

# Kinetic Arrest Originating in Competition Between Attractive Interaction and Packing Force

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We discuss the situation where attractive and repulsive portions of the interparticle potential both contribute significantly to glass formation. We introduce the square-well potential as prototypical model for this situation, and *reject* the Baxter model as a useful model for comparison to experiment on glasses, based on our treatment within mode coupling theory. We present explicit results for various well widths, and show that, for narrow wells, there is a useful analytical formula that would be suitable for experimentalists working in the field of colloidal science. We raise the question as to whether, in a more exact treatment, the sticky-sphere limit might have an infinite glass transition temperature or a high but finite one.

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**KEY WORDS:** Colloidal systems; Baxter model; disordered systems; glass transition; mode coupling theory.

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## 1. INTRODUCTION

Kinetic arrest phenomena at a transition temperature  $T_c$  occurring just prior to the thermodynamic glass transition,  $T_g$ , are well known and have been studied extensively using the mode-coupling theory and simulation methods. Without being exhaustive, we can point to a number of reviews<sup>(1,2)</sup> and papers<sup>(3-5)</sup> in the literature. There has also been considerable experimental work on this field.<sup>(6-13)</sup> Typically such phenomena are considered to be driven primarily by packing effects where the repulsive part of the potential is of primary importance, with the attraction providing merely a modulation of the overall phenomena. In this case the hard

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sphere system exhibits most of the relevant phenomena and may be viewed as the prototypical model of this type of kinetic arrest.<sup>(14)</sup>

However, there has recently been interest<sup>(15, 16)</sup> in cases where the attractive part of the potential, or rather its interplay with repulsion, is more deeply implicated in the arrest phenomenon. This can lead to glasses with much richer structure, including long-ranged density correlations that are frozen into the system. New dynamical phenomena might also be expected in such systems, especially where there is subtle interplay between attraction and repulsion near the glass transition. As in the repulsive case, it is natural to seek a prototypical model that can be conveniently studied within mode-coupling theory with the aim of elucidating the special features of such a system. It is in particular desirable to consider those aspects that represent more than simple modulations of hard-core behaviour. One such choice is represented by the Baxter model<sup>(17)</sup> which has been studied by some of the authors<sup>(15, 16)</sup> in previous publications using the Percus–Yevick approximation<sup>(18)</sup> for the static structure factor, and the mode-coupling theory. The results are promising in that novel dynamical phenomena do emerge, and also it is possible to create kinetic arrest where a long correlation length scale is quenched into the system.

Of course, some of the limitations of a model with hard-core potential and delta-function like attractive potential, as treated by Percus–Yevick<sup>(18)</sup> are evident. For example, it is believed that such a potential would lead only to disordered and crystalline phases, rather than the liquid-gas phase separation implied by the P-Y approximation.<sup>(19)</sup> On the other hand, it may still be possible to make some progress with this approach. For example, in the disordered phase the P-Y approximation is reasonably good for the structure factor,<sup>(20)</sup> so in those cases where the kinetic arrest arises, prior in temperature or time to a crystallization, we may expect reasonable results. It may even be the case that the capability to study arrest near what is believed to be a “metastable” liquid-gas transition may be of some practical interest.<sup>(21–24)</sup> Here we discuss some unsatisfactory features originating from the large- $q$ -tail of the static structure factor, in conjunction with the study of the ideal glass transition in the frame of the mode coupling theory (MCT).

It is perhaps prudent to mention at this stage that the use of Mode Coupling Theory (MCT) for such questions is itself not without controversial aspects. There are numerous criticisms of MCT, and in any case, even if one does accept it as a viable mean-field-type theory, there remains the criticism that it neglects such effects as “hopping” and other phenomena.<sup>(25)</sup> These may be relevant in square-well systems.

However, we shall further argue that, within the MCT, the P-Y approximation and possibly even the exact structure factor of the Baxter

model, leads to very high or infinite glass transition temperature for a broad range of packing fractions in the region where attractive interactions dominate. The outcome of our deliberations shall be that we shall propose as our prototypical model the “narrow” square well potential, treated by P-Y and MCT. We shall show that, for this case, the structure factor is damped at large- $q$  due to the finite well width, and that this leads to finite values of  $\tau_c$ , the effective transition temperature, throughout the phase-diagram. Moreover, the “narrow” square well potential seems to share most of the features of the kinetic arrest discussed in earlier works.<sup>(15, 16)</sup> We shall conclude that the underlying phenomena reported there are therefore *robust* and likely to be observed experimentally, even though the Baxter model is flawed.

