

## Sticky Spheres and Related Systems

George Stell<sup>1</sup>

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Some properties of a system of hard-core particles with attractive wells in the Baxter sticky-sphere limit and a related limit are considered, as is the approach to these limits. A demonstration of the result of Stell and Williams that sticky spheres of equal diameter in the Baxter limit are not thermodynamically stable is given, and the way in which size polydispersity can be expected to restore thermodynamic stability is discussed. The implications of these results for the PY sticky-sphere approximation and recent sticky-sphere computer simulations are then examined. It is concluded that the Baxter PY sticky-sphere approximation for a monodisperse system may well be a reasonable one for a slightly polydisperse system of sticky spheres and that existing simulation results may also be relevant to such a system. How polydisperse a system must be in quantitative terms in order for the PY approximation to be useful remains to be seen, however. The question of whether the PY sticky-sphere approximation may prove to be useful and appropriate in describing monodisperse systems with pair potentials for which the attractive wells are *not* extremely narrow is also considered; it is noted that firm evidence concerning this question also appears to be lacking. Implications for systems near, but not in, the limit of zero attractive-well width are also considered, especially in terms of the relative size of the well width and the degree of size polydispersity in the repulsive cores. The possible pertinence of such considerations to colloidal systems is observed. The importance of taking into consideration the extremely long equilibration times that can be expected for systems with very narrow attractive wells is also pointed out, in connection both with real colloidal systems and in computer simulations. It is further observed that in the Baxter limit sticky spheres described quantum mechanically are indistinguishable from hard spheres so described; near the zero-well-width limit, the quantal behavior hinges on the number of bound states and thus the well depth as well as the relative size of the de Broglie thermal wavelength and the well width. Related results and investigations relevant to the issues described above are cited.

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<sup>1</sup>Departments of Chemistry and Mechanical Engineering, State University of New York, Stony Brook, New York 11794.

## 1. INTRODUCTION

In 1968 Rodney Baxter published<sup>(1)</sup> the analytic solution of the Percus–Yevick (PY) approximation for a three-dimensional system of adhesive spheres in thermal equilibrium, treated classically. In 1985, with G. O. Williams, we found that the model, when treated exactly rather than in the PY approximation, is not thermodynamically stable in two or more dimensions. This result was announced and briefly discussed at the 57th Statistical Mechanics meeting at Rutgers,<sup>2</sup> but an analysis has not appeared heretofore in print. We give here the result using a simple argument that does not require the tedious combinatoric details of the original Stell–Williams demonstration. The argument shows directly that the partition function for  $N$  sticky spheres does not exist when  $N \geq 12$ . We also discuss some other extensions of the initial result—in particular, those relating to polydisperse systems of spheres. Since Baxter’s work appeared, a thriving cottage industry has grown up around the use of the solution of the PY equation for this “sticky-sphere” model.<sup>3</sup> The Stell–Williams result calls into question the significance of that solution, and one of the purposes of this paper is to examine some of the issues this raises.

The model Hamiltonian considered by Baxter is defined by the limiting case of a pair potential  $\varphi(r)$  with a hard core and square-well tail for which the well width  $w$  goes to zero as the well depth  $\varepsilon$  goes to infinity in such a way that the contribution of the well to the second virial coefficient remains finite but nonzero. We can realize this limit by letting

$$-\beta\varphi(r) = \begin{cases} -\infty, & r < R \\ \ln\left(\frac{1 + Rw^{-1}}{12\tau}\right), & R < r < R + w \\ 0, & r > R + w \end{cases} \quad (1)$$

where  $\beta = 1/kT$ ,  $k$  is Boltzmann’s constant, and  $T$  is the absolute temperature. Then, taking  $w \rightarrow 0$ , we find that the limiting Boltzmann factor becomes simply

$$\begin{aligned} \exp -\beta\varphi(r) &= \frac{R}{12\tau} \delta(r - R), & r \leq R \\ &= 1, & r > R \end{aligned} \quad (2)$$

<sup>2</sup> The program of this meeting was published in *J. Stat. Phys.* **49**:403 (1987).

<sup>3</sup> There were probably a few dozen such papers in the 1970s and early 1980s (see, e.g., ref. 2 and references therein, which include a comprehensive set of 14 articles on sticky spheres published prior to 1977). Interest in the model and various extensions rapidly increased in the middle 1980s, in part due to the growing perception that it might be of considerable use as a colloid model. The rate of publication on the model continues to increase. We cite here only some representative examples.<sup>(4)</sup> A few more are cited in connection with specific issues below.

where  $\delta$  is a Dirac delta function. For convenience we shall take  $R=1$  below unless we state otherwise. The second virial coefficient is then, in the thermodynamic limit,

$$B_2 = -\frac{1}{2} \int [e^{-\beta\phi(r)} - 1] d\mathbf{r} = (2\pi/3) - (\pi/6\tau) \quad (3)$$

where the integration is over an infinite volume. In this limit, the potential energy of interaction among  $N$  particles is taken to be the sum over the  $N(N-1)/2$  pair potentials. For a finite system in a box of volume  $V$ , the wall-particle interaction that keeps each particle in the box must also be taken into account in the usual way.

The model is easily generalized to  $d$  dimensions; it is convenient to normalize the well-strength parameter  $\tau$  so that for all  $d$ ,  $B_2 = 2^{d-1}v - v\tau^{-1}$ , where  $v$  is the volume of a hypersphere of diameter  $R$ . [In particular, for  $d=1$ , we have  $v=1$  and the  $12\tau$  in Eqs. (1) and (2) becomes  $\tau$ . For  $d=2$ ,  $v=\pi/4$  and the  $12\tau$  becomes  $4\tau$ .]

