The superfluid transition in helium clusters

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We address cluster size effects on the λ temperature (T_λ) for the rounded-off transition for the Bose–Einstein condensation and for the onset of superfluidity in $(^4\mathrm{He})_N$ clusters of radius $R_0 = aN^{1/3}$, where $a = 3.5$ Å is the constituent radius. The phenomenological Ginsburg–Pitaevskii–Sobaynin theory for the order parameter of the second-order phase transition, in conjunction with the free-surface boundary condition, results in a scaling law for the cluster size dependence of T_λ, which is defined by the maximum of the specific heat and/or from the onset of the finite fraction of the superfluid density. This size scaling law $(T_\lambda^0 - T_\lambda)/T_\lambda^0 \propto R_0^{-1/\nu} \propto N^{-1/3\nu}$, where ν (=0.67) is the critical exponent for the superfluid fraction and for the correlation length for superfluidity in the infinite bulk system, implies the depression of the finite system T_λ relative to the bulk value of T_λ^0. The quantum path integral molecular dynamics simulations of Sindzingre, Ceperley, and Klein [Phys. Rev. Lett. **63**, 1601 (1989)] for $N = 64$, 128, together with experimental data for specific heat of ^{4}He in porous gold and in other confined systems [J. Yoon and M. H. W. Chan, Phys. Rev. Lett. **78**, 4801 (1997); G. M. Zahssenhaus and J. D. Reppy, *ibid.* **83**, 4800 (1999)], are accounted for in terms of the cluster size scaling theory $(T_\lambda^0 - T_\lambda)/T_\lambda^0 = (\pi\xi_0/a)^{3/2} N^{-1/2}$, where $\xi_0 = 1.7 \pm 0.3$ Å is the ''critical'' amplitude for the correlation length in the bulk. The phenomenological theory relates T_λ for the finite system to the correlation length $\xi(T)$ for superfluidity in the infinite bulk system, with the shift $(T_\lambda^0 - T_\lambda)$ being determined by the ratio $R_0/\xi(T)$, in accord with the theory of finite-size scaling. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1622651]

I. PROLOGUE

Cluster chemical physics focuses on the energy landscapes, spatial structures and shapes, phase changes, energetics, nuclear-electronic level structure, spectroscopy, response, dynamics, and chemical reactivity of large, finite systems.[1–3] Central issues in this broad, interdisciplinary, research area pertain to the bridging between the properties of molecular, surface, and condensed phase systems and the utilization of cluster size equations as scaling laws for the nuclear-electronic response of nanostructures.[4–7] When is such size-scaling partial and incomplete? Several examples come to mind in the context of energetics, nuclear dynamics, and cooperative effects. First, specific cluster size effects,[4] involving self-selection and existence of ''magic numbers'' for moderately sized clusters, manifest an irregular variation of structure and energetics, which is not amenable to size scaling. Second, structural characterization and specification of distinct phase-like forms, e.g., solid (rigid) and liquid (nonrigid), or solid (rigid) and solid (rigid) configurations, and ''smeared'' (rounded-off) phase changes between them in clusters and nanoparticles, may differ from the corresponding feature in bulk matter.[8–10] Third, nuclear adiabatic dynamics of clusters manifests new collective excitations, e.g., bulk compression modes,[5,6] and exhibits novel fragmentation patterns, such as cluster fission[11,12] and Coulomb explosion,[13,14] which are unique for finite systems and do not have an analogue in the dynamics of the corresponding bulk matter. A striking example constitutes the dynamics of Coulomb explosion, whose energetics is characterized by a divergent scaling size equation.[15,16]

Notable recent developments in the realm of low-temperature large, finite, quantum systems pertain to the exploration of homonuclear molecular clusters (aggregates or nanodroplets), where the nuclear dynamics is dominated by quantum effects and by permutational symmetry.[17–33] Landmark examples involve $(^4\mathrm{He})_N$ $(N \geqslant 2)$ and $(^3\mathrm{He})_N$ $(N \geqslant 25)$ quantum clusters, which exhibit large zero-point energy motion, being the only clusters (and bulk materials) which are liquid and correspond to floppy nonrigid structures down to $T = 0$.[17–19,34–46] These clusters manifest boson (for ^{4}He) or fermion (for ^{3}He) permutational symmetry.[17–46] The two most important properties for the finite boson $(^4\mathrm{He})_N$ systems (which are well established in the corresponding homogeneous bulk systems) are superfluidity and Bose–Einstein condensation.[17,30,33–47] Superfluidity pertains to the hydrodynamic effects of the response to a slow movement of the system's boundaries,[30,33–48] while Bose–Einstein condensation manifests off-diagonal long-range order, with the occupation number of the ground state becoming proportional to the number density of the atoms.[33,47,48] While the properties of superfluidity and of Bose–Einstein condensation are distinct, both phenomena manifest the implications of boson permutation symmetry and are characterized by the same transition temperature.[31,33,48] Some of the features of the finite $(^4\mathrm{He})_N$ boson systems[17,30,33,49–55] are as follows.