The organization of these observations is as follows. We shall first consider the static structure factor of the square well potential as the input to the MCT. This will permit us to explain new features introduced by a finite well-width. Next we shall consider the effects of these features on the MCT prediction of the transition. Finally we shall discuss the general behaviour of the arrest phenomenon as a function of well-width.

## 2. THE PY APPROXIMATION TO THE SQUARE-WELL POTENTIAL

We consider a square well potential with repulsive core of diameter  $R$  and total range  $R'$ . The well width is therefore parametrized by  $\varepsilon = (R' - R)/R'$ , and the well depth by  $u$ . Note that by taking the appropriate limit of well depth to width we may recover the Baxter model which possesses an analytical solution for the structure factor. By the Baxter sticky sphere model<sup>(17)</sup> we mean  $\varepsilon \rightarrow 0$  and the well depth becomes infinite according to  $(1/\beta) \ln(12\tau\varepsilon)$ ,  $\tau$  being an effective temperature and  $\beta = 1/k_B T$ . To solve the Baxter model within PY an external parameter  $\lambda$  is introduced to define  $h(r)$  within the range of the attraction. It is then easily calculated through a second order equation arising from the matching conditions that have to be verified. Since the limit  $\lambda \rightarrow 0$  corresponds to the hard sphere limit, it may be thought as an attractive energy scale.

Although no analytic solution exists for the square well problem, this model potential is simple enough to be exhaustively studied. Thus the integral equation for the square well problem is readily derived using Baxter's approach. The equations are

$$rc(r) = -Q'(r) + 2\pi\rho \int_r^{R'} dt Q'(t) Q(t-r) \quad (1)$$

for  $0 < r < R'$ , and

$$rh(r) = -Q'(r) + 2\pi\rho \int_0^{R'} dt(r-t)h(|r-t|)Q(t) \quad (2)$$

for  $r > 0$ , where  $c(r)$  is the direct correlation function,  $h(r)$  is the indirect correlation function and  $Q'$  is the derivative of  $Q(r)$ .<sup>(26)</sup> The function  $Q(r)$  is related to  $S(q)$  via

$$S(q)^{-1} = \tilde{Q}(q) \tilde{Q}(-q) \quad (3)$$

and

$$\tilde{Q}(q) = 1 - 2\pi\rho \int_0^{R'} dr e^{iqr} Q(r) \quad (4)$$

This equation can be solved numerically using the P-Y approximation as closure, and it is via this expression that the potential enters the formulation. Of course, the PY closure has many limitations. However, it is quite acceptable for hard spheres, and it is expected to be reasonable for short-ranged potentials.<sup>(20)</sup>

Instead of a numerical solution, the P-Y theory may be solved in a series expansion for small well-width,  $\varepsilon$ , a program that was partially carried out by Menon *et al.*<sup>(27)</sup> The result for the structure factor is,

$$\begin{aligned} \frac{1}{S(q)} - 1 = & 24\eta \left[ \alpha f_2(\bar{q}) + \beta f_3(\bar{q}) + \frac{1}{2} \eta \alpha f_5(\bar{q}) \right] + 4\eta^2 \lambda^2 \varepsilon^2 \left[ f_2(\varepsilon\bar{q}) - \frac{1}{2} f_3(\varepsilon\bar{q}) \right] \\ & + 2\eta^2 \lambda^2 [f_1(\bar{q}) - \varepsilon^2 f_1(\varepsilon\bar{q})] - \frac{2\eta\lambda}{\varepsilon} [f_1(\bar{q}) - (1-\varepsilon)^2 f_1((1-\varepsilon)\bar{q})] \\ & - 24\eta [f_2(\bar{q}) - (1-\varepsilon)^3 f_2((1-\varepsilon)\bar{q})] \end{aligned} \quad (5)$$

where  $\bar{q} = qR'$ ,  $\eta = (\pi/6) \rho R'^3$  and  $\alpha$ ,  $\beta$  and  $\mu$  are given by

$$\begin{aligned} \alpha &= \frac{(1-2\eta-\mu)^2}{(1-\eta)^4} \\ \beta &= -\frac{3\eta(2+\eta)^2 - 2\mu(1+7\eta+\eta^2) + \mu^2(1+\eta)}{2(1-\eta)^4} \\ \mu &= \lambda\eta(1-\eta) \end{aligned} \quad (6)$$

