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# The energy–density landscape for soft spheres

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## Abstract

For soft spheres the number of minima on the potential energy landscape is independent of the volume, and the shape of each basin in the potential energy landscape varies with volume in a predictable way. Two simple assumptions, (1) that the basins are harmonic and (2) that the distribution of basin depths is Gaussian, yield a model for the cold dense states of matter: crystals, glasses, the supercooled fluid and the glass transition. The model agrees with simulation data at temperatures below freezing but fails above the freezing temperature, where the harmonic approximation breaks down.

## 1. Introduction

The focus of this discussion is the potential energy landscape formalism [1–3] which expresses the free energy of a fluid in terms of the free energy of the many glasses, or inherent structure basins, that the fluid samples. Two-dimensional pictures of the multi-dimensional potential energy landscape [3], often rather fanciful, have inspired many discussions [3, 4] of the dynamic and thermodynamic properties of liquids. The same formalism applies with density, rather than energy, as the independent variable and a picture [5] of the density landscape for hard discs pre-dates the more familiar potential energy landscape pictures.

Over the last decade, methods have been developed to measure the entropy and free energy,  $A_g$ , of model glasses in simulation experiments, to quantify the density and energy landscapes. To outline the general strategy [6–8] of these studies, the fluid free energy is expressed as

$$A_f(V, T) = A_g(V, T, z) - TS_c(z) \quad (1)$$

which shows that measuring  $A_f$  and  $A_g$  gives the configurational entropy [9]

$$S_c(z) = k \ln\{N_g(z)\}, \quad (2)$$

and counts the number  $N_g(z)$  of glasses, configurations [9], potential energy minima [1, 2] or basins, of the type  $z(V, T)$ , that have the same energy and pressure as the fluid at the same volume  $V$  and temperature  $T$ .  $k$  is the Boltzmann constant. The internal parameter [10]  $z$  is

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included to distinguish between glasses that have different properties at the same  $V$  and  $T$ . Measuring  $N_g(z)$  quantifies the broad structure of the landscape.

In studies of the density landscape in simple models such as hard spheres [11], hard discs [12, 13] and saturated square-well [7] particles, the internal parameter,  $z$ , was chosen to be the density of a glass at its close-packed limit. In studies of the energy landscape on isochores in the simulated models of Lennard-Jones fluids [8, 14, 15], orthoterphenyl [16], water [17, 18] and silica [19],  $z$  was chosen to be the energy of a glass at zero temperature. With the exception of those for silica [19], all the results are consistent with a Gaussian distribution [7, 20]:

$$N_g(z) = \exp\{N[\alpha - \gamma(z - z_m)^2]\} \quad (3)$$

which is the result expected from the central limit theorem if each macroscopic glass is viewed as a collection of many uncorrelated microscopic parts. For Lennard-Jones models the constants,  $\alpha$ ,  $\gamma$ ,  $z_m$  in equation (3), vary with density [15], so the distribution depends on both density and energy.

To get some insight into how the density and energy landscapes might be combined into a unified picture, we examine a soft-sphere model in which the density dependence of the isochoric potential energy landscape is predictable.

In condensed phases at high pressure, the interaction between molecules is dominated by repulsions and the properties of crystals, glasses and dense fluids might be captured by a soft-sphere model [21]. We show that the form of a supercooled soft-sphere fluid equation of state can be predicted with two simple assumptions:

- (1) that the glasses are harmonic and
- (2) that the number of glasses conforms to equation (3) with an appropriate choice of  $z$ .

These assumptions provide a model for the dense states of matter, which includes an ideal thermodynamic glass transition as the low-temperature limit of the fluid state.

Adding a van der Waals attractive potential to the model yields a liquid–gas spinodal line as the upper temperature limit to the liquid state. The spinodal and ideal glass lines meet with the same slope at the maximum tension that the metastable stretched liquid can sustain. The harmonic approximation is not accurate above the equilibrium freezing temperature but the model can be extended to higher temperatures, to describe a gas and boiling more accurately, by using pressures measured by computer simulations of a soft-sphere fluid.