(1) The onset of the superfluid transition in the finite system.[17,30,33] This transition is referred to as the λ point in the bulk system. What is the analogy in a finite system? The

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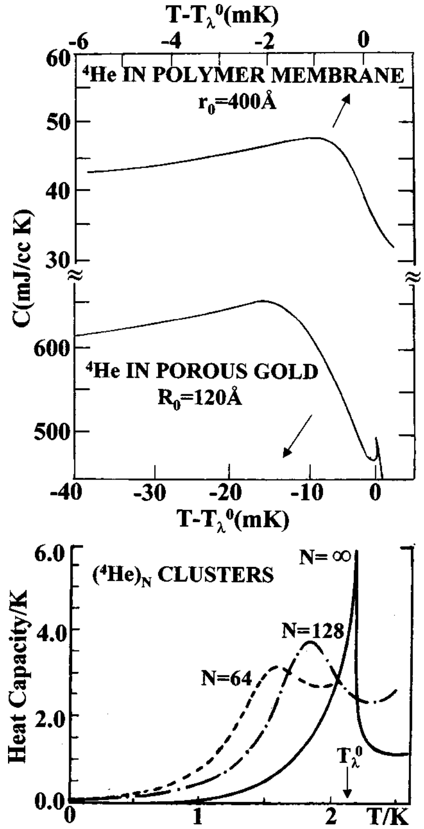

FIG. 1. The temperature dependence of the specific heat of $(^4\mathrm{He})_N$ clusters (lower panel for $N=64$ and $N=128$) obtained from quantum simulations (Ref. 30), and from experimental data for ^{4}He in porous gold (pore radius $R_0=120$ Å, upper panel, Ref. 52) and for ^{4}He in cylindrical channels in polymer membrane (cylinder radius $r_0=400$ Å, upper panel, Ref. 52). The bulk infinite system specific heat ($N=\infty$) is presented in the lower panel.

pioneering quantum path integral Monte Carlo simulation of Sindzingre, Ceperley, and Klein[30] established the appearance of a rounded-off (smeared) λ transition in finite $(\mathrm{He})_N$ ($N=64$ and 128) clusters, as manifested by a maximum in the temperature dependence of the specific heat (Fig. 1), which occurs at the temperature T_λ, with $\Delta T_\lambda = T_\lambda^0 - T_\lambda > 0$, where $T_\lambda^0 = 2.172$ K is the temperature of the λ transition in the bulk,[48] while experimental values of ΔT_λ were recorded[50–55] down to $\Delta T_\lambda \geqslant 2\times 10^{-4}$ K. Early experimental studies[49] of the heat capacity of ^{4}He confined in microscopic bubbles (cavities) in Cu foils indicated the occurrence of the superfluid transition with the lowering of T_λ in the confined space, however, pressure effects and size effects on the superfluid transition cannot readily be separated. Relevant in this context of superfluidity in finite systems[50–55] are several experimental studies of the superfluid transition interrogated by the density and specific heat of ^{4}He in confined geometries,[50–55] i.e., films,[50] cylinders,[50,52] and pores.[52,53] These confined geometries involve polymer membranes (nucleopore filters), with films of 20–80 Å thickness[50] and cylindrical channels of 10^2–10^3 Å diameter[50] (Fig. 1), porous gold with pore diameter of 240 Å (Fig. 1),[52] vicor glass involving a highly intercorrelated network of pores of average diameter of 70 Å,[53] and confinement between sheets of Myler[54] separated by 4600 Å and ^{4}He between Si wafers.[55] These specific heat data manifest the rounding off of the transition and the shift of its maximum (T_λ) to lower values, i.e., $\Delta T_\lambda > 0$. Alternatively, the onset of the appearance of a finite fraction of the superfluid density can be taken as a measure of the λ transition in the finite system. From the available simulation data for $(^4\mathrm{He})_N$ ($N=64{,}128$) clusters[30] the maximum of the specific heat is manifested at $T_\lambda = 1.58$ K for $N=64$, and at $T_\lambda = 1.82$ K for $N=128$, while the onsets of the superfluid density are $T_\lambda = 1.75\pm 0.10$ K for $N=64$, and $T_\lambda = 2.0\pm 0.10$ K for $N=128$. Thus the T_λ values inferred from the maximum of the specific heat are nearly (within numerical uncertainty) equal to the temperatures corresponding to the onset of the superfluid density. The experimental data for ^{4}He confined in porous gold[52] and vicor glass[53] also reveal an approximate coincidence of the temperatures corresponding to the maximum of the specific heat and to the onset of the superfluid density. Both observables characterize the rounded-off λ transition in the finite system. Fisher[8] has advanced the concept of finite size scaling in a confined system, relating the lowering of T_λ to the smallest confining dimension L, by