and  $f_n(x)$  are defined as:

$$\begin{aligned}
 f_1(x) &= \frac{1 - \cos x}{x^2} \\
 f_2(x) &= \frac{\sin x - x \cos x}{x^3} \\
 f_3(x) &= \frac{2x \sin x - (x^2 - 2) \cos x - 2}{x^4} \\
 f_5(x) &= \frac{(4x^3 - 24x) \sin x - (x^4 - 12x^2 + 24) \cos x + 24}{x^6}
 \end{aligned} \tag{7}$$

a formula that was derived by Liu *et al.*<sup>(28)</sup> Note that  $\eta$  is the effective volume fraction calculated according to the large length,  $R'$ , that defines the full range of the potential. Sometimes we shall also use the real volume fraction calculated with  $R$ , the hard core diameter, and this is named  $\phi$ . The two quantities are the same in the limit of Baxter spheres.

In fact, one can push this asymptotic theory a little further than has been done previously. That is, we can solve all parts of the theory to order  $\varepsilon$ , including the  $\lambda$ -equation, obtaining the following,

$$\begin{aligned}
 \lambda^2 \left( 1 + \frac{3\varepsilon\eta}{1-\eta} \right) - 12\lambda \left[ \frac{\tau}{\eta} + \frac{1}{1-\eta} - \varepsilon \frac{1 - (11/4)\eta + \eta^2}{(1-\eta)^2} \right] \\
 + \frac{6}{(1-\eta)^2} \left( \frac{2}{\eta} + 1 - 12\varepsilon(1-\eta) \right) = 0
 \end{aligned} \tag{8}$$

where the physical solution  $\lambda(\varepsilon)$  is now of the form:

$$\begin{aligned}
 \lambda(\varepsilon) &= 6 \left[ \left( \frac{1}{1-\eta} + \frac{\tau}{\eta} \right) \left( 1 - \frac{3\varepsilon\eta}{1-\eta} \right) - \varepsilon \frac{1 - (11\eta/4) + \eta^2}{(1-\eta)^2} \right] \\
 &\pm \left\{ 36 \left[ \left( \frac{1}{1-\eta} + \frac{\tau}{\eta} \right) \left( 1 - \frac{3\varepsilon\eta}{1-\eta} \right) - \varepsilon \frac{1 - (11\eta/4) + \eta^2}{(1-\eta)^2} \right]^2 \right. \\
 &\quad \left. - \frac{6}{(1-\eta)^2} \left[ \left( \frac{2}{\eta} + 1 \right) \left( 1 - \frac{3\varepsilon\eta}{1-\eta} \right) - 12\varepsilon(1-\eta) \right] \right\}^{1/2}
 \end{aligned} \tag{9}$$

It is fairly straightforward then to compare the results of Eq. (5) where  $\lambda = \lambda(\varepsilon)$  with numerical solution of Eqs. (1)–(4). It is also possible to illustrate differences between the Baxter sticky sphere and the square well model. We shall here present a representative selection of results from three values of  $\varepsilon$  ( $\varepsilon = 0.01$ ,  $\varepsilon = 0.03$ , and  $\varepsilon = 0.09$ ), chosen to illustrate various

aspects of the mode-coupling calculations. The smallest value of  $\varepsilon$  is representative of *sticky-sphere* type behaviour, but with a finite temperature transition. The largest value ( $\varepsilon = 0.09$ ) already exhibits properties closer to that of a square well. We note first that, for  $\varepsilon = 0.01$ , the agreement between the numerical calculation of Eqs. (1)–(4) and the leading order in the well-width expansion is essentially perfect (Fig. 1), and we may accept Eq. (5) as defining the P-Y approximation to the small well-width problem. As one might expect for such small  $\varepsilon$ , the moderately small- $q$  (corresponding to the nearest neighbour distances) behaviour of the structure factor in Eq. (5) is in good agreement also with the Baxter model. However there are some very important differences for the large- $q$  behaviour of  $S(q)$  as illustrated in Fig. 2. There are two points to note here that relate to later MCT calculations. Firstly the MCT calculations are sufficiently delicate at large- $q$  for it to be necessary to include many momentum points on the numerical grid. It is therefore highly advantageous to have a formula such as Eq. (5), rather than a numerical solution. Secondly from Fig. 2 (and later comparison of Fig. 4) we see that beyond  $q_\lambda$ , the structure factor of the square

