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Statistical Analysis of Classical Few-Particle Systems*

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The three examples of ideal gas, square well, and harmonic oscillator particles illustrate the equivalence of the constant-energy and constant-temperature descriptions of statistical mechanics if the number of degrees of freedom is large. Significant differences between these descriptions appear, however, in the opposite extreme, i.e., the few-particle limit. The analysis presented here supports the conclusion that three degrees of freedom are necessary to localize a particle in the oscillator potential. This result is discussed in connection with the stability (finite rms particle displacement) of three-dimensional harmonic crystals.

I. INTRODUCTION

From the viewpoint of thermodynamics, the state variables describing large systems with many particles are constant. Thus, constant-energy systems are thermodynamically indistinguishable from the corresponding constant-temperature systems. The viewpoint of statistical mechanics, however, reveals fluctuations in state variables. Applied to small, few-particle systems, the statistical approach exhibits interesting distinctions between the constant-energy and con-

stant-temperature descriptions. These statistical distinctions provide insight into the stability of real three-dimensional crystals.

As a particular example, consider a single particle in a classical one-dimensional harmonic oscillator potential. For such a system, with fixed energy E , the oscillating particle is most likely to be found at its turning points (where the velocity vanishes). From the momentum viewpoint, the most likely value is again the maximum (where the force vanishes). For the same system maintained at temperature T with mean energy E , however, the particle is most likely to be found at the potential energy minimum with x and p both zero. (See Fig. 1.)

As the number of degrees of freedom increases, how is the thermodynamic limit (where the energy and temperature descriptions agree) approached? We illustrate the correspondence between fixed-energy and fixed-temperature results by working out three examples: particles which are free, particles bound by nonuniform square well potentials, and particles bound by oscillator potentials. We find that three degrees of freedom are necessary to localize a particle near its potential minimum. This result is useful in understanding the well-known stability of three-dimensional crystals and the less well-known instability of one and two-dimensional crystals. (The stability question is discussed, for example, by Frenkel.¹)

II. FREE PARTICLES IN ONE DIMENSION

Consider N classical noninteracting particles confined to a potential-free one-dimensional box of length L . If the box is maintained at temperature T , then the probability density for momentum $-\infty < p < \infty$ of any particle is given by

$$\text{Prob}(p) dp = (2\pi mkT)^{-1/2} \exp[-p^2/(2mkT)] dp. \tag{1}$$

If, instead of the temperature, we maintain the

total energy between E and $E+dE$, we find that the momentum distribution depends on N . For a single particle ($N=1$) the momentum can only have the values $\pm(2mE)^{1/2} = \pm E^{1/2}$. (Here and in what follows we shall take $m=1/2$ to simplify notation.) For $N \geq 2$, the energy is given by $p_1^2 + p_2^2 + \dots + p_N^2$ and we can represent all allowed momentum states as the set of points (i.e., the volume) lying between two N -dimensional hyperspheres:

$$E \leq p_1^2 + p_2^2 + \dots + p_N^2 \leq E + dE.$$

If we focus attention on a single particle with momentum p_1 , this relation becomes $E - p_1^2 \leq p_2^2 + p_3^2 + \dots + p_N^2 \leq E + dE - p_1^2$, and we are concerned with the volume in hyperspace between $(N-1)$ -dimensional spheres of radius $E - p_1^2$ and $E + dE - p_1^2$. Since the volume of an $(N-1)$ -dimensional sphere of radius r is proportional to r^{N-1} , we find (omitting redundant subscripts):

$$\begin{aligned} \text{Prob}(p) dp &\propto [(E + dE - p^2)^{(N-1)/2} \\ &\quad - (E - p^2)^{(N-1)/2}] dp \\ &\simeq [(E - p^2)^{(N-1)/2} \\ &\quad + \frac{1}{2}(N-1)(E - p^2)^{(N-3)/2} dE \\ &\quad + \dots - (E - p^2)^{(N-1)/2}] dp. \quad (2) \end{aligned}$$

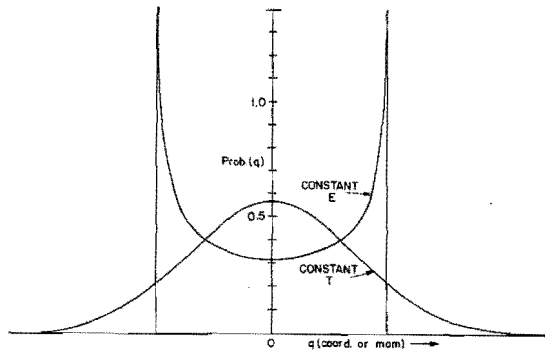


FIG. 1. Constant-energy and constant-temperature probability distributions (coordinate or momentum) for a single particle in a one-dimensional harmonic oscillator potential. The curves have been normalized to the same area.