## 2. Soft spheres

Hoover *et al* [21] studied a crystal and fluid of soft spheres defined by the pair potential

$$u(r) = \varepsilon(\sigma/r)^n \quad (4)$$

where  $u(r)$  is the potential energy of interaction between two spheres separated by  $r$  and where  $\varepsilon$ ,  $\sigma$  and  $n > 3$  are constants.

A special property [21] of this potential is that if any configuration,  $\mathbf{r}^N$ , of  $N$  spheres in a volume  $V_0$  with potential energy  $E(V_0)$  is expanded uniformly to a new volume  $V$ , such that all the pair separations change by a factor of  $(V/V_0)^{1/D}$ , where  $D$  is the spatial dimension, the new potential energy is  $E(V) = (V_0/V)^{n/D} E(V_0)$ . Hoover *et al* [21] show that, for potentials with this property, the excess free energy depends on a single independent variable. We need not repeat their derivation [21], but merely state the result.

A reduced excess free energy,  $a(x)$ , is defined by

$$a(x) \equiv \frac{A(N, V, T) - A_{ig}(N, V, T)}{RT} \quad (5)$$

where  $A$  and  $A_{ig}$  are the Helmholtz free energies of the soft-sphere model and an ideal gas, respectively, and  $R = Nk$  is the gas constant. The free energy of an ideal gas of structureless particles is

$$A_{ig}(N, V, T) = -RT \ln \left\{ \frac{Ve}{N\Lambda^D} \right\} \quad (6)$$

where  $\Lambda = (h^2/2\pi mkT)^{1/2}$  is the de Broglie wavelength,  $h$  is Planck's constant and  $m$  is the mass of a particle. The hybrid independent variable is defined by

$$x \equiv (V_0/V)(\varepsilon/kT)^{D/n} \quad (7)$$

where  $V_0$  is any reference volume.

The important point is that, for soft spheres,  $a(x)$  depends only on  $x$ , regardless of whether  $x$  changes by varying  $T$  or by varying  $V$ . Consequences of that scaling are that the total energy,  $U = (\partial(A/T)/\partial(1/T))_V$ , is

$$\frac{U}{RT} = \frac{D}{2} + \frac{D}{n}x \frac{da(x)}{dx} \quad (8)$$

and the pressure,  $P = -(\partial A/\partial V)_T$ , is

$$\frac{PV}{RT} = 1 + x \frac{da(x)}{dx}. \quad (9)$$

### 3. Harmonic solids

Simulations show that crystals and glasses of soft spheres are nearly harmonic. Hoover *et al* [21] included anharmonic corrections to fit precise simulation results for a soft-sphere crystal, but the corrections are small and they are ignored here.

The Helmholtz free energy of a classical harmonic solid, in which each particle moves independently in a harmonic well, is [22]

$$A(V, T, z) = U(V, 0, z) + DRT \ln\{\theta(V, z)/T\} \quad (10)$$

where  $\theta(V, z)$  is a volume-dependent Einstein temperature,  $U(V, 0, z)$  is the energy at zero temperature and  $z$  is an internal parameter needed to distinguish between crystals and glasses with different properties. It would be more realistic to express the free energy in terms of the lattice vibration frequencies,  $\nu_i$ ,  $i = 1, \dots, 3N - 3$ , but that is not important for the present purpose because equation (10) is regained if an effective Einstein temperature is defined by  $\theta \equiv h\bar{\nu}/k$ , where  $\bar{\nu}$  is the geometric mean of the  $\nu_i$ . It would also be more realistic to use the quantum mechanical, rather than classical, form of equation (10) but the classical form is appropriate for the following comparisons with classical simulation results. The quantum mechanical form is approximated by equation (10) when  $\theta/T \ll 1$ . Simple harmonic models for solids do not account for volume changes [22], but Grüneisen [23] showed how thermal expansion can be explained by allowing for the volume dependence of the vibrational frequencies.