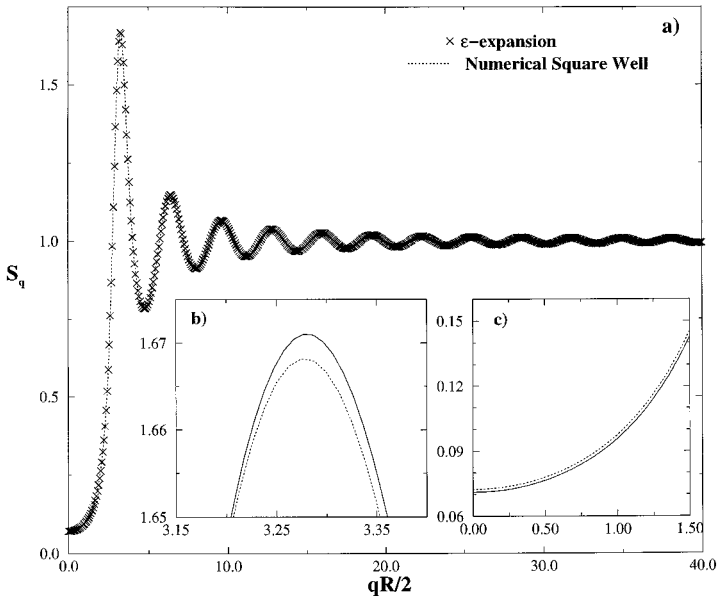


Fig. 1. (a) Square well plotted versus  $\varepsilon$ -expansion for  $\varepsilon = 0.01$ . (b) Detail of the first peak of the structure factor (the dotted line is the square well, the continuous line is the  $\varepsilon$ -expansion). (c) Detail of the *small-q* region of the structure factor.  $\phi = 0.35$  and  $T = 1.0$ .

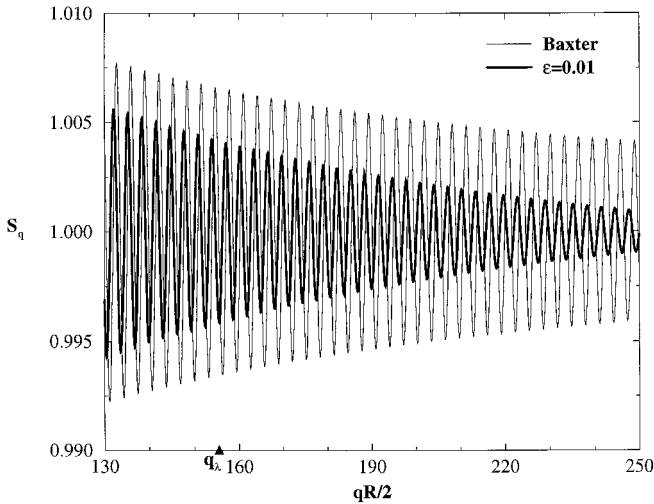


Fig. 2. Structure factor at large- $q$  of the Baxter model and  $\varepsilon$ -expansion for  $\varepsilon=0.01$ . The value  $q_\lambda = \pi/\varepsilon R'$  and by the examination of Fig. 4 it is evident that much beyond this point there is little contribution to the transition temperature.  $\phi=0.35$  and  $\tau=0.5$ .

well model decreases more rapidly than that of the Baxter model. In fact consideration of finite well-width leads, for many purposes, to the effective introduction of a *cut-off* at a momentum corresponding to twice the well width,

$$q_\lambda = \frac{\pi}{(R' - R)} \quad (10)$$

It is this reduction of the range of  $S(q)$  that leads ultimately to meaningful mode-coupling calculation.

Further comparisons between the  $\varepsilon$ -expansion and the numerical results from Eq. (1) are also possible. As might be expected, at  $\varepsilon=0.09$  the deviation between the two results becomes significant (Fig. 3), both for small- $q$  and the first peak, and thereafter one must rely on the numerical solution. Even so, it is interesting to note that the large- $q$  behaviour is still quite well represented by Eq. (5).