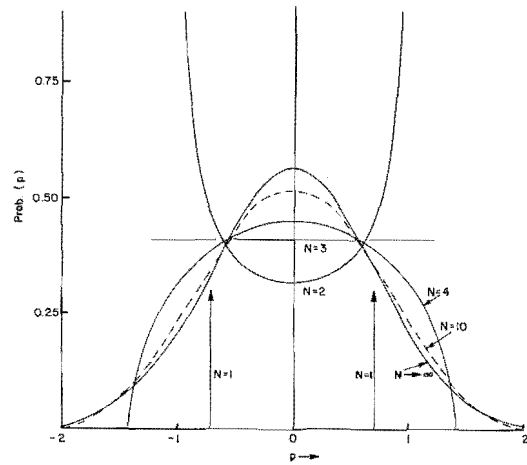


FIG. 2. Normalized momentum distributions for free particles of fixed total energy in one dimension; a sequence of curves for various N (number of particles) showing the approach to the fixed-temperature result, $\pi^{-1/2} \exp(-p^2)$, as N goes to infinity.

If we keep only the first order term in dE , we have

$$\text{Prob}(p) dp = C_N (E - p^2)^{(N-3)/2} dp.$$

We can identify C_N from the normalization condition,

$$\int_{-\sqrt{E}}^{\sqrt{E}} \text{Prob}(p) dp = 1,$$

arriving at the following expression for the probability:

$$\begin{aligned} \text{Prob}(p) dp &= \frac{\Gamma(N/2)}{\sqrt{(E\pi)} \Gamma(N \cdot 1/2)} \\ &\quad \times (1 - p^2/E)^{(N-3)/2} dp \end{aligned}$$

with

$$\Gamma(n) \equiv \int_0^\infty \exp(-x) x^{n-1} dx.$$

For large N this distribution approaches the constant-temperature result [Eq. (1)] with $E = \frac{1}{2}NKT$; i.e., the usual correspondence between kinetic energy and temperature for a one-dimensional system. The approach is illustrated graphically in Fig. 2 for $N=1, 2, 3, 4, 10$, and $N \rightarrow \infty$, where we have set $kT=1$ for simplicity. The

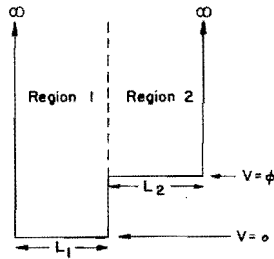


FIG. 3. The non-uniform square well potential discussed in Sec. III.

transition to Eq. (1) for $N \rightarrow \infty$ is obtained mathematically by means of the following correspondence:

$$\begin{aligned} \text{Prob}(p) dp &\underset{N \rightarrow \infty}{\propto} (1 - p^2/\frac{1}{2}NkT)^{(N-3)/2} dp \\ &\simeq [\exp(-p^2/\frac{1}{2}NkT)]^{N/2} dp \\ &= \exp(-p^2/kT) dp. \end{aligned}$$

The error in this replacement is of order $1/N$, which vanishes in the limit $N \rightarrow \infty$.

The distributions for $N=1, 2$, and 3 are clearly distinct, while for $N=4$ a qualitative resemblance to the thermodynamic large-system limit has already begun to emerge. The $N=3$ case is an interesting and significant boundary between systems in which high momenta are more probable and systems in which low momenta prevail. Momentum independence of the distribution for $N=3$ arises from the quadratic dependence of kinetic energy on momentum, and while it occurs here in connection with $N=3$, the result is clearly peculiar to the momentum space of two particles. The probability of a given value of p_1 is determined by the volume in momentum space available to the remaining two particles, a quantity which turns out to be independent of p_1 [see Eq. (2)]:

$$\begin{aligned} \text{Prob}(p_1) &\propto [(E + dE - p_1^2)^{1/2}]^2 \\ &\quad - [(E - p_1^2)^{1/2}]^2 = dE. \end{aligned}$$

There is a simple geometric analog for the constancy of the $N=3$ probability distribution: the cross-sectional area of a plane cut through an

idealized three-dimensional orange peel (spherical, uniform thickness) is independent of the cut's location so long as it does not lie entirely within the peel.

