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# Singularities of the pressure for hard-core systems

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It is shown that the divergence of the pressure at the close-packed volume for the metastable supercooled fluid branch may be less singular than that of a first-order pole—the result of the free-volume theory. Such weaker singularity gives a possible explanation of why the numerical values found for the close-packed volume are always less than Bernal's random close-packing volume.

A question of constant interest for a classical continuous system of particles with purely repulsive hard-core potential is the nature of the singularity of the pressure $P$ at the density of amorphous close packing[1,2] (extended fluid branch), and at the density of closest packing[3] (solid phase). In what follows we show that the singularity at the density of closest packing in the solid phase, viz., $\rho_0 = N/V_0$, where $V_0$ is the minimum volume enclosing $N$ particles with hard cores, is of the form

$$P_{\text{solid}}/\rho_0 kT \simeq \frac{A}{(1-V_0/V)^{\lambda}} \quad \text{as } V \rightarrow V_0, \tag{1}$$

with $A > 0$ and $\lambda \geq 1$. In addition, if a singularity exists with $N/V_1 \equiv \rho_1 < \rho_0$ in an extended fluid branch, then

$$P_{\text{fluid}}/\rho_1 kT \simeq \frac{B}{(1-V_1/V)^{\mu}} \quad \text{as } V \rightarrow V_1, \tag{2}$$

with $B > 0$ and $\mu > 0$. For a macroscopic system of hard disks, $V_0 = N\sigma^2\sqrt{3}/2$, as given by the hexagonal close-packed arrangement. In three dimensions, the densest possible packing for a macroscopic system of hard spheres is assumed to be the regular close-packed arrangement, viz., either hexagonal close packing or face-centered-cubic packing, and so $V_0 = N\sigma^3/\sqrt{2}$. Notice that for macroscopic systems the shape of the volume is of no thermodynamic consequence.

The partition function for the purely repulsive hard-core potential in any spatial dimension $d$ is given by[4]

$$Z(V,N,T) = (N!\lambda^{Nd})^{-1}\int_V d\mathbf{r}_1 \cdots \int_V d\mathbf{r}_N \times \prod_{1 \leq i < j \leq N} S(|\mathbf{r}_i - \mathbf{r}_j|)\ , \tag{3}$$

where

$$S(|\mathbf{r}|) = \begin{cases} 1 \text{ if } |\mathbf{r}| > \sigma, \\ 0 \text{ if } |\mathbf{r}| < \sigma \end{cases} . \tag{4}$$

(The variable $\sigma$ is the length of the hard rods or the diameter of the hard disks or spheres.) Note that[4]

$$Z(V,N,T) = 0 \quad \text{when } \rho \geq \rho_0\ . \tag{5}$$

It is important to remark that in computer experiments the partition function is obtained[3] by integrating the equation of state [defined by Eq. (7) below]. Therefore, a metastable supercooled phase and the solid phase possess different partition functions. However, a single mathematical analysis suffices to consider both cases. Suppose the pressure is singular at some density $\rho = \rho_c \leq \rho_0$, and

$$P/\rho_c kT \simeq \frac{C}{(1-V_c/V)^{\omega}} \quad \text{as } V \rightarrow V_c\ , \tag{6}$$

with $C > 0$ and $\omega > 0$. The assumed form (6) for the behavior of the pressure near a singularity includes also possible multiplicative logarithmic singularities. (This is quite similar to the way critical-point exponents are defined[4] in the theory of phase transitions.) It is clear that one can consider all sorts of more complicated singularities, e.g., essential singularities, limit point of different types of singularities, and so on, and carry through a more general analysis. However, even the simple form (6) is much more general than anything assumed in the literature, and, in fact, allows us to prove that the possibility $\mu < 1$ cannot be ruled out for random close packing. Now, by definition,

$$\frac{P}{kT} \equiv \left(\frac{\partial}{\partial V}\ln Z(V,N,T)\right)_{N,T}\ , \tag{7}$$

and so

$$Z(V,N,T) = \begin{cases} e(N,T)\exp\{[CN/(1-\omega)](1-V_c/V)^{1-\omega}\}; & \omega \neq 1\ , \\ f(N,T)(1-V_c/V)^{CN}, & \omega = 1\ , \end{cases} \tag{8}$$

as $V \rightarrow V_c$, where $e(N,T)$ and $f(N,T)$ are constants of integrations. (It should be remarked that the pure numbers $C$, $\omega$, and $V_c/V_0$ depend weakly on $N$ and become strictly independent of $N$ only in the thermodynamic limit.) For $\rho_c = \rho_0$, $Z_{\text{solid}}(V,N,T)$ must vanish by (5) as $V \rightarrow V_0$, and so $\omega = \lambda \geq 1$, thus establishing result (1) with $C = A$. (The free-volume approximation gives[5] $\lambda = 1$ and $A = d$, which is exact for hard rods.) However, for $\rho_c = \rho_1$, $Z_{\text{fluid}}(V,N,T)$ need not vanish as $V \rightarrow V_1$, and so $\omega = \mu > 0$, and result (2) follows with $C = B$.