We now turn to the thermodynamic aspects of the P-Y solution of the finite well problem. We have noted earlier some intrinsic failings of the P-Y approximation of the Baxter model in that liquid-gas rather than the expected crystallization transition is produced.<sup>(19)</sup> There are other unusual features of the P-Y solution, such as the asymmetry of the phase diagram with respect to the spinodal (see, for example, refs. 30–32) and the uncertain status of the phase diagram to the left of the critical point. In fact, a careful analysis of the expansion in square-well width leads to a few new

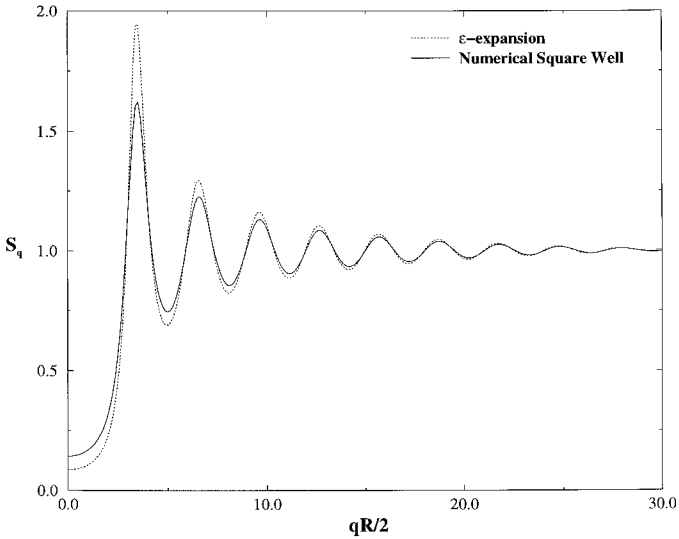


Fig. 3. Square well versus  $\varepsilon$ -expansion for  $\varepsilon = 0.09$ ,  $\phi = 0.35$  and  $T = 1.0$ .

features, not present in the Baxter solution. Amongst them there is the observation that the phase diagram is no longer so asymmetric with respect to the critical point, and there is a finite region of real solution beneath the spinodal curve, near the critical point.<sup>(33)</sup> These details need not concern us here, since we shall be interested in points of the phase diagram above the P-Y phase separation. For our present purpose it is possible to use the P-Y structure factors for temperatures and densities to the stable (right) side of the high density branch of the spinodal line.

In summation, then, we believe that the P-Y approximation, and in particular the leading order of the small *well-width* expansion given by Eq. (5) is, at least, a useful approximation to the structure factor for an interesting range of parameters of the square well potential. We shall now study this range within MCT.

### 3. THE MODE COUPLING THEORY

The mode coupling theory provides a description of the kinetic arrest phenomenon. For certain values of the interaction parameters the density-density correlation function

$$\phi_q(t) = \frac{\langle \delta\rho^*(\mathbf{q}, t) \delta\rho(\mathbf{q}, 0) \rangle}{NS_q} \quad (11)$$



possesses a long-time decay with a non-zero infinite time limit. When this occurs, diffusion slows dramatically and the viscosity diverges: the glass transition occurs. The Zwanzig and Mori<sup>(34)</sup> formalism and MCT ideas<sup>(1)</sup> lead to the equations

$$\ddot{\phi}_q(t) + \Omega_q^2 \phi_q(t) + \nu_q \dot{\phi}_q(t) + \Omega_q^2 \int_0^t m_q(t-t') \dot{\phi}_q(t') dt' = 0 \quad (12)$$

where  $m_q(t)$  is given by

$$m_q(t) = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} V(\mathbf{q}, \mathbf{k}) \phi_k(t) \phi_{|\mathbf{q}-\mathbf{k}|}(t) \quad (13)$$

the vertex function is

$$V(\mathbf{q}, \mathbf{k}) = \frac{\rho}{q^4} (\mathbf{q} \cdot (\mathbf{q} - \mathbf{k}) c_{|\mathbf{q}-\mathbf{k}|} + \mathbf{q} \cdot \mathbf{k} c_k)^2 S_q S_k S_{|\mathbf{q}-\mathbf{k}|} \quad (14)$$

and the two quantities  $\Omega_q$  and  $\nu_q$  are respectively, the characteristic frequency and a white noise term due to the fast part of the memory function; they are defined as,

$$\Omega_q = \frac{q^2 k_B T}{m S(q)}$$

$$\nu_q = \nu_1 q^2$$

and  $\nu_1 = 1$  in our calculations. In the limit  $t \rightarrow \infty$  we find the equation for the static problem

$$\frac{f_q}{1-f_q} = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} V(\mathbf{q}, \mathbf{k}) f_k f_{|\mathbf{q}-\mathbf{k}|} \quad (15)$$

where  $f_q$  is the *Edwards–Anderson* factor:

$$f_q = \lim_{t \rightarrow \infty} \phi_q(t) \quad (16)$$

$S_q$  is the static structure factor and  $c_q = (S_q - 1)/\rho S_q$  is the Fourier transform of the direct correlation function following the Ornstein–Zernike relation.