The Stell-Williams analysis is based upon an examination of the radial distribution function  $g(r)$ , which we write as a Boltzmann factor times a cavity function,  $g(r) = e(r) y(r)$ ,  $e(r) = \exp -\beta\phi(r)$ . In order for the system to be thermodynamically stable, certain integrability conditions on  $g(r)$  must be satisfied. For example, from the virial theorem (with  $P$  the pressure, and  $\rho$  the number density),

$$\frac{\beta P}{\rho} = 1 - \frac{\rho}{2d} \int g(r) \beta \frac{d\phi(r)}{dr} r d\mathbf{r} \quad (4)$$

the volume integral of  $rg(r) \beta d\phi(r)/dr$  [or equivalently, of  $ry(r) de(r)/dr$ ] must exist.<sup>4</sup> For the adhesive-sphere model, for which  $e(r) = H(r) + \text{const} \cdot \tau^{-1} \delta(r-1)$ ,  $H(r)$  a step function, this means that the volume integral of  $ry(r)[\delta(r-1) + \text{const} \cdot \tau^{-1} d\delta(r-1)/dr]$  must exist, which requires that  $y(1)$  be finite. Stell and Williams found that it is not. Expanding  $y(r)$  in  $\rho$ , one finds a  $\delta(r-1)$  singularity of  $O(\rho^{10})$  for  $d=3$  [ $O(\rho^5)$  for  $d=2$ ] and increasingly more singular terms in all higher orders of  $\rho$ , not just at  $r=1$ , but for an infinite discrete set of  $r$  values that becomes arbitrarily dense for sufficiently large  $r$ . [As a result, the volume integral over  $g(r)-1$  is nonintegrable, and the isothermal compressibility is well defined for no thermodynamic state.] In the  $\rho$  expansion of the pressure, for  $d=3$  no virial coefficients beyond the 11th are finite and for  $d=2$  none beyond the sixth are finite.

<sup>4</sup> The internal energy associated with the potential given by Eq. (1) has a logarithmic divergence in the sticky limit, as already noted by Baxter.<sup>(1)</sup> Since only changes in the internal energy are typically of thermodynamic importance, the "infinite additive constant" this weak divergence represents does not in itself constitute a serious impediment to the use of the model.

The possibility of thermal stability in the absence of convergent Taylor-series representations of pressure or correlation functions—a possibility that is realized in model fluids of charged particles as a result of shielding in the correlation functions—is not available in this model. The singularities that appear are far too robust to be resummed away. As we shall see below, the mechanism hinges crucially on the geometry of certain close-packed clusters of equal-sized hyperspheres involving 12 or more spheres in three dimensions and seven or more disks in two dimensions. If we were considering a polydisperse system of hyperspheres with a continuous size distribution, the probability associated with the singularity-producing clusters of equal-sized particles would drop to zero and the stability-destroying mechanism that we have found would disappear. If one backs away from the sticky-sphere limit, one sees that what determines the thermal behavior of a polydisperse square-well model is the size of two length ratios—the square-well width  $w$  relative to the sphere diameter  $R$  and the standard deviation  $\sigma(R)$  of the core diameter distribution about the mean diameter  $\bar{R}$ . When one takes the sticky limit for fixed  $\sigma(R) \neq 0$  one enters a regime [ $w \ll \sigma(R)$ ] in which thermodynamic stability is retained in the sticky limit, and for some range of  $\sigma(R)$  the PY approximation may well be as serviceable and reliable an approximation as it is for less singular potentials. If one then lets  $\sigma(R) \rightarrow 0$ , however, one can expect to lose thermodynamic stability, with the PY result becoming increasingly poor for sufficiently small  $\sigma$ . Just *how* small, however, remains unclear. If instead one considers first taking the monodisperse limit  $\sigma(R) \rightarrow 0$  with arbitrarily small but fixed  $w \neq 0$  [and well depth tuned as a function of  $w$  according to Eq. (1)], one can expect to enter a regime,  $\sigma(R) \ll w$ , in which one has thermodynamic stability, but with anomalous thermodynamics—the smaller  $w$ , the more anomalous the thermodynamics—that is not well described by the PY approximation for  $w \ll \bar{R}$ . If one then takes the sticky limit, the thermodynamics can be expected to become more and more anomalous, and one loses stability in this limit. How small  $w/R$  can be before the PY approximation becomes useless remains to be seen.

We shall discuss some implications of these observations after giving some technical details concerning the singular sticky-sphere behavior.

## 2. SOME TECHNICAL DETAILS

We begin by summarizing the Stell–Williams analysis of  $\gamma(r)$ , which utilizes the well-known graphical representation<sup>(5)</sup> of its density expansion in terms of  $f$  bonds, unlabeled (black)  $\rho$ -vertices, and two white 1-vertices labeled 1 and 2, respectively. (In our Figs. 2 and 3, we suppress the labels

1 and 2 for visual clarity.) The graphs represent integrals divided by their symmetry numbers, with each  $f$  bond representing a function

$$f(r_{ij}) = e^{-\beta\varphi(r_{ij})} - 1$$

each black vertex representing integration over a volume as well as a number-density factor,  $\rho \int d\mathbf{r}_i$ , and the two white vertices representing unintegrated-over variables  $\mathbf{r}_1$  and  $\mathbf{r}_2$ .

In any spatial dimension  $d$ , the most singular contributions associated with each graph of the expansion of  $y(r)$  come from integrand configurations in which the arguments  $r_{ij}$  of some or all of the  $f(r_{ij})$  are of unit magnitude, so that  $f(r_{ij}) = \text{const} \cdot \delta(r_{ij} - 1)$ , and the arguments of all the other  $f(r_{ij})$  are less than unity, for which the corresponding  $f$ 's have the value  $-1$ . All such configurations can be themselves represented by graphs with straight-line  $f$  bonds of unit length and a prefactor  $(-1)^n$  associated with the  $n$  bonds evaluated at  $r_{ij} < 1$ . In one dimension, only graphs that can be embedded in a line need be considered; in two dimensions, only planar graphs, etc. We shall these graphs representing the subset of integrand configurations that contribute to the singularities of the integrands the embedded graphs. Embedded graphs can be thought of as linkages consisting of rigid bonds of unit length joined with rotational freedom at the vertices. The subclass of such graphs that represent rigid bodies turns out to be the most important ones in our analysis—for a given number of vertices they prove to be the most singular ones. [Here we shall be primarily interested in embedded graphs associated with  $y(r)$  and with the  $Q_{N-2}$  (12) of Eq. (5), but it is also useful to consider embedded graphs associated with the  $Q_N$  of (7) and with the density and activity coefficients of  $\ln \Xi$ , where  $\Xi$  is the grand partition function. There again the rigid graphs play a key role.]

