

42-48
JK

Exact Dynamical Basis for a Fluctuating Cell Model*

WILLIAM G. HOOVER

Lawrence Livermore Laboratory and Department of Applied Science, University of California at Davis-Livermore, Livermore, California 94550

AND

WILLIAM T. ASHURST

Sandia Livermore Laboratory and Department of Applied Science, University of California at Davis-Livermore, Livermore, California 94550

AND

RICHARD GROVER

Lawrence Livermore Laboratory, Livermore, California 94550

(Received 25 April 1972)

Cell-like models for many-body thermodynamic properties can be derived by considering the motion of a single very light particle in a classical system. Because the configuration probabilities are mass independent, the pressure and the energy calculated for such a light particle are identical with thermodynamic values. In the special case of hard spheres it is shown that the pressure from collisions is proportional to the surface-to-volume ratio of the hard sphere free volume.

I. INTRODUCTION

The basic aim of any cell model is to find a "one-particle" or "free-volume" model which successfully mimics the equilibrium properties of a many-body system. Ever since Lennard-Jones and Devonshire introduced the cell-model approximation to thermodynamics, a variety of such models has been hopefully applied to gas, liquid, and solid properties, but with indifferent success.¹ An important reason for this disappointment is that information is lost in the step of converting a many-body description to a one-body model, so that even at best there will be widely differing errors and inconsistencies in properties calculated in this way. Nevertheless, considerable effort at various levels of sophistication has been lavished on the cell model. From the simplest model, in which a single particle sweeps out a free volume in the field of its fixed neighbors, have evolved more complicated models including interparticle correlations, correlations between rows or planes of moving particles, vacancies, and hybrid crystal structures.

Here we suggest that a new and relatively sophisticated cell model should produce accurate pressures and energies for dense fluids. This prediction is based on analysis of a dynamical classical system in which a single light particle will actually execute cell-like motion in the fixed background of its more massive neighbors. Because the configuration probabilities are mass-independent the time-averaged properties of that single moving particle are the same as those in a system where all particles have the same mass and average motion. Thus the properties of the moving particle can be related to many-particle thermodynamics.

We illustrate the correspondence between one-particle and many-particle properties by working out two detailed examples. The examples show that the moving particle occupies a *distribution* of cell sizes and shapes which is relatively broad. This observation

suggests ways in which the predictions of cell models should be improved.

II. DYNAMICAL BASIS FOR THE CELL MODEL

In a classical system of N identical particles the energy and pressure can be calculated as the long-time averages of one-particle quantities:

$$\begin{aligned} E/NkT &= \frac{3}{2} + \langle \phi_1/kT \rangle; \\ PV/NkT &= 1 + \langle v_1/kT \rangle, \end{aligned} \quad (1)$$

where ϕ_1 is Particle 1's share of the total potential energy and v_1 is the analogous contribution of Particle 1 to PV . In the case that the potential energy is a sum of pair terms $\Phi = \sum \phi_{ij}$, ϕ_1 and v_1 are as follows:

$$\begin{aligned} \phi_1 &= \frac{1}{2} \sum_{j=2}^N \phi_{1j}; \\ v_1 &= -\frac{1}{6} \sum_{j=2}^N r_{1j} \phi'_{1j}. \end{aligned}$$

Now consider a slightly modified system in which the *mass* of Particle 1 is much less than that of the other particles, $m_1 \ll m_2 = m_3 \cdots m_N = m$. The average kinetic and potential energies of Particle 1 are mass-independent in a classical system so that (1) still holds. Because the average speed of any particle varies as the inverse square root of its mass, Particle 1 now travels much faster than the rest. As we approach the limit $m_1 \rightarrow 0$ Particle 1 moves naturally at high speed, with $\frac{1}{2} m_1 v_1^2 + 2\phi_1$ constant, while all the others appear frozen. Thus the dynamical situation, with a single light particle, corresponds to a cell-model picture. Notice though that the average potential part of the energy governing the motion of Particle 1 is exactly *twice* the average potential energy per particle.