It is clear that  $f_q = 0$  is always a solution of the Eq. (16). In fact it is possible to show<sup>(1)</sup> that, where the potential is purely repulsive and at low densities, this is the stable solution, and the system is in the liquid phase.

Above a certain  $\phi_c$  (that depends on the parameters of the system) non-zero solutions begin to appear and non-ergodic behaviour appears. The ideal glass line, moreover, can be defined studying the behaviour of the eigenvalues of the stability matrix of the system.<sup>(1)</sup> Here we have bracketed the transition line by iteratively solving Eq. (15). Where more precise results have been required we have studied the stability matrix. Of course, all these calculations are subject to numerical error, particularly with respect to the numerical momentum cut-off in the integrals. Since the attractive glass requires consideration of both repulsive and attractive parts of the potential, the former length scale being set to be the well-width, we have carried out finite-size analysis of our results to check their validity. Now we are in a position to solve the kinetic arrest temperature,  $\tau_c$ , as a function of well parameters and the structure factor. From now on we shall refer to the *effective* temperature  $\tau$  as introduced by Baxter and related (for small  $\varepsilon$ ) to the temperature via:  $\tau = (1/12\varepsilon) \exp(u/k_B T)$ .<sup>(27)</sup> The first point to note is that, for the Baxter model in the region where attractions are relevant (previously labelled as  $B_2$  in refs. 15 and 16), there are, strictly speaking, very substantial contributions from the long tail of the Baxter solution, not taken into account in earlier works. The apparent transition observed previously is a consequence of truncating the long tail of the Baxter solution. Indeed, we find that the apparent  $\tau_c$  rises with the number of  $q$ -vectors taken into account in the calculation.

For example, in the case of Fig. 4 ( $\varepsilon = 0.01$  and  $\phi = 0.3881$ ) we see that the  $\tau_c$  continues to change with the number of points in the numerical grid until we reach a well-width cut-off equal to twice the well width ( $\pi/\varepsilon R'$ ). Of course, the cut-off required is somewhat dependent on the property of the system chosen. However the general outline of the observation is clear. The attractive glass transition is strongly *finite-size* dependent due to the contribution to the integral Eq. (15), from momentum scales up to around  $q_\lambda = \pi/\varepsilon R'$ . Thus, for very small well widths the calculations require many thousands of points, and for the Baxter model there appears to be no useful number of points that can ensure convergence of the transition temperature in the attractive region of the transition. The implication is clear. It is the (small) finite-well-width model that is the appropriate prototype of the system we discuss rather than the literal Baxter Model. However, we make another observation, illustrated quite well by Fig. 4. That is, paradoxically, the Baxter model solution can be applied in the mode coupling theory to study attractive glasses providing the appropriate well-width cut-off ( $q_\lambda$ ) is applied. We can see this because  $\tau_c$  from the Baxter solution truncated at  $q_\lambda$  is comparable to  $\tau_c$  from the true P-Y square well potential of width  $\varepsilon = \pi/q_\lambda R'$ . In some cases in the literature we have therefore the interesting situation that the Baxter structure factor appears to work due to numerical

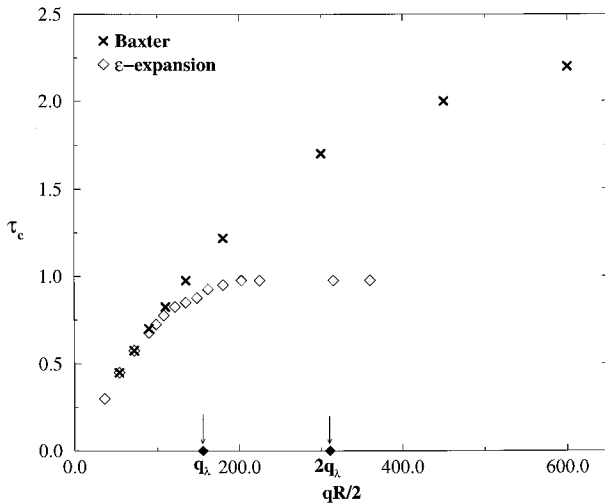


Fig. 4. Behaviour of  $\tau_c$  in function of the cut-off as evaluated from Eq. (11).  $\varepsilon=0.01$  and  $\phi=0.3881$ . As before  $q_\lambda=\pi/\varepsilon R'$ .

cut-off, even though the full model has an unrealistic glass transition temperature. The discussion is not purely academic since experimentalists fit data to such models. In future we recommend that Eq. (5) be applied up to around  $\varepsilon=0.03$  for the case of attractive colloidal particles. Beyond this value of  $\varepsilon$ , more care must be taken.