III. PARTICLES IN A NON-UNIFORM SQUARE WELL

In this section we extend the preceding discussion to include a potential of the form shown in Fig. 3. Momentum distributions can be derived by straightforward extension of the methods developed in Sec. II. Here we shall determine instead the expectation values $\langle n_1 \rangle_{av}$ and $\langle n_2 \rangle_{av}$, the average number of particles in regions 1 and 2. We determine the equilibrium numbers by statistical weighting of the various possible configurations for a given value of the total energy. A configuration is specified by giving the number of particles in regions 1 and 2, n_1 and n_2 . The phase space statistical weight associated with the partition $[n_1, n_2]$ consists of two elements. The coordinate space statistical weight, given by $L_1^{n_1} L_2^{n_2}$ can be set equal to unity if we choose $L_1 = L_2 = 1$. The momentum space statistical weight is given as in Sec. II by the volume in N -dimensional space between hyperspheres corresponding to the maximum momenta $(E - \Phi + dE)^{1/2}$ and $(E - \Phi)^{1/2}$. The potential energy Φ is equal to $n_1 \phi_1 + n_2 \phi_2 \equiv n_2 \phi_2$ (see Fig. 3). Hence,

$$\begin{aligned} \Delta V_p &\propto [(E - n_2 \phi + dE)^{1/2}]^N - [(E - n_2 \phi)^{1/2}]^N \\ &\propto (E - n_2 \phi)^{(N-2)/2} dE + O(dE^2). \end{aligned}$$

The resulting expression for the expectation value $\langle n_1 \rangle_{av}$ can then be written

$$\langle n_1 \rangle_{av} = \frac{1}{Z} \sum_{n=0}^N n \frac{N!}{n!(N-n)!} [E - (N-n)\phi]^{(N-2)/2}$$

with

$$Z = \sum_{n=0}^N \frac{N!}{n!(N-n)!} [E - (N-n)\phi]^{(N-2)/2}. \quad (3)$$

The binomial coefficients give the number of ways N distinguishable particles can be partitioned into groups of n and $N-n$. If $[E - (N-n)\phi]$ becomes negative, it means that the

corresponding partition is energetically forbidden. Such terms are simply omitted in the sum over n for both Z and $\langle n_1 \rangle_{av}$.

We can find $\langle n_2 \rangle_{av}$ by a similar calculation, or more directly from $\langle n_2 \rangle_{av} = N - \langle n_1 \rangle_{av}$. The behavior of the ratio $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ as a function of N is most easily illustrated graphically. However, to define the parameters E and ϕ it is useful to consider first the limiting form of $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ for $N \rightarrow \infty$. From Sec. II, we know that for large N the system becomes equivalent to one for which the temperature is specified. The ratio $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ is therefore determined by the Boltzmann factor corresponding to the potential energy difference ϕ ; $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av} = \exp(-\phi/kT) = \exp(-\phi/2\epsilon)$. ϵ represents the average kinetic (thermal) energy per particle and corresponds to $\frac{1}{2}kT$ for a one-dimensional system. Therefore, if we wish to observe the approach to this limit in a consistent manner as N goes from 1 to ∞ , we should evaluate $\langle n_1 \rangle_{av}$ and $\langle n_2 \rangle_{av}$ in each case for fixed ϵ . This requires an iterative procedure since ϵ depends on the value of $\langle n_2 \rangle_{av}$, i.e., $\epsilon = (E - \langle n_2 \rangle_{av}\phi) / N$. We choose a value of E , calculate $\langle n_1 \rangle_{av}$ and $\langle n_2 \rangle_{av}$, and then