It should be noted that the analysis, with equation-of-state data from molecular dynamics (MD) and Monte Carlo studies is based on a linear behavior[6] of $\rho kT/P \sim (\eta_{\text{RCP}} - \eta)$ near the vicinity of random close packing (RCP), where the packing fraction $\eta = \rho\pi\sigma^3/6$ for hard spheres. Also, Padé approximants, as applied to date,[6] can only give rise to simple or higher-order poles. Notice that the value of the critical-packing fraction obtained from a linear extrapolation would, according to (2), with $0 < \mu < 1$, give that $\eta_{\text{ext}} > \eta_{\text{RCP}}$. Therefore, it may be that for hard spheres $\eta_{\text{RCP}} \equiv 2/\pi \cong 0.6366$—the limiting high density[6] for amorphous packing of hard spheres—and so the extrapolated values of $\eta_{\text{ext}}$ reflect already the behavior demanded by (2) for $0 < \mu < 1$. For instance, $\eta_{\text{ext}} = 0.644$ from MD computations[1] with a 32-particle system, $\eta_{\text{ext}} = 0.637 \pm 0.002$ from a lengthy MD computation,[2] with a 500-particle system, and $\eta_{\text{ext}} = 0.64 \pm 0.02$ in a recent[6] method of calculating $\eta_{\text{RCP}}$.

The thermodynamic identity (7) gives, with the aid of (3), that $P/kT$ is a function of $N$ and $V$ only, which in the thermodynamic limit becomes $P/kT = F(\rho)$. Therefore, the singularities appearing in (1) and (2) correspond to the limits $T/P_{\text{solid}} \rightarrow 0$ at $V = V_0$—the volume of close packing for the crystal—and $T/P_{\text{fluid}} \rightarrow 0$ at $V = V_1$—the volume of close packing of the equilibrium liquid—respectively. The existence of this latter singularity in the equation of state for the hard-sphere fluid would result from the supercooled metastable fluid branch. The singularity of $P_{\text{fluid}}/kT$ at $V = V_1$ is usually identified[6] with the random close packing of hard spheres at $T = 0$ which occurs (to 0.06%) at Bernal's volume $V_{\text{RCP}} = N\sigma^3\pi^2/12$. Result (1) together with Eq. (2) with $0 < \mu < 1$ imply[7] that the configurational entropy $S_c(P_0,T) \equiv S(\text{liquid}, P_0, T) - S(\text{crystal}, P_0, T) > 0$, possesses a minimum at $T = T_g > 0$, and is such that $S_c(P_0,T)/Nk \rightarrow +\infty$ as $T \rightarrow 0$ for fixed $P = P_0$. These results corroborate the metastable nature of the (supercooled) liquid branch, and strengthen further the identification of the random close-packed state with the metastable state for very low temperature packing of hard spheres. Herein lies the importance of the possibility $\mu < 1$—even if $\mu = 1 - \epsilon$ with $0 < \epsilon << 1$. It implies that the configurational entropy $S_c$ is infinite at the absolute zero of temperature. Note that at constant pressure $P = P_0$, $S(\text{liquid}, P_0, T) \rightarrow \frac{3}{2} Nk \ln T$ as $T \rightarrow 0$, for $\mu < 1$. (Recall that the classical hard sphere system does not satisfy the third law of thermodynamics.) Consequently, the configurational entropy of the supercooled liquid, viz., $S_c(\text{liquid}, P_0, T) \equiv S(\text{liquid}, P_0, T) - \frac{3}{2} Nk \ln T$, is finite in the metastable (random-close-packed) state at zero temperature. [It should be remarked that in the free-volume theory, $S_c(\text{liquid}, P_0, T) \rightarrow 3Nk \ln T$ as $T \rightarrow 0$, for fixed $P = P_0$.] Note also that the minimum configurational entropy $S_c(P_0, T_g)$, which is[7] approximately $Nk$, would correspond to the residual entropies of ordinary laboratory glasses. In the solid phase, at constant pressure $P = P_0$, $S_c(\text{crystal}, P_0, T) \sim -T^{(1-\lambda)/\lambda}$ as $T \rightarrow 0$, for $\lambda > 1$, where $S_c(\text{crystal}, P_0, T) \equiv S(\text{crystal}, P_0, T) - \frac{3}{2} Nk \ln T$. If, however, $\lambda = 1$, then $S_c(\text{crystal}, P_0, T) \sim \ln T$ as $T \rightarrow 0$. Therefore, $\lambda > 1$ leads to an infinite heat capacity as $T \rightarrow 0$, while $\lambda = 1$ gives rise to a finite heat capacity as $T \rightarrow 0$. Accordingly, the value $\lambda = 1$ is clearly preferred in the solid phase.[3] (A similar argument can be used to eliminate the possibility $\mu > 1$ for the extended fluid branch.)

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