In the usual cell model the neighbors of the moving central particle are thought of as fixed only for con-

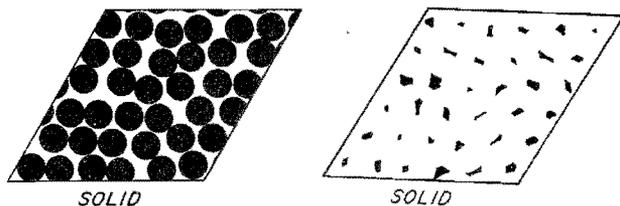


FIG. 1. A typical equilibrium configuration for 36 hard disks in the solid phase at three-fourths the close-packed density. Part A of the Figure shows the disks, Part B indicates the free volume obtained for the disks. Each free volume represents the area available to the center of a disk if all of the remaining disks were held fixed. This single snapshot gives 36 typical light-particle free volumes.

venience, and one particle only is arbitrarily allowed to move. By contrast our model, by giving Particle 1 a small mass, allows that Particle naturally to move faster relative to its heavier neighbors. Of course the neighbors will gradually move too, for any finite m_1 , so that in order to calculate the long-time averages specified in Eq. (1) we would need to include a *distribution* of cell shapes and sizes.

By considering our special system with one light particle we have shown that a cell model *can* actually predict correct thermodynamic properties. Exactly the same conclusion is reached if one considers instead the alternative "Monte Carlo" evaluation² of the configurational averages. In the Monte Carlo average a single particle could be moved many times in succession, holding the rest fixed. Provided that the other particles are *eventually* moved, the single-particle energy and pressure averages will not differ from those calculated with either sequential or random choices of the particle to be moved.³

From either the dynamical or the configurational viewpoint we see that correct energy and pressure predictions depend on the *distribution* of cell sizes and shapes enclosing a typical particle. Thus the central problem of a realistic one-particle cell theory is to describe cell distributions properly.

III. APPLICATION TO HARD SPHERES

Cell models are particularly easy to visualize for classical hard spheres, disks, and rods, because such hard particles are confined to definite "free volumes" with sharp boundaries. Inside the free volumes the potential energy vanishes. See the Figs. 1 and 2 for some typical free volumes in the two-dimensional hard-disk system. "Hard" particles are entirely excluded from the infinite-energy regions in which they could overlap other particles. A light "soft" particle in a system with more realistic forces would have a free volume depending on the total energy $\frac{1}{2}m_1v_1^2 + 2\phi_1$.

For D -dimensional hard spheres the thermodynamic properties are particularly simple:² The average energy is entirely kinetic, $DkT/2$ on the average, and the pressure is simply related to the radial distribution

function $g(r)$ evaluated at the particle diameter σ , or equivalently to the average collision rate $\langle \Gamma \rangle$:

$$PV/NkT = 1 + B_2(N/V)g(\sigma) = 1 + B_2(N/V)\langle \Gamma \rangle / \langle \Gamma \rangle_0. \quad (2)$$

Both ways of writing the hard-particle equation of state express the nonideal part of the pressure in terms of the probability for finding two colliding particles in contact. Because the collision rate depends on mass, the last expression in (2) holds only if the collision rate and the low-density-limit collision rate $\langle \Gamma \rangle_0$ are evaluated for particles with the same mass. In Eq. (2) B_2 is the second virial coefficient, $\frac{2}{3}\pi\sigma^3$ for spheres, $\frac{1}{2}\pi\sigma^2$ for disks, and σ for rods.

In our modified system containing one particle much lighter than all the rest, and hence faster, the equation of state can be expressed equivalently in terms of the mean free path for a light particle, $\langle \lambda \rangle$, and its low-density limit $\langle \lambda \rangle_0 = V/(\pi N\sigma^2)$ for $D=3$; $V/(2N\sigma)$ for $D=2$, and V/N for $D=1$:

$$PV/NkT = 1 + B_2(N/V)\langle \lambda \rangle_0 / \langle \lambda \rangle; \quad m \rightarrow 0. \quad (3)$$

In the three-dimensional hard-sphere case, for example, Eq. (3) simplifies to $PV/NkT = 1 + \frac{2}{3}\sigma / \langle \lambda \rangle$, with the understanding that $\langle \lambda \rangle$ is evaluated for a light particle.