The internal parameter,  $z$ , is chosen to be the dimensionless energy of a crystal or glass at zero temperature, and at a reference volume  $V_0$ ,

$$z \equiv U(V_0, 0, z)/N\varepsilon = (V/V_0)^{n/D}U(V, 0, z)/N\varepsilon. \quad (11)$$

With this choice,  $z$  is a constant, independent of volume and temperature, for a particular crystal or glass, and the constants  $\alpha$ ,  $\gamma$ ,  $z_m$  in equation (3) do not vary with density.

#### 4. Harmonic solids of soft spheres

The scaling implied by equations (5)–(7) requires [21] that the Einstein temperature in equation (10) varies with volume as

$$k\theta(V, z)/\varepsilon = b(z)(V_0/V)^{(n/2+1)/D} \quad (12)$$

where  $b(z)$  is a dimensionless constant for a particular solid but might vary with  $z$ .

Equations (5), (10)–(12) give the excess free energy of a harmonic solid of soft spheres as

$$a_s(x, z) = zx^{n/D} + (n/2) \ln\{x\} - S_0(z) \quad (13)$$

where  $S_0(z)$  is constant for a particular glass or crystal, but might vary with  $z$  if  $b(z)$  in equation (12) changes with  $z$ . For a classical solid it is necessary to measure the entropy to determine  $S_0(z)$  [24].

Equations (8), (9), (13) give the energy and pressure of harmonic solids of soft spheres:

$$\frac{U}{RT} = D + zx^{n/D} \quad (14)$$

$$\frac{PV}{RT} = 1 + n/2 + (n/D)zx^{n/D}. \quad (15)$$

Equations (14), (15) are useful at low temperature and volume (large  $x$ ) but the harmonic approximation breaks down at high temperature and volume. For instance, equation (15) requires that  $PV/RT \geq n/2 + 1$  at high volume or temperature, which is unphysical.

#### 5. Soft-sphere fluids

The excess free energy of the fluid, from equations (1) and (5), is

$$a_f(x) = a_g(x, z) - S_c(z)/R \quad (16)$$

and the configurational entropy, from equations (2) and (3), is

$$S_c(z)/R = \alpha - \gamma(z - z_m)^2. \quad (17)$$

The equilibrium value of  $z(x)$  minimizes the free energy of the fluid [10], so

$$(\partial[a_g(x, z) - S_c(z)/R]/\partial z)_x = 0. \quad (18)$$

Equations (13), (16)–(18) give

$$z(x) = z_m + (dS_0/dz)/2\gamma - x^{n/D}/2\gamma \quad (19)$$

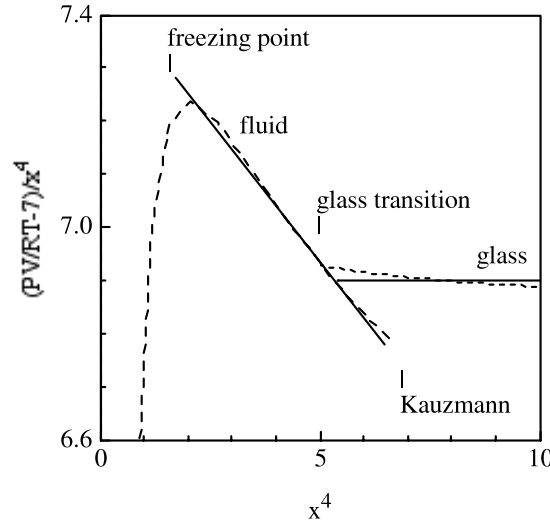
which is the value of  $z(x)$  for those glasses that have the same energy and pressure as the equilibrium fluid at  $x$ . To simplify the following equations, it is assumed that  $dS_0(z)/dz$  is either constant or small enough to neglect. If it is constant, then  $z_m + (dS_0/dz)/2\gamma$  is constant and the form of the equations that follow is not changed if  $z_m$  is redefined to absorb the constant  $(dS_0/dz)/2\gamma$ . The assumption needs further study.

