \gg |J_0|$, so that the limiting expressions under Eq. (39) may be used, we find

$$\Delta^2 = \Delta_0^2/\{1 - 96c_0^2[2\ln 2(1-c_0) - 1]/2\ln^2 2\}\ . \tag{40}$$

The maximum enhancement occurs at $c_0 = 0.185$ where $\Delta = 1.34\Delta_0$. If $c_0 < 0.01$ the concentration dependence of $\Delta$ can safely be ignored and $\mu$ may be expressed in the normalized form

$$\beta\mu = \ln[(1-y)/y] - 4(1-y)/t\ , \tag{41}$$

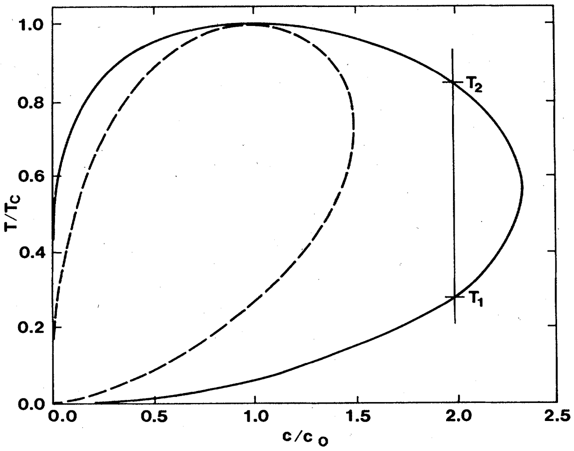

FIG. 5. Normalized phase boundary given by Eq. (41). Dashed curve, spinodal boundary; solid curve, boundary from Maxwell construction. Temperatures $T_2$ and $T_1$ are upper and lower boundary points in connection with Fig. 6.

where $t = T/T_c$ and $y = \exp(-\tilde{c}\ln 2/t)$ with $\tilde{c} = c/c_0$, from which the isotherms can readily be plotted. One can show from Eq. (41) that $c_1 \propto t^2$, $c_2 \propto t\ln(1/t)$, and $\bar{c} \propto t$, where $c_1$, $c_2$, and $\bar{c}$ are, respectively, the two roots of $\partial\beta\mu/\partial c = 0$ and the value of $c$ where $\partial^2\beta\mu/\partial c^2 = 0$. Thus $T = c = 0$ represents a lower critical point so that the diagram is a special case of a closed loop with upper and lower critical points. The resulting phase diagram for both the spinodals and Maxwell equal areas construction[13] are presented in Fig. 5.

## V. DISCUSSION

The above theory has predicted phase separation at arbitrarily large values of the site energy width $\Delta$, whereas MF gives no separation for $\Delta$ larger than the mean-field interaction energy. A closed-loop, retrograde-solubility phase diagram is found for large $\Delta$ instead of the dome-shaped figure generally associated with lattice-gas models. As mentioned in the Introduction, closed-loop diagrams with a finite lower critical temperature and concentration are often found in binary-liquid mixtures. They have been explained[10-12] by orientationally-dependent interactions between molecules of the two species. The following argument, borrowed from the Introduction of Ref. 12, gives a physical picture.

Suppose the system consists of type-$A$ and type-$B$ molecules. There are $A$-$A$ and $A$-$B$ attractive interactions $-J_{AA}$ and $-J_{AB}$, respectively, with $-J_{AB} > -J_{AA}$ so that an $AB$ mixture is energetically favored over an $AA$ segregated phase. (For the purpose of making later analogy with the amorphous hydride, we ignore any $BB$ interaction.) Suppose further, however, that the reduction in entropy associated with ordering via the $AB$ interaction is much greater than that associated with the $AA$ interaction. Then although $AB$ ordering is favored energetically over $AA$ and thus is the lowest temperature configuration, its free energy is disfavored so that $AA$ ordering can be preferred at higher temperatures. The resulting free-energy difference at a fixed $A$ concentration is as sketched in Fig. 6, where temperatures $T_1$ and $T_2$ are as shown in Fig. 5. Above $T_2$ the $AB$ system is mixed with maximum entropy, i.e., the sites are randomly occupied. Below $T_1$ there is again the $AB$ mixture, but it is now ordered so as to take advantage of the $AB$ attraction and has a lower entropy than in the phase separation region $T_1 < T < T_2$, where $AA$ attraction dominates the free energy. The large entropy reduction associated with $AB$ interaction is accomplished in the binary liquid by having a $J_{AB}$ only when the molecules are properly oriented. Thus advantage can be taken of the strong $AB$ attraction only at the expense of a sharp reduction in the number of possible molecular configurations.

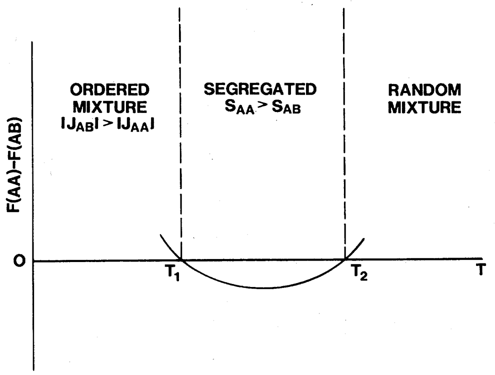

FIG. 6. Schematic free-energy difference vs temperature for $AB$ mixture. $F(AB)$ equals free energy with $A$ uniformly mixed in $B$; $F(AA)$ equals free energy with $A$ molecules clustered together. $J$ and $S$ refer to respective interaction energies and entropies. See text for further details.