$$\Delta T_\lambda / T_\lambda^0 \sim L^{-1/\nu}, \tag{1}$$

where $\nu = 0.67$ is the characteristic exponent for the divergence of the correlation length.[50–53] Similarly, the region δT_λ of the rounding off of the specific heat curve is expected to be determined by the relation[8] $\delta T_\lambda \sim L^{-1/\nu}$, whereupon the ratio $\delta T_\lambda / (\Delta T_\lambda / T_\lambda^0) = \mathrm{const}$, being size independent. When these relations for $\Delta T_\lambda / T_\lambda^0$ and δT_λ were originally subjected to experimental scrutiny,[50] it was found that the specific heat data in polymers, films, and cylinders (over a small size domain) obey the Fisher relation,[7] Eq. (1), however, the scaling exponent was lower[50] than the value $\nu = 0.67$. A possible resolution of this finite size scaling problem was considered[51] by replacing T_λ^0 by a size-dependent reference temperature. A more elaborate scrutiny of specific heat and superfluid fraction data for finite systems over a larger size domain is called for.

(2) Superfluidity in the finite systems. The quantum path integral simulations[30] for the $(^4\mathrm{He})_N$ ($N=64{,}128$) clusters indicate the onset of the superfluid fraction ϕ_λ at $T \simeq T_\lambda$, with a gradual increase of ϕ_λ with decreasing temperature, reaching a large finite value ($\phi_\lambda \simeq 0.9$) at $T=0$. Even more interesting is the use of molecular spectroscopic probes for superfluidity in large $(^4\mathrm{He})_N$ clusters ($N=10^4$–10^6) at 0.4 K (where $\phi_\lambda \simeq 1$).[38–42] Another microscopic probe for superfluidity in large $(^4\mathrm{He})_N$ clusters ($N \geqslant 10^5$) at 0.4 K involves a transport probe, i.e., electron tunneling from the electron bubble,[56,57] which provided evidence for vanishingly low viscosity of the superfluid finite system.

(3) Elementary excitation in the superfluid clusters. The existence of a roton-type collective excitation spectrum in large $(^4\mathrm{He})_N$ clusters ($N=10^4$–10^5) at 0.4 K was established from electronic spectroscopy of large molecules, e.g., glyoxal.[36]

While the characteristics of superfluidity and of the elementary excitations in the large, cold ($T=0.4$ K) $(^4\mathrm{He})_N$ clusters ($N=10^4$–10^6) were considered in analogy to the properties of the corresponding bulk system,[34–46,56,57] the interesting problem of size effects on the phenomena of Bose–Einstein condensation and superfluidity in finite boson systems[30,31,37,38,50–55] is not yet fully elucidated. The available information emerges from the path integral Monte Carlo simulations of $(^4\mathrm{He})_N$ ($N=64{,}128$) clusters[30] and experimental specific heat data of ^{4}He in confined porous systems.[50–53] In this paper we address the issue of the size scaling of the λ point in finite $(^4\mathrm{He})_N$ clusters. As a starting point, we shall utilize the phenomenological theory of Ginzburg, Pitaevskii, and Sobaynin,[58,59] for the λ transition with proper boundary conditions for free surfaces, to explore the cluster size dependence of T_λ in $(^4\mathrm{He})_N$ clusters. The cluster size scaling theory for superfluidity in $(^4\mathrm{He})_N$ clusters provides a satisfactory semiquantitative account of the results of the path integral Monte Carlo simulations results[30] and experimental specific heat data of ^{4}He confined in pores[50–53] for the lowering of T_λ with decreasing the size of the $(^4\mathrm{He})_N$ clusters. The phenomenological theory relates the intensive property (T_λ) of the finite system (of size L) to the correlation length $\xi(T)$ for superfluidity in the corresponding bulk system, with the shift $(T_\lambda^0-T_\lambda)$ depending on the ratio $L/\xi(T)$. This result of the phenomenological model for the size dependent λ transition is related to the theory of finite size scaling,[8,9,60–64] which is extensively used to interpret simulations of phase transitions, e.g., liquid–vapor critical point[8,62] and Bose–Einstein condensation in liquid ^{4}He and in a hard sphere gas.[61,63,64] While the finite size scaling theory routinely allows one to deduce the transition point for the infinite system from simulations for finite-size samples,[61,63,64] one can invert the argument using finite size scaling for the estimate of the "smeared" λ point in the finite quantum boson system.