The energy and pressure of the fluid are the same as those of a glass, from equations (14), (15) with  $z(x)$  from equation (19), so, for the fluid,

$$\frac{U}{RT} = D + (z_m - x^{n/D}/2\gamma)x^{n/D} \quad (20)$$

$$\frac{PV}{RT} = 1 + n/2 + (z_m - x^{n/D}/2\gamma)(n/D)x^{n/D}. \quad (21)$$

Equation (15) shows that  $(PV/RT - 1 - n/2)/x^{n/D}$  is constant in a harmonic solid and equation (21) predicts that it varies linearly with  $x^{n/D}$  in the fluid. Figure 1 tests these



**Figure 1.**  $(PV/RT - 1 - n/2)/x^{n/D}$  versus  $x^{n/D}$  for a soft-sphere fluid and glass ( $D = 3, n = 12, V_0 = N\sigma^3$ ). The dashed curve for the fluid is calculated from a polynomial (equation (13) from [25]) which fits the equilibrium fluid ( $x^4 \leq 1.75$ ) pressure precisely but is less accurate [25] for the supercooled fluid. The dashed curve for the glass is from [33]. The straight solid lines show the forms predicted by equation (15) with  $z = 1.72$  for the glass and equation (21) with  $z_m = 1.86, \gamma = 20$  for the fluid. Hoover *et al* [21] locate the equilibrium freezing point at  $x^4 = 1.75$ . Cape and Woodcock [25] locate the kinetic glass transition near  $x^4 \approx 5$  and the Kauzmann point, where the fluid entropy extrapolates to that of the crystal, near  $x^4 \approx 7$ .

predictions for a one-component fluid and glass of soft spheres and shows that equation (21) fits the supercooled fluid data between the freezing point and the glass transition. The failure of equation (21) at higher temperature (smaller  $x$ ) is expected because the harmonic approximation breaks down when  $x$  is small. Hoover *et al* [21] and Cape and Woodcock [25] note that the superheated crystal is unstable near the freezing temperature, even on very short timescales, and it seems likely that glasses are also unstable there.

Equation (15) fits the soft-sphere crystal pressures [21, 25], to within about twice the uncertainty in the measurements, with  $z = 1.48$ .

The one-component fluid is prone to freezing and more precise data are available for mixtures. Figure 2 shows the results of Yu and Carruzzo [26] for an equimolar binary mixture of soft spheres with diameters in the ratio 1.4. The equilibrium freezing temperature for this mixture has not been determined, but it is likely that equation (21) fits all the supercooled fluid measurements.

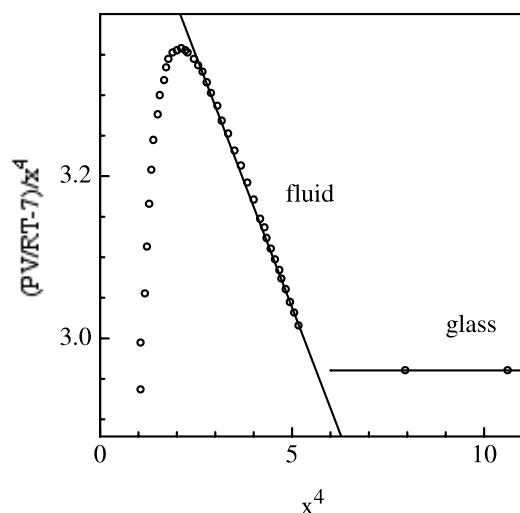
Figure 3 shows Perera's [27] results for an equimolar binary mixture of soft discs with diameters in the ratio 1.4. In this case the freezing point has been located [27] and the figure confirms that equation (21) fits all the supercooled fluid measurements precisely.