For the present situation we identify the $B$ "molecules" with rigid lattice sites so that $J_{AB}$ corresponds to the site energy $\epsilon$, while $J_{AA}$ is the hydrogen-hydrogen interaction. For large $\Delta$, $J_{AB}$ is the dominant interaction but, if there is to be an analogy with the binary liquid, there should be a greater lowering of entropy associated with ordering among the low-energy sites than with ordering to take advantage of attractive hydrogen-hydrogen interactions. It is not immediately obvious that this is true. Consider, however, the partial ordering which can occur with competing interactions. If the concentration of hydrogen at sites which interact attractively with a central occupied site is increased by a small amount $\epsilon$, and the concentration at repulsive-interaction sites is decreased by $\epsilon$, one can show that the energy is lowered by an amount of the order of $J\epsilon$ while the entropy is lowered by the order of $\epsilon^2$. Thus $\delta S_{AA} \sim \delta E^2/J^2$ gives the reduction in entropy required to lower energy by an amount of $\delta E$. On the other hand, a small increase in the concentration of hydrogen at lower energy sites produces the same order changes in entropy and energy; so $\delta S_{AB} \sim \delta E/\Delta$ for the reduction in entropy associated with a lowering of site energy. Hence for a sufficiently low change in energy $\delta E < J^2/\Delta$, a greater entropy reduction is required for the $AB$ interaction and analogy with the binary liquid model is established. Note that for $\delta E \sim k_B T$ the condition $\delta E < J^2/\Delta$ is roughly equivalent to $T \le T_c$ [see Eq. (39)].

The spatial distribution of hydrogen may look random both for $T \gg T_2$ and $T \ll T_1$, but the entropy is quite different. Well above $T_2$, any site may be occupied and a large number of configurations are possible. Well below $T_1$, only a small number of configurations are allowed which minimize the total site energy, but if the static positions of low site energy are arranged at random the hydrogen locations will appear as random also. Only in the intermediate region $T_1 < T < T_2$ is there a relative ordering of the hydrogens.

What is the likelihood of detecting phase separation in amorphous or random metal hydrides? This depends on the values of interaction $J$ and site energy width $\Delta$. The latter has been predicted[14,15] to be

$$\Delta \propto K V_H \,,$$

where $K$ is the bulk modulus and $V_H$ is the volume change upon addition of hydrogen. Measurements[14] show $\Delta$ to be between about 0.16 and 0.23 eV for Pd-Si and Ni-Zr amorphous hydrides and in numerical agreement with the above relation when various constants are put in. Thus if the interactions are the same as used in the $PdH_x$ model for Fig. 1, we should expect to see phase separation below 200—250 K. This is lower than generally studied by pressure versus composition isotherms but still sufficiently high for the hydrogens to establish thermal equilibrium without being "frozen" into a quenched distribution. Thus one might see the phase separation by thermodynamic measurements, such as heat capacity, which are not hindered by surface effects and/or too low a hydrogen equilibrium vapor pressure.

Spectroscopic techniques, such as NMR, Mössbauer, and neutron scattering might also be able to detect local variations in the hydrogen concentration. The retrograde feature presents a problem in that no phase separation will be seen if the hydrogen concentration is too high. Based on Fig. 3, one should keep $c<0.15$. Since $c$ is the concentration per interstitial site, the relation to $H/M$ ratio $x$ is not obvious. If hydrogen occupies tetrahedral sites, of which about 2.5 per metal atom have been estimated to be occupiable,[16,17] the criterion would imply $x<0.4$. But if, for Pd dominant systems, hydrogen, as in the crystal, occupies only octahedral sites[15] of which there are only about 0.25 per metal atom,[16] the figure is reduced to a very small $x<0.04$.

The elastic interaction strength[6] $J$ is of the order of

$$J \propto P^2/K \propto KV_H^2$$

where $P \sim KV_H$ is the dipole force constant. As a consequence the parameter $J/\Delta$ which measures relative importance of the randomness is given by $J/\Delta \propto V_H$.

Since $V_H$ is nearly the same for all hydrides,[18] we expect $J/\Delta$ to be about the same for all amorphous hydrides which have the same relative width of the radial distribution function, the other parameter which determines[14,15] $\Delta$. This would imply that, according to MF, if one amorphous hydride shows no phase separation down to 0 K, all will have similar vanishing of $T_c$. The model here, however, predicts $T_c \propto J^2/\Delta$ for large $\Delta$ and therefore

$$T_c \propto KV_H^3 ,$$

so that one should look for amorphous hydrides with a large bulk modulus. Based on properties of the elements[19] this, for example, would favor Rh and disfavor La as constituents.

The above argument, however, assumes that the elastic interaction is dominant. The picture could change if electronic interactions are important or, as proposed by RG, there is an additional concentration dependence of the chemical potential from a hydrogen-dependent electron density of states.

The calculation presented here is unrealistic in the sense that the interaction $J_{ij}$ has not been taken as random. However, this should not make much difference for the many competing interactions since we already have large variations in $J_{ij}$. In particular, the results of Sec. IV would apply with the simple replacement $J_e^2 = \sum_j J_{ij}^2 \to \sum_j \{J_{ij}^2\}$ where $\{J_{ij}^2\}$ represents a configurational average, and it was already shown there that a net mean field, such as might be destroyed by random interactions, is *not* required to produce the novel phase diagram.

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