For rigid embedded graphs it is convenient to introduce the notion of a degree of singularity  $b - dv + \theta$ , where  $b$  is the number of bonds,  $v$  the number of black vertices, and  $\theta$  represents the number of orientational degrees of freedom available to the graph when the positions of the white vertices are fixed. For graphs with two white vertices,  $\theta = 0$  when  $d = 1$  and 2. When  $d = 3$ ,  $\theta = 1$ , except for the graph consisting of a single bond, for which  $\theta = 0$ . (For graphs with one white circle, which are of interest in analyzing the equation of state,  $\theta = 0$  for  $d = 1$ ,  $\theta = 1$  for  $d = 2$ . For  $d = 3$ ,  $\theta = 3$ , except for the single-bond graph, for which  $\theta = 2$ .) One expects the rigid graphs associated with  $y(1)$  to have a positive index; when  $b - dv + \theta = 1$ , there is a  $\delta$ -function singularity. When  $b - dv + \theta > 1$ , the singularity is nonintegrable. When one considers the graphs associated with  $y(1)$  for  $d = 1$ , it is instructive to consider the case  $v = 2$  in some detail, and we illustrate this case in Fig. 1, which has been drawn and captioned to be

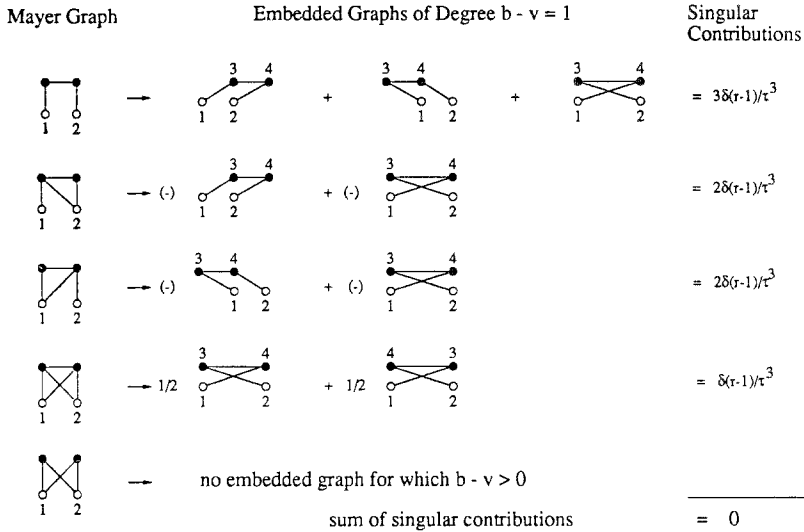


Fig. 1. Graphs of order  $\rho^2$  contributing to  $\gamma(r)$  at  $r=1$  in one dimension. There are  $\delta$ -function contributions from three of the four cluster integrals (Mayer graphs) contributing to  $\gamma(1)$ , but they cancel. Note that all of the embedded graphs represent configurations that are not physically realizable for four particles labeled 1, 2, 3, 4 because of their hard cores. Such unrealizable configurations do not contribute to  $\gamma(1)$ , which for  $d=1$  proves to be nonsingular.

largely self-explanatory. We see there that all the singular  $\delta$ -function contributions cancel, so they do not appear in  $\gamma(1)$ ; they are all associated with configurations of four particles that are physically unrealizable because of the hard cores of the particles. It turns out that for any  $d$  such unrealizable configurations do not contribute to  $\gamma(1)$ ; only realizable configurations can contribute to the singular structure of  $\gamma(r)$  or to the virial coefficients of the equation of state. We note that the results in Fig. 1 immediately imply that for  $d=1$  both the PY and HNC (hypernetted chain) approximations yield no thermodynamics for  $d=1$  because they are both lacking the bridge diagram shown on the fourth line of graphs. (This was first pointed out by Hiroike in a nongraphical analysis of the fourth virial coefficient.<sup>(6)</sup>)

The Stell-Williams analysis hinges on the “realizability theorem” that only realizable particle configurations contribute to sticky-sphere thermodynamics, the term-by-term verification of which proves to be extremely tedious. One can profitably use the Ree-Hoover<sup>(7),5</sup>  $f$ -bond,  $(f+1)$ -bond resummation of Mayer graphs to obtain the result through the seventh virial coefficient for  $d=2$ . Wertheim’s<sup>(9)</sup>  $z$ -vertex,  $f_R$ -bond,  $(s\text{-mer})$ -hyper-

<sup>5</sup> See ref. 8 for the extension to graphs in  $\gamma(r)$ .

vertex expansions for  $\ln \Xi$ ,  $\rho_1$ , and  $\rho^2 g(r)$  provide the most powerful general means we have found for obtaining the result. His representation can be used conveniently to analyze the additivity expansions of those functions, since all singularities appear in the structure of the hypervertices. The results then can be used to immediately yield the singularities in the density expansions of  $\ln \Xi$  and  $g(r)$  and to show that only realizable configurations can contribute to the singular structure of both the activity and virial coefficients.

Here we shall follow a simpler approach to demonstrate directly the singularity in the cavity function at  $r = 1$  and the lack of thermodynamic stability for a system of  $N$  particles when  $N \geq 7$  for  $d = 2$  and  $N \geq 12$  for  $d = 3$ . It begins with the observation that for a canonical system of  $N$  particles in a box  $\Omega$  of volume  $V$  the pair distribution function  $g(\mathbf{r}_1, \mathbf{r}_2)$  is given for  $\mathbf{r}_1$  and  $\mathbf{r}_2$  in  $\Omega$  by

$$g(\mathbf{r}_1, \mathbf{r}_2) = V^2 Q_{N-2}(12) / Q_N \quad (5)$$

where  $Q_{N-2}(12)$  is the configuration integral for two fixed particles in the system

$$Q_{N-2}(12) = \int e^{-\beta\Phi(1 \cdots N)} d\mathbf{r}_3 \cdots d\mathbf{r}_N \quad (6)$$

and  $Q_N$  is the configuration integral for free particles in the system

$$Q_N = \int e^{-\beta\Phi(1 \cdots N)} d\mathbf{r}_1 \cdots d\mathbf{r}_N \quad (7)$$