It is clear enough that the pressure calculated from (2) or from (3) could be evaluated in a dynamical simulation of light-particle motion. How can the resulting (exact) one-particle equation of state be related to the properties of a one-particle cell model? We can relate the pressure to the light particle "free volume" by noting that the collision frequency for a light particle confined to a free volume must be proportional to the frequency with which it strikes the boundary surface s_f and inversely proportional to the accessible volume v_f :

$$\Gamma \propto s_f / v_f.$$

The density-independent proportionality constant can be determined from the low-density limit where s_f is $4\pi N\sigma^2$ and v_f is V . The resulting equation of state, for D -dimensional hard spheres, is

$$PV/NkT = 1 + (\sigma/2D)\langle s_f/v_f \rangle. \quad (4)$$

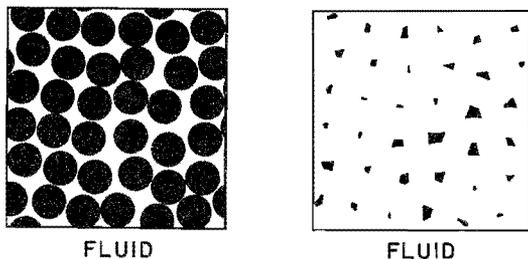


FIG. 2. A "fluid" configuration for 36 disks at three-fourths the close-packed density. Although traces of the initial square-lattice configuration still persists, this figure indicates that the free volume distribution in the fluid phase is characterized by greater fluctuations than that of the solid.

We can illustrate the application of Eq. (4) in the one-dimensional case. Consider a "Tonks gas" of N hard rods of length σ confined to a line of length V .⁴ A slight modification of Tonks' 1936 calculation shows that the probability of finding a hard rod with the free volume v_f within dv_f (where v_f is now the one-dimensional length over which the center of a rod is free to move) is, in the large- N limit of thermodynamics,

$$\text{Prob}(x)dx = xe^{-x}dx.$$

where

$$x = Nv_f/(V - N\sigma).$$

If we calculate the average surface-to-volume ratio using the distribution from Eq. (4) with $s_f=2$, we find $\langle s_f/v_f \rangle = 2N/(V - N\sigma)$. This value, substituted into the general light-particle relation (4), reproduces Tonks' exact equation of state for the many-body system:

$$PV/NkT = 1 + N\sigma/(V - N\sigma) = V/(V - N\sigma).$$

It ought to be pointed out that although we can calculate pressure directly in terms of the free volume and its surface, we cannot so easily calculate the entropy.⁵ The entropy is a collective many-body property which has to be determined by integrating the equation of state from a starting point at which the entropy is known. The usual starting point for an entropy integration would be the low density limit, at which the entropy approaches the known ideal gas limit.

What happens for two or three-dimensional hard spheres? The free volume behaves in an interesting way in these cases. At low density $\langle v_f \rangle$ is obviously extensive, of order V , while at high density $\langle v_f \rangle$ is just as obviously intensive, of order V/N . We expect, but cannot prove, that the sudden change from extensive to intensive free volume occurs at a density well below the freezing density. Of course $\langle s_f \rangle$ would simultaneously change sharply from extensive to intensive so that the quotient in the equation of state (4) would be a continuous function of density. For a realistic potential and at a fixed density the transition from extensive to intensive would occur at a characteristic value of the energy $2\phi_1$. The hard-particle transition density, which could probably be located by computer experiments, would be analogous to the critical densities associated with percolation, network connectivity, and related problems in which the probability for having a path of infinite length changes discontinuously from zero to one at a particular density of links between lattice sites.⁶

In the Figures we show two configurations of 36 hard disks at a density close to the freezing density. For the small 36-disk system it is possible to observe either the fluid phase or the solid phase at this density. Figure 1 shows a periodic arrangement of 36 disks in the triangular (close-packed) crystal structure characteristic of the high-density solid phase. We