II. PHENOMENOLOGICAL THEORY OF T_λ IN $(^4\mathrm{He})_N$ CLUSTERS

The Ginzburg–Pitaevskii theory[58] for bulk liquid ^{4}He near the λ point rests on Landau's theory of second-order phase transitions.[65] This theory was extended by Ginzburg and Sobaynin[59] for the treatment of the λ transition in finite systems, e.g., thin films, narrow channels, confined space and vortices, exploring size effects, and confinement on the superfluid transition, which is pertinent for the analysis of the onset of superfluidity in $(^4\mathrm{He})_N$ clusters. This phenomenological theory[58,59] rests on the introduction of a macroscopic complex wave function ψ, which is used as an order parameter for the superfluid transition. The (complex) order parameter ψ is related to the superfluid density ρ_s, and is normalized in the form

$$\rho_s=m|\psi|^2, \tag{2}$$

where m is the mass of the helium-4 atom. The normal He fluid is considered to be at rest and the free energy density $f^{(0)}$ (which depends on the pressure p and temperature T) of the homogeneous infinite fluid can be expanded in terms of powers of $|\psi|^2$, while the local free energy density $f(\mathbf{r})$ for an inhomogeneous finite system can be expressed in terms of powers of $|\psi(r)|^2$. Thus for a homogeneous system

$$f^{(0)}(P,T,\psi)=f_1(P,T)+A|\psi|^2+(B/2)|\psi|^4+\cdots, \tag{3}$$

where f_1 is the free energy density of normal ^{4}He, while the coefficients A and B depend on T and P.[66] From the equilibrium condition for the homogeneous fluid $(\partial f^{(0)}/\partial|\psi|^2)_{P,T}=0$ Ginzburg and Pitaevskii[58,59] established the relation $A+B|\psi|^2=0$, which results in an explicit relation between the homogeneous system superfluid density ρ_s and the coefficients A and B, so that $\rho_s=-A/B$. At this stage the phenomenological theory of Ginzburg and Sobaynin can be adopted, representing the bulk order parameter and its superfluid density ρ_s in terms of a critical exponent

$$\rho_s/\rho_\lambda=t^\nu, \tag{4}$$

with

$$t=(T_\lambda^0-T)/T_\lambda^0, \tag{5}$$

where the critical exponent for the superfluid fraction is $\nu=0.6702$,[67] i.e., manifesting the "2/3 scaling law." T_λ^0 is the λ point temperature of the infinite system. Here the superfluid effective density is $\rho_\lambda=0.351\ \mathrm{g\,cm^{-3}}$,[67] while $\rho(T_\lambda)=0.146\ \mathrm{g\,cm^{-3}}$ is the experimental density at T_λ^0. The equilibrium condition results in $|\psi|^2=-A/B$, which from Eq. (4) implies that $\rho_s/\rho_\lambda=-A/B\propto t^\nu$. In the temperature range below T_λ^0, i.e., $(T_\lambda^0-T_\lambda)>0$, the parameter A is negative.[56,57] The temperature dependence of the expansion parameters is expressed in the form

$$A=-\alpha t^{2\nu}\quad(\alpha>0), \tag{6}$$

$$B=\beta t^\nu. \tag{7}$$

Equations (6) and (7) are consistent with the scaling relations (4). All the terms in the expansion (3) exhibit the same t dependence, and the parameters α and β are temperature independent.[59,66]