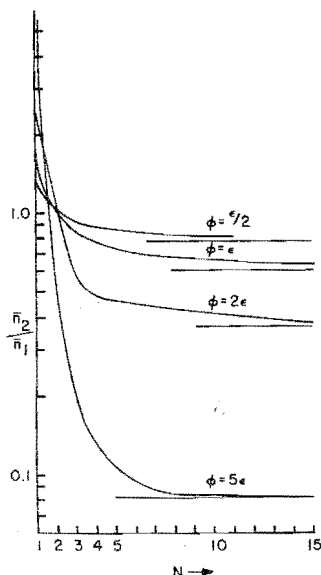


FIG. 4. The particle number ratio $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ as a function of N for fixed mean kinetic energy ϵ in the potential of Fig. 3. The curves for different ϕ approach the corresponding value of $\exp(-\phi/2\epsilon)$ as N becomes large.

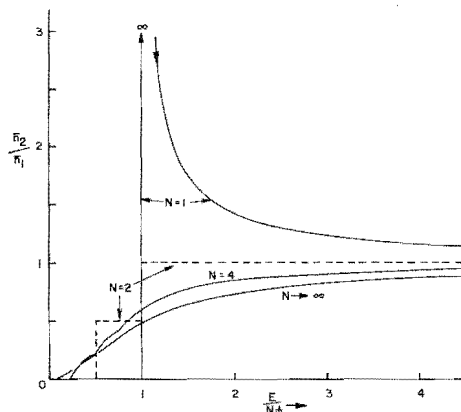


FIG. 5. The particle number ratio $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ as a function of mean total energy for various values of N . The limiting curve for $N \rightarrow \infty$ corresponds to the Boltzmann factor $\exp(-\phi/kT)$ with $\frac{1}{2}kT = \epsilon$.

find the corresponding value of ϵ from the relation just given. A few iterations of this procedure with suitably revised values of E will usually produce the desired value of ϵ to sufficient accuracy.

Figure 4 is a plot of the ratio $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ as a function of N for four values of ϕ ranging from $\epsilon/2$ to 5ϵ . In each case, the only value of N for which the particle density is greater in the region of higher potential occurs for $N=1$. For a single particle, the value of $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ as given by Eq. (3) is, just as one expects, the ratio τ_2/τ_1 of the times spent in region 2 and region 1 for a particle with total energy E :

$$\frac{\langle n_2 \rangle_{av}}{\langle n_1 \rangle_{av}} = \frac{\tau_2}{\tau_1} = \frac{v_1}{v_2} = \left(\frac{E}{E-\phi} \right)^{1/2}$$

For $N=2$, we have $\langle n_1 \rangle_{av} = \langle n_2 \rangle_{av}$ for any choice of ϕ so long as $E > 2\phi$. Since $E = N\epsilon + \langle n_2 \rangle_{av}\phi$, this condition cannot be satisfied for $\phi > 2\epsilon$, and we note that the curve for $\phi = 5\epsilon$ passes through $\frac{1}{2}$ at $N=2$ instead of 1. The equality of $\langle n_1 \rangle_{av}$ and $\langle n_2 \rangle_{av}$ (for $N=2$ and $\phi < 2\epsilon$)² is another manifestation of the unusual behavior of a two particle system resulting from the quadratic energy-momentum relationship. The specific value $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av} = \frac{1}{2}$ for $\phi = 5\epsilon$ can also be traced to the same cause. For $N > 2$, $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ is less than one for all N , decreasing monotonically in each

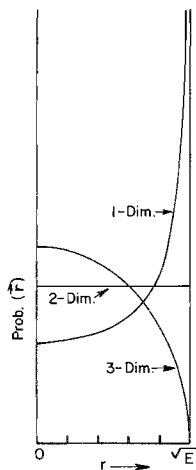


FIG. 6. Coordinate probability distributions for a single particle of total energy E in the one-, two-, and three-dimensional harmonic oscillator potentials. The curves have been normalized to the same area. In two and three dimensions, we distinguish $\text{Prob}(r)$ from $\text{Prob}(|\mathbf{r}|)$; e.g., in three dimensions, $\text{Prob}(|\mathbf{r}|)dr = 4\pi r^2 \text{Prob}(r)dr$.

case to the limiting value $\exp(-\phi/2\epsilon)$ for large N .