We now turn to another aspect of this question. We have calculated the asymptotic  $\tau_c$  as a function of  $\varepsilon$  for  $\phi=0.2$  (Fig. 5). Evidently, as  $\varepsilon$  decreases the glass temperature rises sharply (due to the large- $q$  tail) so that at  $\varepsilon=0.001$  the effective temperature  $\tau_c$  is very high, roughly seventeen times higher than the Baxter gas-liquid critical temperature. For numerical calculation, we are unable to conclusively show the asymptotic limit  $\tau_c$  ( $\varepsilon \rightarrow 0$ ). However, we believe that the glass appears to be the stable solution for all effective temperatures where the system does not behave as a herd-sphere fluid. This is quite a practical question. Colloidal particles with vanishing well-width, but large well-depths would therefore not undergo the expected fluid-solid transition,<sup>(19)</sup> but would generally found to be a glass, up to temperature where attractions are irrelevant in any case, and the particles behave as hard spheres. Since, for finite  $\varepsilon$ , we now have finite values of  $\tau_c$ , it is natural to ask if the important dynamical features of the model described in ref. 15 are recovered. The existence of a logarithmic decay of density-density correlation, associated to the presence of a cusp singularity in the parameter space in the case of “narrow” square well potentials is under investigation.

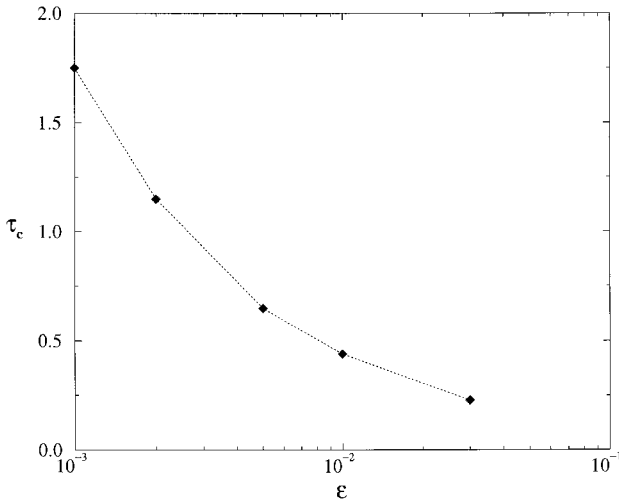


Fig. 5. Behaviour of  $\tau_c$  in function of  $\epsilon$  at  $\phi = 0.2$ .

#### 4. CONCLUSIONS

As we have noted earlier, it is of interest to identify a simple model, and treatment of that model that exhibits the principal phenomena where the attractive part of the potential is important in glass formation. We have seen that one good candidate is the square well potential where, for very narrow wells, important new properties are already evident. Thus, glasses with frozen density fluctuations, including those where the correlation lengths  $\xi$  is quite large, appear beneath the attractive glass curve. In addition we have seen that well-width is quite an important parameter. Truly sticky spheres in the Baxter sense, or experimental approximations to these, probably are nearly always found as glasses, perhaps the powdery precipitates found in particle glasses being examples of this. For more moderate square-well parameters we may expect interesting glass behaviour, and the details of the transition and attendant dynamics are under examination. We have also noted that, from the experimental point of view, the finite-well structure factor formula (5) represents a more realistic approach to the dynamics of such system, though indication of this were already clear much earlier.<sup>(28)</sup> Finally, we offer the conjecture that the exact model of Baxter spheres would be a glass for any effective temperature which preserves the presence of the attractive interactions in the potential. This could be in agreement with Stell's<sup>(19)</sup> clustering ideas for the

Baxter model. In addition, however, we have illustrated how the situation evolves away from the Baxter limit. Proof, or modification, of the Baxter limit scenario may be an interesting challenge to some of the readers of this paper.

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