Here  $\Phi(1 \cdots N)$  is the potential energy of the system. For convenience we shall consider a system of  $N - 2$  sticky spheres and 2 particles labeled 1 and 2, respectively, that interact as sticky spheres with the other  $N - 2$  spheres but interact with each other as ideal-gas particles. Then  $g(\mathbf{r}_1, \mathbf{r}_2)$  is the cavity function  $y(\mathbf{r}_1, \mathbf{r}_2)$ . [In fact, one could let particles 1 and 2 interact as hard spheres without any change in our analysis, since we are only concerned with  $y(\mathbf{r}_1, \mathbf{r}_2)$  for  $r \geq 1$ .] The wall-particle interaction will not enter our discussion, but for simplicity we shall assume it to be a hard-sphere/hard-wall interaction for all particles, so that all the  $\int d\mathbf{r}_i$  in (6) and (9) are over the volume  $V$  available to the center of a hard sphere in the box, which is the same  $V$  that appears in Eq. (5). Then  $\Phi$  can be taken to be simply a product of two-particle Boltzmann factors

$$e(r_{ij}) = e_R(r_{ij}) + e_A(r_{ij}) \quad (8)$$

for all  $i < j$  except  $i = 1, j = 2$ , where  $e_R$  is the repulsive hard-sphere term and  $e_A$  the attractive  $\delta$ -function term. The  $e(r_{12})$  is 1. The integral in the

numerator of (5) can be expressed as a graph with  $N$  vertices,  $N-2$  of which are black and unlabeled and 2 of which are white and labeled 1 and 2, respectively, with  $e$ -bonds representing the  $e(r_{ij})$  of (8) between all pairs of particles except 1 and 2.

It is clear that the most singular contribution to  $y(\mathbf{r}_1, \mathbf{r}_2)$  from  $Q_{N-2}(12)$  will come from the  $\delta$ -function parts of the interaction. It is also clear that the  $e_R$  parts of the Boltzmann factors prevent nonrealizable configurations of particles 1, ...,  $N$  from contributing to the integrands of both  $Q_{N-2}(12)$  and  $Q_N$ . Thus when we consider the embedded graphs with  $e_A$ -bonds associated with  $Q_{N-2}(12)$  and  $Q_N$  we need consider only realizable configurations. For simplicity, we shall also limit our discussion to rigid embedded graphs, which we can most simply order with respect to degree of singularity. For a given  $N$ , the most singular graphs are rigid.

For  $d=1$ , the only singular graph for each  $N$  is the chain graph and the  $\delta$ -function singularity is integrable. There is no realizable embedded graph corresponding to  $y(\mathbf{r}_1, \mathbf{r}_2)$  at  $r_{12}=1$ , however. For  $d=2$  the smallest  $N$  for which there is a  $\delta$ -function singularity in a realizable embedded graph of  $Q_{N-2}(12)$  is  $N=4$ . The  $\delta$ -function is loaded at  $r_{12}=\sqrt{3}$ . The smallest  $N$  for which one finds a  $\delta$ -function singularity at  $r_{12}=1$  is  $N=7$ . For  $d=3$  the smallest  $N$  for which there is a  $\delta$ -function singularity in a realizable embedded graph of  $Q_{N-2}(12)$  is  $N=5$  and it is loaded at  $r_{12}=(8/3)^{1/2}$ . The smallest  $N$  for which one finds a  $\delta$ -function singularity at  $r_{12}=1$  is  $N=12$ . The graphs corresponding to these singularities are shown in Fig. 2. For  $d=2$  and  $d=3$  there is an infinite number of graphs associated with  $Q_{N-2}(12)$  for large  $N$  that have nonintegrable singularities, both at  $r_{12}=1$  and at an infinite number of other  $r_{12}>1$ . Two of these are shown in Fig. 3.

Instead of investigating  $y(r_1, r_2)$  through  $Q_{N-2}(12)$  as we have just done, one can alternatively examine  $Q_N$  directly for a system of  $N$  sticky spheres. Since the configurational Helmholtz free energy of the system is given by

$$-\beta F^{\text{CONF}} = \ln Q_N \quad (9)$$

one can determine for each  $d$  the smallest  $N$  for which  $Q_N$  is not finite. This determines the  $N$  for which the system becomes thermodynamically unstable for fixed  $V$ . The analysis is much like that of  $Q_{N-2}(12)$ , since the graphs are the same, except that all vertices are unlabeled and there is an additional  $e$ -bond. One finds that when  $d=2$ ,  $Q_N$  becomes infinite for  $N \geq 7$ . When  $d=3$ ,  $Q_N$  becomes infinite for  $N \geq 12$ ; this is fully consistent with the results for  $Q_{N-2}(12)$  and is probably the most direct approach to establishing the thermodynamic instability of the Baxter sticky-sphere model for  $d \geq 2$ . It immediately implies that one loses stability in the ther-



modynamic limit for both  $d=2$  and  $d=3$ . We note that it is clear that one similarly has no stability for  $d>3$ . We also note that for the system used in analyzing  $Q_{N-2}(12)$ ,  $Q_N$  is still finite for  $N=7$  when  $d=2$  and for  $N=12$  when  $d=3$  because of the absence of the  $e$ -bond between particles 1 and 2. It is for this reason that we did not have to bring into the picture the behavior of the  $Q_N$  in the denominator of (5) when determining the  $N$  for which the behavior of  $y(\mathbf{r}_1\mathbf{r}_2)$  becomes singular at  $r_{12} = 1$ .