The free energy density $f(\mathbf{r})$ of the inhomogeneous finite system with a local order parameter $\psi(\mathbf{r})$ was expressed[59] by adding to $f^{(0)}$, Eq. (3), an even expansion of the gradient term, so that

$$f(\mathbf{r})=f_1+(\hbar^2/2m)|\nabla\psi(\mathbf{r})|^2+A|\psi(\mathbf{r})|^2+(B/2)|\psi(\mathbf{r})|^4+\cdots. \tag{8}$$

The total free energy $F=\int d^3\mathbf{r}f(\mathbf{r})$ is minimized with respect to the order parameter. The minimization with respect to ψ^* results in the Schrödinger-type equation

$$-(\hbar^2/2m)\nabla^2\psi+A\psi+B|\psi|^2\psi+\cdots=0. \tag{9}$$

At this stage the correlation length $\xi(T)$ for superfluidity in the bulk is introduced

$$\xi(T)=(\hbar^2/2m|A|)^{1/2}, \tag{10}$$

which according to Eq. (6) is

$$\xi(T)=\xi_0 t^{-\nu}, \tag{11}$$

where

$$\xi_0=(\hbar^2/2m|\alpha|)^{1/2}. \tag{12a}$$

The critical exponent ν for the correlation length, Eq. (11), is identical to that for the superfluid fraction,[8,52,53,58,67] Eq. (4). ξ_0, Eq. (12a), is the "critical" amplitude for the correlation length. ξ_0 can be related to the superfluid density by the Josephson relation[68]

$$\xi_0=k_B T_\lambda^0 m^2/\hbar^2\rho_\lambda, \tag{12b}$$

where ρ_λ is the superfluid effective density,[67] Eq. (4). Equation (12b) results in $\xi_0 = 3.1$ Å for bulk ^{4}He. Note that this short "critical" amplitude for the correlation length implies that ξ_0 is comparable to the interatomic spacing $a = 3.5$ Å in liquid ^{4}He.

The application of Eq. (9) for the order parameter in a finite system, e.g., clusters, requires the introduction of the appropriate boundary condition, with the vanishing of the order parameter, i.e., $\psi = 0$ at the boundaries of the cluster. This boundary condition explicitly invokes a step function approximation for the cluster surface profile, while the realistic description of $(^4\mathrm{He})_N$ clusters involves a broadened profile with a full width at half maximum (FWHM) of 4.5 Å.[4] Introducing the reduced coordinates

$$\mathbf{r}_* = \mathbf{r}/\xi(T) \tag{13}$$

and using Eqs. (10) and (12a), Eq. (9) is then expressed in the form

$$-\nabla_*^2 \psi + [-1 + (B/A)|\psi|^2 + \cdots]\psi = 0, \tag{14}$$

where ∇_*^2 is the Laplacian in the reduced coordinates, Eq. (13).

Equation (14) was advanced by Ginzburg and Sobaynin for superfluidity in confined finite systems.[59] This theory will be applied herein for the onset of superfluidity of ^{4}He confined in a sphere of radius R_0. Adopting the step function approximation, the boundary condition for the order parameter at the free surface is taken as $\psi(R_0) = 0$. For low values of ψ the first-order linear form of Eq. (9) is

$$\frac{1}{R_*^2} \frac{d}{dR_*}\left(R_*^2 \frac{d\psi}{dR_*} \right) + \psi = 0, \tag{15a}$$

where

$$R_* = R/\xi(T) \tag{15b}$$

with the lowest solution $\psi(R_*) = \sin R_*/R_*$. The free-surface boundary condition $\psi(R_0/\xi) = 0$ results in $R_0/\xi(T) = \pi$, so that $R_0 = \pi \xi_0 t^{-\nu}$ with t is given by Eq. (5). This result implies that the order parameter in the finite system vanishes at the boundary, marking the onset of the superfluid transition in the cluster at the temperature T_λ when

$$(T_\lambda^0 - T_\lambda)/T_\lambda^0 = (\pi \xi_0 / R_0)^{1/\nu}. \tag{16}$$

Equation (16) implies that the lowering of the λ temperature T_λ in the finite clusters is given by

$$(T_\lambda^0 - T_\lambda)/T_\lambda^0 = (\pi \xi_0)^{1/\nu}/R_0^{1/\nu}. \tag{17a}$$

Setting $R_0 = aN^{1/3}$, where N is the number of the He atoms and a $(= [m/\rho(T_\lambda)^{1/3}])$ is the constituent radius (the average interatomic distance $a = 3.5$ Å), results in

$$(T_\lambda^0 - T_\lambda)/T_\lambda^0 = (\pi \xi_0 / a)^{1/\nu}/N^{1/3\nu}. \tag{17b}$$

Equations (17a) and (17b), together with $\nu \simeq 2/3$, provide the size scaling of the λ point in clusters.