## 6. Soft spheres with van der Waals attractions

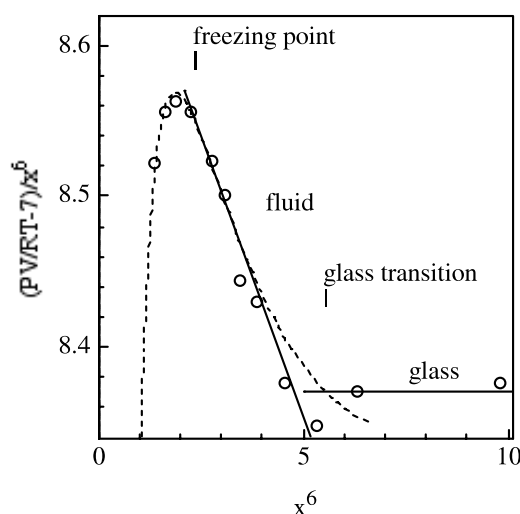
One modified van der Waals equation of state [28] is

$$P = P_{ss} - a(V_0/V)^2 \quad (22)$$

with  $P_{ss}$  the pressure of the soft-sphere crystal, fluid or glasses. Including the attractive term  $-a(V_0/V)^2$  allows the model to describe a liquid–gas transition. Because the harmonic



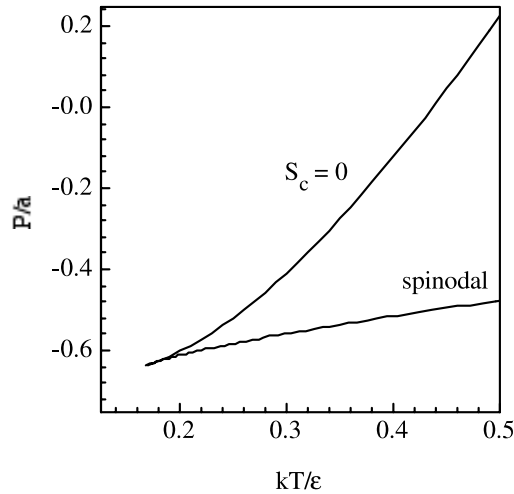
**Figure 2.**  $(PV/RT - 1 - n/2)/x^{n/D}$  versus  $x^{n/D}$  for an equimolar binary soft-sphere mixture ( $D = 3$ ,  $\sigma_b/\sigma_s = 1.4$ ,  $n = 12$ ,  $V_0 = N(\sigma_b^3 + \sigma_s^3)/2$ ). Circles show simulation data from [26]. The straight solid lines show the forms predicted by equation (15) with  $z = 0.75$  for the glass and equation (21) with  $z_m = 0.92$ ,  $\gamma = 16$  for the fluid.



**Figure 3.**  $(PV/RT - 1 - n/2)/x^{n/D}$  versus  $x^{n/D}$  for an equimolar binary soft-disc mixture ( $D = 2$ ,  $\sigma_b/\sigma_s = 1.4$ ,  $n = 12$ ,  $V_0 = N(\sigma_b^2 + \sigma_s^2)/2$ ). Circles show simulation data from [27] (table 4.2 of [27]) and the dashed curve is calculated from a polynomial (equation (4.6) of [27]) which fits the fluid ( $x^6 \leq 5$ ) pressure with a maximum deviation of 0.3% (which corresponds to about four times the symbol size in the figure). The straight solid lines are the forms predicted by equation (15) with  $z = 1.39$  for the glass and equation (21) with  $z_m = 1.45$ ,  $\gamma = 42$  for the fluid.

approximation breaks down above the freezing temperature, the simple model with  $P_{ss}$  given by equations (15) or (21) does not describe a gas accurately.