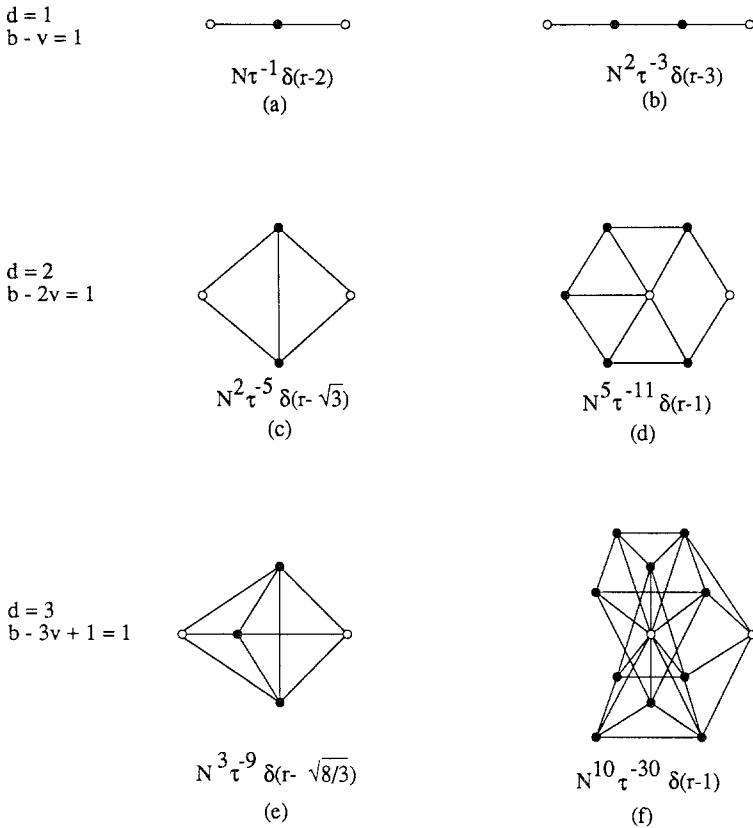


Fig. 2. The simplest realizable embedded graphs with  $\delta$ -function singularities in  $y(\mathbf{r}_1\mathbf{r}_2)$  for  $d=1$  (a, b),  $d=2$  (c, d), and  $d=3$  (e, f). The order in  $N$  and  $\tau$  of the  $\delta$ -function and the  $r = |\mathbf{r}_1 - \mathbf{r}_2|$  at which it is loaded is shown below each graph. The graphs for which the  $\delta$  is loaded at  $r=1$  are the lowest-order graphs (in both  $N$  and  $\tau^{-1}$ ) that contribute to thermodynamic instability. With a bond between the pair of white vertices and those vertices blackened (increasing the power of both  $N$  and  $\tau^{-1}$ ), these graphs carrying  $\delta(r-1)$  become the embedded graphs that give rise to the lowest-order singularities in the  $N$ -particle partition functions and in the activity ( $z$ ) and density ( $\rho$ ) expansions of  $\beta P$ , the order in  $N$  corresponding to the order in  $z$  and  $\rho$ , respectively.

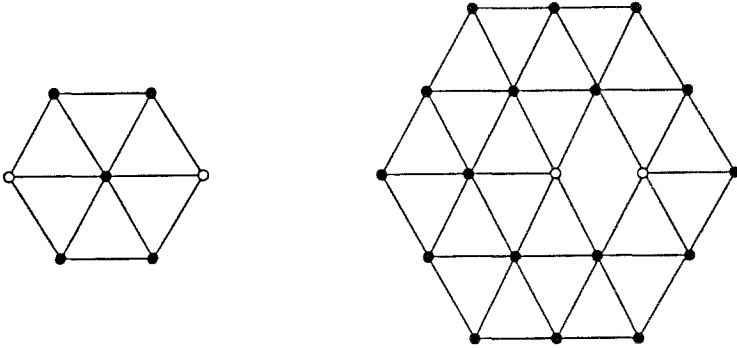


Fig. 3. Two of the infinite numbers of dangerous embedded graphs in  $d=2$  that represent nonintegrable terms in  $y(r)$ . The first has a nonintegrable singularity at  $r=2$ , the second at  $r=1$ . Upon integration over the white vertices the graphs represent nonintegrable terms in the configuration integrals  $Q_7$  and  $Q_{19}$ , respectively.

An analogous analysis in the grand ensemble can be similarly made. Instead of a single  $Q_{N-2}(12)$  and  $Q_N$  for a given  $V$ , one must consider all the  $Q_N$  and  $Q_{N-2}(12)$  for  $N$  up to the close-packing  $N$  and form the grand partition function  $\Xi$  and the corresponding activity series of  $Q_{N-2}(12)$  that defines the  $\Xi(12)$  in the numerator of the fraction  $\Xi(12)/\Xi$  that defines the two-particle density function  $\rho(\mathbf{r}_1, \mathbf{r}_2)$ . The divergences in  $Q_N$  for  $N \geq 7$  when  $d=2$  and  $N \geq 2$  when  $d=3$  mean that one always has these infinities in the  $\Xi$  (unless  $V$  is miniscule) and thus will have these infinities in  $\ln \Xi$  for *any* value of the activity (unless  $V$  is miniscule). This again demonstrates thermodynamic instability.

One can ask questions that require one to go beyond the analyses we have so far made here. They pertain to the structure of the density and activity expansions for an infinite system of square-well particles with a pair potential given by Eq. (1), as one goes to the sticky limit by letting  $w \rightarrow 0$ . Which terms in the expansions diverge? And how do they grow as a function of  $w$ ? We have already directly verified that the seventh coefficient in two dimensions and the 12th coefficient in three dimensions are the lowest-order coefficients to diverge in both the density and activity expansions of the equation of state. The question of how fast the divergent coefficients grow as  $w \rightarrow 0$  is a much more subtle question that we are currently investigating with Branko Borstnik.

### 3. WHAT DOES IT ALL MEAN? SOME REMARKS

(i) In light of our analysis, what is one to make of the PY approximation for sticky spheres, or of the existing Monte Carlo simula-

tion results<sup>(10)</sup> for sticky particles? With regard to the latter, it is clear that the “dangerous” large close-packed clusters that yield the singularities responsible for loss of thermodynamic stability have simply not been sampled. Here the situation is not too different from that which one would have for a slightly polydisperse system, where clusters such as those associated with the graphs of Fig. 2c for  $d=2$  and Fig. 2e for  $d=3$  will still occur with appreciable probability, because they can be realized by having four disks and five spheres all in contact, respectively, even when all the disks and all the spheres have different diameters. The bonds will no longer all be of unit length, but each bond  $f(r_{ij})$  will still be of length equal to  $(R_i + R_j)/2$ , where  $R_k$  is the diameter of the sphere centered at  $\mathbf{r}_k$ . However, the “dangerous” clusters [associated with nonintegrable terms in  $g(r)$ ] will only be found with zero probability in a polydisperse system, since they involve the geometry of equal-sized particles in order to be realized. [Thus, for example, the graph of Fig. 2d with each  $f(r_{ij})$  bond of length  $(R_i + R_j)/2$ ,  $R_k$  all different, cannot be realized, and the graph of Fig. 2f cannot be realized with each  $f(r_{ij})$  of length  $(R_i + R_j)/2$  such that  $r = (R_1 + R_2)/2$ .]