In the original Ginzburg–Sobaynin[58] analysis of ^{4}He superfluidity in confined spaces, the λ transition in a cylinder of radius r_0 and length ℓ ($\ell \gg r$) was considered making use of Eq. (14) together with the appropriate boundary conditions $\psi(r_0) = 0$ and $(d\psi/dr)_{r_0} = 0$. This treatment results in[58]

$$(T_\lambda^0 - T_\lambda)/T_\lambda^0 = (\alpha \xi_0 / r_0)^{1/\nu}, \tag{18}$$

where $\alpha = 2.405$ is the first root of the Bessel function. Equations (17a) and (18) provide explicit expressions (with appropriate numerical coefficients [$\pi = 3.14$ for spherical clusters, Eq. (17), and $\alpha = 2.41$ for cylinders, Eq. (18)]) for the relation $(T_\lambda^0 - T_\lambda) \propto L^{-1/\nu}$, where $L = R_0$ or $L = r_0$, in accord with Eq. (1).[8,9]

III. SIZE SCALING OF THE λ POINT IN CLUSTERS AND FINITE SYSTEMS

From the preceding analysis we infer that the depression $\Delta T_\lambda = T_\lambda^0 - T_\lambda$ of the λ point in $(^4\mathrm{He})_N$ clusters, Eq. (17), size scales as $\Delta T_\lambda / T_\lambda^0 \propto R_0^{-1/\nu} \approx R_0^{-3/2}$, and similarly in cylindrically confined systems, Eq. (18) (of radius r_0) $\Delta T_\lambda / T_\lambda^0 \propto r_0^{-1/\nu} \approx r_0^{-3/2}$. For $(^4\mathrm{He})_N$ clusters the dependence of ΔT_λ on the number of constituents, Eq. (17b), is given in the form $\Delta T_\lambda / T_\lambda^0 \propto N^{-1/3\nu} \approx N^{-1/2}$. The relative depression of the λ point in clusters provides a proper cluster size equation, i.e.,

$$\Delta T_\lambda / T_\lambda^0 = \delta / N^{1/2} \tag{19a}$$

$$= \gamma / R_0^{3/2}, \tag{19b}$$

where $\delta = (\pi \xi_0 / a)^{3/2}$ and $\gamma = (\pi \xi_0)^{3/2}$, with $\Delta T_\lambda \to 0$ for R_0, $N \to \infty$.

The scaling relation, Eq. (19), with the proper critical exponent ($\nu \simeq 2/3$), will be utilized to establish the validity of this cluster size equation over a large range of finite spherical $(^4\mathrm{He})_N$ systems ($R_0 = 14$–400 Å, $N = 64 - 1.5 \times 10^6$) from isolated clusters[30] to supported pores in metals,[52] and glasses[53] (Table I and Fig. 2). Concurrently, the scaling relation, Eq. (18), will be applied with the same critical exponent ($\gamma = 2/3$) to account for the depression of the λ point for ^{4}He confined in cylindrical channels of polymer membranes[52] and nucleopore filters[50] (Table I and Fig. 2). Spherical geometry was taken for the isolated clusters,[30] for pores in metals[52] and in glasses,[53] while cylindrical geometry was taken for the polymers.[50,52] From this analysis an estimate of the "critical" amplitude ξ_0 for the bulk correlation length will emerge. The fit of the quantum simulations results of Sindzingre, Ceperley, and Klein[30] (Table I and Fig. 2) to Eq. (19) results in $\delta = 2.17$ and $\xi_0 = 1.9$ Å for $N = 64$ and $\delta = 1.82$ and $\xi_0 = 1.7$ Å for $N = 128$. Thus the finite size scaling law provides a semiquantitative account of the quantum simulation data for small ^{4}He clusters.[30] The cluster size dependence of $\Delta T_\lambda / T_\lambda^0$, according to Eq. (19), was extended over a considerably larger size domain of spherical cavities, whose size was obtained from structural data,[52] with the analysis of the experimental specific heat data (Table I and Fig. 2) for ^{4}He in porous gold ($R_0 = 120$ Å)[52] and vicor glass ($R_0 = 35$ Å).[53] The analysis for these porous spherical systems and, in particular, for the vicor glass, implies complete pore filling.[50(b)] The values of δ, Eq. (19a), obtained for all the finite spherical systems, are nearly constant within a numerical spread of 30% (Table I and Fig. 2), providing evidence for the validity of the cluster size equation, Eqs. (17) and (19). The values of the "critical" amplitude ξ_0 inferred from this analysis (Table I and Fig. 2) for spherical ^{4}He pores

TABLE I. Specific heat of $(^4\text{He})_N$ finite systems.