Figure 4 shows the form of the liquid stability limits predicted by equations (21), (22) in the pressure–temperature plane. The results shown are for  $x^4 > 2$  where figure 1 suggests that equation (21) is reliable. The model predicts an ideal glass transition [9, 29] where  $S_c(z) \rightarrow 0$ . Along the ideal glass transition curve,  $z = z_m - \sqrt{\alpha/\gamma}$  (from equation (17)) and  $x^{n/D} = 2\sqrt{\alpha\gamma}$



**Figure 4.** The ideal glass transition curve,  $S_c = 0$ , and the spinodal curve for soft spheres in the pressure–temperature plane when  $x^4 \leq 2$ , from equations (21), (22) with constants  $z_m = 1.86$ ,  $\gamma = 20$  (from figure 1) and  $\alpha = 1.06$  [30, 31].

(from equation (19)). The values  $\gamma = 20$ , from figure 1, and an estimate [30]  $\alpha = 1.06$  which is in good accord with estimates from a simulation experiment [31] are used. Adding the mean-field attractive potential to the soft-sphere model does not affect the entropy, so the ideal glass transition is located where  $x^{n/D} = 2\sqrt{\alpha\gamma} \approx 9.2$ . The spinodal curve, where  $(\partial P/\partial V)_T \rightarrow 0$ , is calculated from equations (21), (22).

The ideal glass curve is the low-temperature limit of the metastable liquid state and the spinodal curve is the upper temperature limit. The two curves meet with the same slope at the maximum tension (negative pressure) that the metastable liquid can sustain [32].

Figure 5 shows the prediction of equations (21), (22) at higher temperatures and compares them with a more accurate estimate of the spinodal.

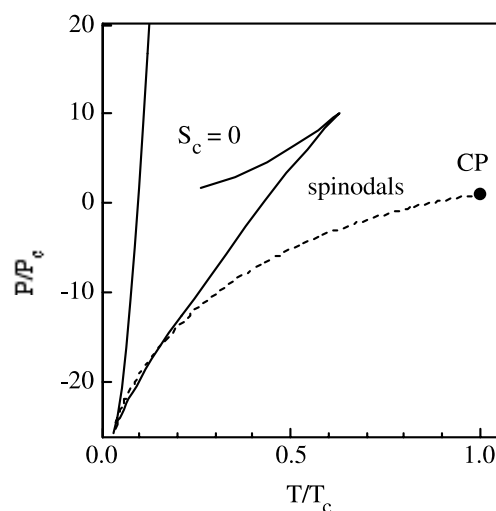
A thermodynamic argument was presented [32] to explain why the curves in figure 4 meet with the same slope. That argument may be flawed in general, but if a single internal parameter is sufficient to distinguish between glasses, which is evidently true for hard spheres and soft spheres, then the curves of constant  $S_c(z)$  must meet a spinodal with the same slope in the  $P, T$  plane. That is because a curve of constant  $S_c(z)$  is also a curve of constant  $z$ , so the fluid samples the same glasses all along the curve. But if  $S_c(z_1, z_2)$  depends on two parameters [10], then  $z_1$  and  $z_2$  may vary along a curve of constant  $S_c(z_1, z_2)$  and the argument becomes more complicated, because changing  $z_1$  and  $z_2$  changes one glass into another, which is not a reversible process in the thermodynamic sense.

## 7. Summary

For soft spheres, the number of minima on the potential energy landscape is independent of the volume, and the shape of each basin in the potential energy landscape varies with volume in a predictable way. Two elementary assumptions:

- (1) that the basins are harmonic and
- (2) that the distribution of basin depths is Gaussian,





**Figure 5.** As figure 4, but extended to higher temperatures where equation (21) is inaccurate (figure 1). The more accurate dashed spinodal curve is calculated using equation (13) from [25] for  $P_{ss}$  in equation (22). The axes are scaled using the critical pressure,  $P_c$ , and critical temperature,  $T_c$ , from the equation from [25].

lead to a simple model for the cold dense states of matter: crystal, glasses, the supercooled fluid and the glass transition.

The model agrees with simulation data at temperatures below freezing but fails above the freezing temperature, where the harmonic approximation breaks down.

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