We can interpret the results for large N as the probability, in a one particle system maintained at temperature T , for finding the particle in region 2 or in region 1. We thereby identify a qualitative difference between one particle systems of given energy and given temperature. The particle "prefers" the region of high potential if the energy is specified, the region of low potential if the temperature is specified.

In Fig. 5, we plot the ratio $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ for $N=1, 2, 4$, and $N \rightarrow \infty$ as a function of $E/N\phi$, the mean total energy in units of ϕ . For $N=1$, the curve is derived from $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av} = (E/E-\phi)^{1/2}$ and can be described as follows: $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$ is zero until E becomes equal to $\phi + \delta$, at which point the particle has velocity $\sim \delta^{1/2}$ in region 2; $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av} \rightarrow \infty$ therefore as $\delta \rightarrow 0$. For $N \geq 2$, a similar description in terms of energetically forbidden configurations applies, with "thresholds" at $E = \phi, 2\phi, \dots$ up to $N\phi$, for permitting an additional particle in region 2. Beyond $N=1$, however, there are no further infinities in $\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av}$; configurations having particles of zero velocity in region 2 are compensated by those configurations having particles

with zero velocity in region 1. Due to the properties of a two particle system noted earlier, the curve for $N=2$ is horizontal between energy thresholds. For $N=4$ there are thresholds at $E = \phi, 2\phi, 3\phi$, and 4ϕ . The slope of the curve between thresholds follows directly from Eq. (3) with the omission of terms corresponding to forbidden configurations. It is apparent that the degree of discontinuity decreases with increasing N as the sequence of curves approaches the limiting result for $N \rightarrow \infty$, which has been derived from the Boltzmann relationship,

$$\langle n_2 \rangle_{av} / \langle n_1 \rangle_{av} = \exp(-\phi/2\epsilon).$$

As $E/N\phi$ becomes large, the influence of the potential difference ϕ decreases and the curves for different N all approach unity.

IV. PARTICLES IN A HARMONIC OSCILLATOR POTENTIAL

We have been dealing thus far with a Hamiltonian of the form

$$E = \sum_{i=1}^N (p_i^2/2m + k_0 x_i^2/2)$$

or

$$E = \sum_{i=1}^{2N} q_i^2$$

if for convenience we choose $m=1/2, k_0=2$, and represent both p and x by q . With the energy bounded between E and $E+dE$, the statistical weight associated with a particular q_i is given by the volume in phase space between hyperspheres corresponding to E and $E+dE$:

$$\Delta V \propto [(E+dE - q_j^2)^{1/2}]^{2N-1} - [(E - q_j^2)^{1/2}]^{2N-1} \\ \simeq C_N (E - q_j^2)^{N-3/2}$$

with C_N a constant of proportionality. Letting $N=1$, we find the distribution proportional to $(1 - q^2/E)^{-1/2}$ which is the usual harmonic oscillator probability function for the particle coordinate or the momentum.

For two particles, it is more interesting to consider the distribution function corresponding to the simultaneous specification of both particle coordinates. The physically realizable space of x_1 and x_2 is a circular disk of radius equal to \sqrt{E} . The probability associated with any point in this disk (value of x_1 and x_2) is proportional to the area in two-dimensional momentum space (p_1 and p_2) corresponding to the energy range dE . As we have already seen, however, this area is energy independent:

$$[(E + dE - x_1^2 - x_2^2)^{1/2}]^2 - [(E - x_1^2 - x_2^2)^{1/2}]^2 = dE.$$

The probability is therefore *uniform* over the disk $x_1^2 + x_2^2 \leq E$, independent of x_1 and x_2 .

We can interpret this result for two particles in one dimension as a description corresponding to one particle in two dimensions. The Hamiltonians are the same for an isotropic oscillator:

$$E = x_x^2 + x_y^2 + p_x^2 + p_y^2 = \mathbf{r}^2 + \mathbf{p}^2.$$

Since all allowed values of \mathbf{r} are equally probable, there is no tendency toward stabilization in any location.