show both the locations of the particles and the free volumes which would be available to each of them if all the others were held fixed. Because a movie rather than just a snapshot would be necessary to determine which particle is the light one, we save time and reduce the number of configurations studied by averaging over *all* particles in the system, treating each in turn as if it were the light particle. A single equilibrium configuration, provided many particles are included, is sufficient for an accurate determination of the pressure.⁷ The "fluid" configuration shown in Figure 2 was constructed by starting out with 36 disks in the mechanically unstable square-lattice structure. We hoped in this way to obtain a disordered fluid arrangement. Unfortunately the original conditions are still quite noticeable in the "fluid" configuration shown. We feel that nevertheless the Figures serve to illustrate an important difference between the free volume distributions characteristic of the solid and fluid phases. The two snapshots reveal that, at the same density, the fluid phase is characterized by (1) smaller free volumes and (2) larger fluctuations in the distribution of free volumes relative to the solid phase. A systematic investigation of free volume geometry, using fast computers, is feasible, and should prove particularly rewarding in developing cell theories able to distinguish between the solid and fluid phases.

IV. APPLICATION TO HARMONIC CRYSTALS

Having studied the totally anharmonic hard-sphere case, we now consider softer forces for which energy, as well as pressure, can be determined from a cell model. We consider explicitly a one-dimensional harmonic chain of N particles with the nearest-neighbor interaction energy $\frac{1}{2}\kappa(x_i - x_{i+1})^2$ where the x variables indicate *displacements* from the minimum-energy configuration and where N is much greater than 1. This model, like the one-dimensional hard rod model treated in Sec. III, has an intensive free volume at all energies because each particle is confined between its nearest neighbors. To avoid the complications of surface effects we join Particle 1 to Particle N so that the system can be viewed as being either periodic or confined to the perimeter of a large circle. Then, if we focus attention on Particle 1, assumed again to be the light particle, we can write its potential energy in either of two equivalent ways:

$$\begin{aligned} \frac{1}{4}\kappa[(x_1 - x_N)^2 + (x_1 - x_2)^2] &= \phi_1 \\ &= \frac{1}{2}\kappa[(x_1 - \frac{1}{2}x_2 - \frac{1}{2}x_N)^2 + \frac{1}{4}(x_2 - x_N)^2]. \end{aligned}$$

In either form for ϕ_1 (each of the terms in parentheses has an average value $\frac{1}{4}kT$). The second way of writing the one-particle energy ϕ_1 is particularly instructive because it separates the potential energy into rapidly varying and slowly varying components. The first term varies rapidly about its average value, half the average kinetic energy of Particle 1, on the time scale of light-particle motion. The second term, viewed

on the same time scale, is constant and plays the role of a static increase in potential energy due to a local density fluctuation. The average value of the second term, on the time scale of heavy-particle motion, is also $\frac{1}{2}kT$, as exact evaluation shows. An *approximate* calculation leading to the same result is helpful in understanding the origin of the slowly varying static energy: if standard thermodynamic fluctuation theory⁸ is applied to evaluate the second term $\langle \frac{1}{8}\kappa(x_2 - x_1)^2 \rangle$, by using $\langle (\delta V/V)^2 \rangle = kT/BV$, where B is the bulk modulus, the exact value $\frac{1}{2}kT$ is obtained. In the harmonic chain case, just as in the anharmonic hard sphere case, the one-particle model predicts exact thermodynamic properties. The pressure calculation for the harmonic chain is very similar to the energy calculation just carried out. The major difference between the hard-sphere and the harmonic-chain free volume distributions is that the oscillators have a narrower (Gaussian) distribution while the spheres have a wider (exponential) one.

Two- or three-dimensional harmonic crystals can be treated by analogy with the one-dimensional case. If the terms contributing to ϕ_1 are diagonalized the results can be separated into a slowly varying mean-field density fluctuation contribution of $\frac{1}{4}DkT$ and a rapidly varying thermal potential energy $\frac{1}{4}DkT$. The total light-particle energy includes these two equal potential terms plus the kinetic-energy contribution $\frac{1}{2}DkT$.