(ii) With respect to the status of the PY sticky-sphere approximation for  $d=3$ , some of the same considerations appear to be relevant. First of all, one can formulate and solve the PY sticky-sphere approximation for  $d=3$  for a polydisperse system with a continuous size distribution. (In fact the solution is already implicit in the extension of Baxter’s solution to mixtures with a discrete number of species made by Barboy.<sup>(11)</sup>) Such a system is free of dangerous clusters and hence appears to be thermodynamically stable so the PY approximation may well yield a reasonable assessment of some of its thermodynamic and structural properties, in much the same way that the approximation does for a number of other fluid models. There are certain dramatic structural features of the exact  $\gamma(r)$  that are guaranteed to be missed by the PY approximation (such as the  $\delta$ -function contribution from the graphs appearing as Figs. 2c–2f), but such structural features may contribute little to, say, the physically important scattering function in Fourier space, because Fourier transforming will be a smoothing operation for such features and also because one averages over the size distribution in both  $R_1$  and  $R_2$  to get the scattering function. Moreover, when  $\sigma(R) \rightarrow 0$ , the usual (single-diameter) PY result will be recovered from the PY polydisperse result and will be a good approximation to that result for  $\sigma(R) \ll \bar{R}$ , where  $\bar{R}$  is the mean diameter. In terms of certain real systems such as colloids, in which the solvent-averaged  $\varphi(r)$  may have an attractive well of range  $w$  that is very narrow compared to  $\bar{R}$  and for which there can also be appreciable polydispersity, the possible relevance of the sticky-sphere PY approximation hinges in part on the

relative values of  $w$  and  $\sigma(R)$ . For  $w \ll \sigma(R) \ll \bar{R}$  the usual monodisperse PY approximation might well be useful and appropriate, but for  $\sigma(R) \ll w \ll \bar{R}$  the PY approximation will inevitably become poor when the ratios  $\sigma(R)/w$  and  $w/\bar{R}$  both become sufficiently small. An outstanding question is how small. There has been one comparison<sup>(12)</sup> of polydisperse sticky-sphere results for turbidity with experimental colloid results that suggests the sticky-sphere results are sensible and useful for the silica colloids used in that comparison.

(iii) In the case of a strictly monodisperse system, the above considerations lead to the conclusion that as one takes the sticky limit,  $w \rightarrow 0$  in Eq. (1), starting with  $w = 1$ , say, the PY solution will begin to depart more and more drastically from the exact structure of the model, which becomes more and more anomalous, until in the limit, the model loses thermodynamic stability. One is at present hampered in seeing exactly how this comes about by the technical difficulties involved in backing away from the sticky limit in the cluster-integral analysis, but it seems likely that the "dangerous" cluster integrals are negligible until  $w$  becomes quite small, when they begin to diverge very rapidly and nonuniformly with the dangerous graphs of lower index  $b - dv + \theta$  at first numerically dominating the higher-index graphs, but then as  $w$  gets smaller and smaller, the higher-index graphs overwhelming the lower-index graphs. This picture leads to the conclusions—perhaps paradoxical at first glance—that the PY sticky-sphere solution is a much more reasonable approximation for the potential of Eq. (1) when  $w$  is *not* very much smaller than  $R$  than when it is. However, if the limiting catastrophe outlined above is sufficiently nonuniform, one could imagine the thermodynamics becoming anomalous in a pronounced way only when  $w$  is very, very small—say,  $w \approx R/100$  or  $R/1000$  or  $R/10,000$ —so that the PY solution might track the true sticky-sphere behavior reasonably well over a very wide range of  $w$  values. We suspect this is the case.

Our surmise is based in part on numerical studies we have already made with Tooker and with Devore on the behavior of relatively simple graphs (of too low index to be dangerous) as functions of  $T$  as one lets  $w \rightarrow 0$ , and the attendant behavior of the first few virial coefficients,  $B(T)$ ,  $C(T)$ ,  $D(T)$ , etc. One knows that in the  $w \rightarrow 0$  limit,  $B(T)$ ,  $C(T)$ , and  $D(T)$  will be functions that discontinuously drop from their hard-sphere values to  $-\infty$  at a crossover temperature [the  $\beta_0$  of item (vii) below]. Similar discontinuities appear in the limiting behavior of the individual cluster integrals that sum up to give the first few virial coefficients. But one finds that the approach in  $B(T)$  and  $C(T)$  to these discontinuous functions of  $T$  as  $w \rightarrow 0$  is monumentally slow (nonuniform). For example, even at  $w/R = 10^{-4}$  the  $B(T)$  and  $C(T)$  curves look a lot more like square-well

$B(T)$  and  $C(T)$  curves for  $w/R=1$  than like the limiting discontinuous  $B(T)$  and  $C(T)$  curves. One might reasonably expect this nonuniform and sluggish approach to limiting behavior as  $w \rightarrow 0$  to persist in the higher-index integrals. If it does, it could mean that the quantitative effect of dangerous graphs will only be felt when  $w/R$  is extremely small. We are hoping that current work with Borstnik on the higher-index integrals will help illuminate this question.

(iv) A method that has become more or less standard in applying the PY sticky-sphere solution to a potential that has an attractive well of non-zero range is to compute  $B_2(T)$  associated with the potential of interest and then to find a  $\tau(T)$  appropriate to that potential by equating that  $B_2(T)$  with the right-hand side of Eq. (3). (We refer to this as the " $B_2$  device" in our remarks below.) This provides a clean and extremely convenient way of using the sticky-sphere solution to describe the thermodynamics of pair potentials that include attraction that is not necessarily of extremely short range or, for that matter, of the form given by Eq. (1). Our results do not argue against doing this, although they suggest that the rationale for doing it is much more tenuous than heretofore realized. In particular, they make clear that the result can only be justified as a one-step approximation procedure rather than a two-step procedure that first involves approximating the model potential of interest as a sticky-sphere potential.