On considering three particles in one dimension, we can interpret the result as a description of one particle in three dimensions. We omit the now familiar line of reasoning and simply state the result: $\text{Prob}(\mathbf{r}) \propto (1 - |\mathbf{r}|^2/E)^{1/2}$. This function, which ranges over the interior of the sphere $|\mathbf{r}|^2 \leq E$, has a maximum for $\mathbf{r} = \mathbf{0}$ as shown in Fig. 6 where we compare the distributions for the one-, two-, and three-dimensional oscillators. In contrast to the situation for a single particle in one and two dimensions, the distribution function in three dimensions suggests a stable condition in which the particle is most likely to be found near the origin.³

These results have an interesting analog in the theory of crystal stability. A harmonic crystal (meaning that the Hamiltonian is a quadratic form in the coordinates and momenta and that diffusion is not allowed) can have a finite mean squared displacement only in three (or more) dimensions. If x is the displacement along any one

coordinate (for a cubic crystal),

$$\langle x^2 \rangle = (kT/m) \langle \omega^{-2} \rangle.$$

The divergence of $\langle \omega^{-2} \rangle$ in one and two dimensions occurs in exact calculations for finite crystals⁴ and also follows from the Debye model, which is exact for those low frequencies causing the divergence:

$$\left\langle \frac{1}{\omega^2} \right\rangle = \int_0^{\omega_D} \omega^{-2} \omega^{d-1} d\omega / \int_0^{\omega_D} \omega^{d-1} d\omega;$$

where d is the dimensionality (1, 2, or 3) and ω_D is the Debye frequency.

The divergence is very slow in two dimensions; a classical two-dimensional crystal with lattice spacing of three Angstroms stretching from here to the moon would have an rms displacement much less than one micron.

The divergence can be understood in terms of the central limit theorem which implies that the number of particles in a fixed macroscopic region of space must fluctuate by an amount of order $\langle N \rangle^{1/2}$. Since the boundary of a one-dimensional region contains only two particles, the central limit theorem can only be satisfied if particles move (i.e., positions fluctuate) a distance of order $\langle N \rangle^{1/2}$ lattice spacings. In three dimensions, on the other hand, the surface of a sphere is of order $N^{2/3}$ so that individual motions which are vanishingly small, of order $N^{-1/6}$, can satisfy the theorem. The two-dimensional case is on the borderline, requiring displacements on the order of a single lattice spacing, and slowly diverges for $N \rightarrow \infty$ as noted above.

The results we have just found for one-, two-, and three-dimensional oscillators are suggestively similar. The one-dimensional oscillator is most likely to be found at its turning points. The two-dimensional oscillator is equally likely to be found *anywhere* in its allowed coordinate region, $0 \leq x^2 + y^2 \leq E$. For the three-dimensional oscillator the most probable location occurs at the origin with the probability going to zero at the turning radius.

There are a number of anomalies associated with various two-dimensional systems. The neutral stability exhibited here in the two-dimensional

oscillator has a counterpart in the two-dimensional crystal, for which the force constant opposing displacement of a particle vanishes [$k \sim (\ln N)^{-1}$] as the size goes to infinity.⁴ (In this same limit for fluids, the transport coefficients diverge⁵ in two dimensions.) It is interesting to observe that the results derived here on the basis of a simple statistical approach are in qualitative agreement with crystal stability properties derived through more sophisticated treatments.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

¹J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955), p. 119.

²To be precise, we have considered here the case $\phi = 2\epsilon - \delta$ with δ an arbitrarily small number.

³One might argue that we should consider $2\pi r \text{Prob}(\mathbf{r})dr$ and $4\pi r^2 \text{Prob}(\mathbf{r})dr$ in the two- and three-dimensional cases, respectively. While this would change the distributions, it would not alter the conclusion; namely, that the probability maximum occurs at something less than r_{max} only in three (or more) dimensions.

⁴Explicit results for two-dimensional hard disks are tabulated by D. A. Young and B. J. Alder, *J. Chem. Phys.* **60**, 1254 (1974). For two-dimensional classical close-packed harmonic crystals, with nearest-neighbor interactions, the mean squared displacement varies as $(\ln N)$ for N large [W. G. Hoover, W. T. Ashurst, and R. J. Olness, *J. Chem. Phys.* **60**, 443 (1974)].

⁵The divergence is still being studied. For references to recent work, see T. Keyes and I. Oppenheim, *Phys. Rev. A* **8**, 937 (1973).