The division of the potential energy into two parts makes it possible to understand an ambiguity that is present in the usual cell theory.⁹ In that treatment the potential energy for a "wanderer" particle moving in the field of its fixed neighbors is treated in an inconsistent way. The energy $2\phi_w = \sum \phi_{wj}$ is separated into a static part, evaluated in the perfect-lattice configuration with Particle w at its cell center, and a dynamic part, $2\phi_w - 2\phi_w(0)$. The per particle energy from the cell model is then taken to be *half* the static part plus the average value of the *entire* dynamic part, $(\Phi/N)_{\text{cell}} \equiv \phi_w(0) + \langle 2\phi_w - 2\phi_w(0) \rangle = \langle 2\phi_w \rangle - \phi_w(0)$. Although our detailed view of the cell model shows that both parts of the energy should be divided by two, $(\Phi/N)_{\text{exact}} \equiv \phi_1 \equiv \langle \frac{1}{2} \sum \phi_{ij} \rangle$, the *inconsistent* cell-theory treatment leads to the *exact* energy in the harmonic-crystal case. This paradox is resolved by noting that the excess potential energy of the wandering particle included in the cell-theory calculation, $\frac{1}{4}DkT$ more than the consistent treatment would give to Particle 1, is exactly compensated by the omitted $\frac{1}{4}DkT$ which would actually appear in $\phi_w(0)$ due to local fluctuations in density and shape.

V. CONCLUSION

This light-particle study suggests that the usual cell model should be improved by taking the cell-size and cell-shape distributions into account. This could

be done by applying a variational technique, by applying macroscopic fluctuation theory, or by using an empirical form for the cell distribution suggested by computer experiments. Some work along these lines, directed toward the calculation of thermodynamic properties from a cell model incorporating density fluctuations, has already been carried out.¹⁰ It seems likely that similar fluctuation effects could profitably be included in calculations of the electronic band structure of solids.

The approximate work of Gosling and Singer⁵ shows that computer experiments could be devised to measure the dependence of free volume shapes and sizes on density and energy. Such experiments could also provide guidance for distinguishing the solid and the fluid phases on the basis of one-particle properties.

ACKNOWLEDGMENTS

We would like to thank Thomas Gorman for his painstaking execution of the Figures.

Marvin Ross helped our investigation with both criticism and suggestions.

* This work was performed under the auspices of the United States Atomic Energy Commission.

¹ For a comprehensive analysis of cell models see J. A. Barker, *Lattice Theories of the Liquid State* (MacMillan, New York, 1963).

² See the Chapters by W. W. Wood and by B. J. Alder and W. G. Hoover in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (Wiley, New York, 1968).

³ In a computer calculation of the free energy of vacancy formation, the work necessary to uncouple a particle from its neighbors was measured. It was found to be useful to move the nearest neighbors of the coupled particle more frequently than the others; D. R. Squire and W. G. Hoover, *J. Chem. Phys.* **50**, 701 (1969).

⁴ L. Tonks, *Phys. Rev.* **50**, 955 (1936).

⁵ In approximate cell theories the Helmholtz free energy is determined from the one-particle partition function, $-A/NkT = \ln Z_1 + \text{constant}$. In most cases the so-called "constant" actually depends on both V and T . An attempt to calculate the entropy by using free volumes determined with fast computers has been published by E. M. Gosling and K. Singer, *Pure and Applied Chem.* **22**, 303 (1970), and indicates that for liquids approximate entropies can be obtained in this way; the Gosling-Singer work is qualitatively very interesting but should be read with caution because most of the equations in it are actually inequalities. We would like to thank Professor Singer for some stimulating correspondence, including a preprint, "Some Comments on the Free Volume (Cell-) Model of Liquids based on Monte Carlo Calculations." This preprint, submitted to *J. Chem. Soc. Faraday Trans. II*, clarifies and extends the earlier Gosling-Singer work and points out the need for further quantitative study of the cell-model approach.

⁶ J. M. Ziman, *J. Phys. C* **1**, 1532 (1968).

⁷ Bernal has long suggested that the configuration typical of the fluid phase be constructed by randomly close-packing hard spheres. Now that such packings can be generated efficiently, Bernal's ideas can be tested quantitatively. See D. J. Adams and A. J. Matheson, *J. Chem. Phys.* **56**, 1989 (1972).

⁸ See Sec. 111 of L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958).

⁹ The question of whether or not to include a factor of two in the one-particle thermal energy is discussed in Sec. 14-1 of J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940).

¹⁰ R. Grover [unpublished work described in *Bull. Am. Phys. Soc.* **17**, 80 (1971)].