We find that there seems to be only fragmentary evidence in the literature concerning the accuracy provided by the  $B_2$  device. There is a study<sup>(13)</sup> over a few temperatures that suggests the device may be useful when  $w/R=1/25$  at those temperatures. One cannot expect the PY approximation to be reliable for low temperatures (i.e.,  $\tau \ll 1$ ) for any  $w$  if directly applied to the  $\varphi(r)$  of Eq. (1); the graphs it neglects include those that become increasingly important as  $T$  or  $\tau \rightarrow 0$  for any fixed  $w$ . Using the PY sticky-sphere approximation for such a potential via the  $B_2(T)$  device will certainly not remedy this deficiency, so that prudence dictates that the PY sticky-sphere approximation not be taken seriously for  $\tau$  small compared to 1, irrespective of the system to which it is being applied.

(v) Adding Coulombic<sup>(14)</sup> or other soft tails to sticky spheres will not alter the divergences that we have been considering. Adding terms that give rise to steric hinderance effects that prevent the formation of the dangerous clusters will restore stability, however. Cummings and Stell<sup>(15)</sup> and Stell and Zhou<sup>(16)</sup> have considered such "shielded sticky-shell" models, and Stell (unpublished work) has considered the use of  $n$ -body forces for  $n \geq 3$  to produce the same effect. For example, in three dimensions, if one has a four-body potential that turns off the stickiness between all pairs of four

particles when the centers of the four particles are unit distance from one another, one will eliminate all dangerous terms in the cluster integrals. One will also eliminate the  $\delta$ -function contributions from terms like that of Fig. 2e, which are integrable, but missing from the PY approximation. The resulting system could well turn out to be adequately approximated by the three-dimensional PY sticky-sphere approximation and represents another way of making sense of its results, albeit a somewhat artificial one. Still another way is to regard it as an approximation for a shielded sticky-shell model<sup>(15,16)</sup> in which the shell diameter  $L$  is just slightly less than the core diameter  $R$ .

(vi) Restricting the sticky surface associated with binary interactions to small enough areas (e.g., circles) so that there is steric hinderance preventing the dangerous clusters will also restore thermodynamic stability. In these models there is a step function of relative orientation multiplying the  $\delta$ -function in Eq. (2). Such "sticky-spot" models have been considered by us<sup>(17)</sup> and also, in the limit of sticky points, by Wertheim.<sup>(18)</sup> Wertheim's model is also the limit of his more general model<sup>(9)</sup> in which square-well attraction between particles emanates from points within their hard interaction cores. Wertheim's model goes back to Boltzmann, who considered it in detail in Chapter IV of Vol. II of his *Gasttheorie*.<sup>(19)</sup>

A variant of the sticky-spot model is a sticky-sphere model in which the coefficient of the  $\delta$ -function term in Eq. (2) is dependent upon the relative orientation of two particles in a continuous way.<sup>(20)</sup> Whether the dangerous clusters are suppressed or not in such models depends upon the precise form of the orientational-dependent coefficient.

(vii) It is important to point out that the behavior of the hard-core square-well model in which the well width  $w$  is extremely narrow and well depth  $\varepsilon$  is extremely deep but *fixed* involves a number of considerations beyond those upon which we have been focusing. For such a model  $B_2(T)$  will be essentially that of a hard-particle system consisting of the cores alone for all  $T$  above a distinguished value  $T_0$ , below which  $B_2(T)$  has a very large negative value with a very rapid crossover in a small range  $(\Delta T)_0$  about  $T_0$ . Clearly this will also be true of the first few higher virial coefficients (for the same  $T_0$ ). Although the still higher coefficients that include the dangerous cluster integrals are too complicated to analyze in any detail, the picture that emerges irrespective of their precise behavior is that of a resulting thermodynamic phase surface that will have an extremely flat-topped coexistence curve in the  $T$ - $\rho$  plane—almost a step function—out of which will rise a fluid-state/ordered-state coexistence region with nearly vertical boundaries in essentially the same position as the hard-hypersphere fluid-state/ordered-state coexistence curve. In other

words, above a critical temperature  $T_c$  the system will be nearly indistinguishable thermodynamically from one of hard hyperspheres, but slightly below  $T_c$  it will be nearly indistinguishable from a closed-packed solid at zero temperature coexisting with vacuum. One can consider a limiting sequence of such systems by first taking the sticky-sphere limit for one fixed temperature corresponding to a fixed  $\beta_0$  in Eq. (1) and then using this limit to determine a well depth  $\varepsilon$  as a function of well width  $w$  for all temperatures, independent of temperature. In the limit  $w \rightarrow 0$ , which we shall call the  $\beta_0$ -limit here, one expects a perfectly flat horizontal coexistence boundary in the  $T$ - $\rho$  plane for  $0 < \rho < \rho_{FL}$ , where  $\rho_{FL}$  is the density at which the hard-sphere fluid-state/ordered-state coexistence begins. In the Baxter sticky limit,  $\varepsilon = \varepsilon(w, \beta)$  is temperature *dependent*, in contrast to the  $\varepsilon = \varepsilon(w, \beta_0)$  we are contemplating here. If the dangerous cluster configurations were absent [for example, as a result of polydispersity with  $w \ll \sigma(R) \ll \bar{R}$ ], then  $T_0 = (\beta_0 k)^{-1}$  would be expected as the limiting critical temperature  $T_c$  in the  $\beta_0$ -limit. In contrast, the Baxter limit (again, in the absence of the nonintegrable term as in the polydisperse case) is equivalent to an expansion of temperature scale about the temperature  $T_0$  as one lets  $w \rightarrow 0$ . In the Baxter limit, the infinitesimal temperature range  $(\Delta T)_0$  that shrinks to the single temperature  $T_0$  in the  $\beta_0$ -limit instead becomes the whole  $\tau$  range. (Note that, consequently, we lose one-to-one correspondence between  $\beta$  and  $\tau$  values in the Baxter limit, unless we graft on "from the outside" some way of redefining a correspondence, such as the  $B_2$ -device.)

In the presence of the dangerous cluster configuration one can use an argument of Hemmer and Stell<sup>(21)</sup> to assess the  $\beta_0$ -limit. From it one concludes that for all  $d$  there is a transition temperature  $T_T$  for all densities below which one has a two-phase state consisting of essentially close-packed crystal in equilibrium with a vapor that is essentially vacuum. For  $d$  up to at least 8, one expects

$$T_T = qT_0/2d \quad (10)$$

where  $q$  is the number of nearest-neighbor spheres surrounding a  $d$ -dimensional sphere at close packing. Thus  $T_T = T_0$  for  $d=1$ ,  $T_T = 3T_0/2$  for  $d=2$ , and  $T_T = 2T_0$  for  $d=3$ . (For  $d=1$ , one needs an attractive tail of the pair potential that is infinitely weak and long-ranged in order to have a phase transition with a critical temperature  $T_c$  to begin with. But one can expect the "collapse transition" in the  $\beta_0$ -limit even without the tail.)

Boltzmann contemplated a system close to the  $\beta_0$ -limit in Section 73, Chapter VI, Vol. II of *Gastheorie*. Referring to a pair of such atoms as "combined" if their centers are a distance between  $R$  and  $R+w$  of each other and letting  $n_2$  and  $n_3$  refer to the number of dimers and trimers thus

formed, he concluded that "as soon as the atoms begin to combine at all, they will prefer to form aggregates containing a larger number of atoms. Something like liquification of a gas would then occur. Unfortunately, except for the case where  $n_3$  is small compared to  $n_2$ , further calculations encounter difficulties that can scarcely be overcome, so that it remains undecided whether one can obtain under this assumption laws of liquification similar to those provided by the van der Waals equation." For  $w$  not too much smaller than  $R$ , we have indeed come to expect liquification for a square-well system similar to that predicted by van der Waals equation, and as one takes the  $\beta_0$ -limit, Eq. (10) gives one some quantitative measure of the avalanche that Boltzmann foresaw. Many interesting questions still remain. With Hemmer we considered this problem in the light of exact analysis of a one-dimensional model<sup>(21)</sup> and with Tooker<sup>(22)</sup> and J. Devore (unpublished) we are considering the  $\beta_0$ -limit in various perturbative approximations in three dimensions.

(viii) In all of the above analyses, we have been speaking of the equilibrium properties of our models, but in taking the limits with which we have been concerned, the question of equilibration times is of such primary importance that one can scarcely reach a full understanding of the issues we are considering without bringing it into the picture. To see why this is so, one need only ask how long one might expect it to take for the dangerous clusters to destroy thermodynamic stability if one started with a square-well system at a given equilibrium state and then suddenly took the Baxter sticky limit,  $w \rightarrow 0$ . It is perhaps surprising, but not hard to verify, that an elastic binary collision between sticky spheres is indistinguishable from an elastic binary collision between hard spheres of the same diameter and also that the probability of an  $n$ -particle collision,  $n \geq 3$  (necessary for the formation of a bound-state cluster of two or more particles), is zero, because of the zero time duration of a binary collision. One sees therefore that the stickiness is invisible, so to speak—the model will equilibrate into a state of hard-sphere equilibrium. This is also what will happen if we suddenly take the  $\beta_0$ -limit, even if  $\beta_0$  is less than the  $\beta$  of the system.

In order to make thermodynamic sense out of such limits, it is most natural to instead require that they be taken with adiabatic slowness, so the system has a chance to reequilibrate through each step of the limiting process. It is a good thing one can imagine having an infinite amount of time at one's disposal in carrying out such limits, for as one comes closer and closer to the  $w \rightarrow 0$  limit (in the case of either the Baxter sticky limit or the  $\beta_0$ -limit) it can be expected to take a longer and longer time to approach equilibrium.

If instead of rigid particles in a vacuum, one imagines the particles as solute particles in a solvent that can carry away energy (or as particles with



internal degrees of freedom that can absorb translational energy and reemit it in another form), then equilibration to the state dictated by the equilibrium partition function is facilitated because it can take place entirely within the context of binary collisions. One can still anticipate enormously long time scales being necessary for the appearance of the large clusters that destroy thermodynamic stability in the sticky limit. In applying these considerations to real systems (e.g., colloids), where one must back away from the limit, this means that one can anticipate long-time-scale difficulties in attaining true thermodynamic equilibrium for systems that include very deep and narrow contributions to the interpotential potential. In the study of colloids, for which the solvent-averaged colloid–colloid potential can include such a term, this time-scale aspect of the problem is indeed apparent and ubiquitous.

This time-scale problem is closely related to the problem of arriving at configurations representative of true equilibrium states in Monte Carlo sampling. An important difficulty is that one can easily reach a state that has many earmarks of a local equilibrium state in a run that would drift slowly into an increasingly different state if continued indefinitely. Unless there is a definitive way of being assured that one is on some kind of plateau in making such runs, the data they represent can be highly misleading. The problem is particularly severe in systems in which the second virial coefficient is not finite, such as a colloid model with a DLVO pair potential as it is often defined. One knows that there is no true equilibrium for such a system, and it is therefore difficult to assess the significance of Monte Carlo results that describe its structure.

(ix) So far, all our comments have been in terms of a nonquantal description of the systems under discussion. It is amusing to note that all effects of interparticle attraction associated with the Baxter sticky limit disappear when one uses a quantal description. As long as the de Broglie thermal wavelength  $\lambda$  is large compared to  $w$ , the effect of the attractive part of the square-well potential will be greatly attenuated when one passes from a classical to quantal description, and in the Baxter limit, the effect will be totally lost. Thus Baxter sticky spheres viewed quantum mechanically are indistinguishable from hard spheres for all densities and nonzero temperatures. When one backs off from the  $w \rightarrow 0$  limit, interesting questions emerge having to do with the thermodynamic character of the square-well system when both  $w$  and  $\lambda$  are small compared to  $\sigma$ . Some of these have been touched upon in the study by Hemmer and Stell,<sup>(21)</sup> and in a further rigorous investigation made by the author in collaboration with M. Penrose, O. Penrose, and R. Pemantle.<sup>(24)</sup> A new feature that emerges as being crucial in the quantum mechanical picture is the importance of bound states, which will occur for sufficiently large  $w$ .

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