System	N	R_0 (Å)	$\Delta T_\lambda / T_\lambda^0$	δ[f]	ξ_0 (Å)[g]	δt (K)[h]	$\delta t/(\Delta T_\lambda / T_\lambda^0)$ (K)
Isolated cluster quantum simulations[a]	64	14.3	0.271	2.17	1.9	0.372	1.4
Isolated cluster quantum simulations[a]	128	18.0	0.161	1.82	1.7	0.286	1.8
Porous gold experiment[b]	4.03×10^4	120	6.45×10^{-3}	1.29	1.3	1.8×10^{-2}	2.8
Pores in vycor glass experiment[c]	10^3	35	6.5×10^{-2}	2.06	1.8	5×10^{-3}	0.1
Polymer membranes cylindrical channels experiment[d]	⋯	$r_0=400$	3.7×10^{-4}	⋯	0.9[i]	1.5×10^{-3}	4.1
Nucleopore		$r_0=150$	$2.9\times10^{-3}\pm0.5\times10^{-3}$	⋯	1.23 ± 0.13[i]		
Filters	⋯	$r_0=400$	$5.5\times10^{-4}\pm0.5\times10^{-4}$	⋯	1.09 ± 0.06[i]		
Cylindrical channels		$r_0=500$	$3.7\times10^{-4}\pm0.5\times10^{-4}$	⋯	1.04 ± 0.09[i]		
Experiment[e]		$r_0=1000$	$1.1\times10^{-4}\pm0.15\times10^{-4}$	⋯	0.90 ± 0.08[i]		

[a]Reference 30.
[b]Reference 52.
[c]Reference 53.
[d]References 53 and 50.
[e]Reference 50(b).
[f]$\delta=(\Delta T_\lambda/T_\lambda^0)N^{1/2}$, Eq. (19).
[g]$\xi_0=a\,\delta^\nu/\pi$, Eq. (19).
[h]δt determined by FWHM/2 of $C(T)$ in the region $T<T_\lambda$ for $(^4\text{He})_N$ clusters and $T>T_\lambda$ for confined systems.
[i]ξ_0 determined from Eq. (18).

$(R_0=35–120\ \text{Å})$ vary in the range of 1.3–1.8 Å, being close to the values $\xi_0=1.7–1.9$ Å obtained for the small clusters $(R_0=14–18\ \text{Å})$. We have also included in Table I and Fig. 2 the experimental specific heat data for ^{4}He in polymer membranes and nucleopore filters[50] with cylindrical channels (with a radius of $r_0=150–1000$ Å). Making use of Eq. (10) for the analysis of the experimental data for ^{4}He in cylindrical channels,[50(b)] we obtained ξ_0 values in the range $\xi_0=1.23\pm0.13$ Å for $r_0=150$ Å to $\xi_0=0.90\pm0.08$ Å for $r_0=1000$ Å. These values of ξ_0 for the cylindrical channels exhibit a systematic variation of less than 12%, and are lower by about 50% than the average value of 1.7 ± 0.3 Å evaluated for the experimental data for spherical finite systems $(R_0=14–120\ \text{Å})$. When all these experimental specific heat data are taken together we infer that $\xi_0=1.5\pm0.6$ Å. This value of $\xi_0\approx1–2$ Å obtained from the analysis of quantum simulation data $(R_0=14–18\ \text{Å})$ and experimental data for ^{4}He spherical confined systems $(R_0=35–120\ \text{Å})$ in cylindrical channels $(r_0=150–1000\ \text{Å})$, is lower by a numerical factor of $\sim$1.5–3.0 than the value of $\xi_0=3.1$ Å estimated from the Josephson relation, Eq. (12a), for the bulk superfluid. We note in passing that a single value of ξ_0 was used in the analysis of the specific heat data in finite systems. This ξ_0 value corresponds to the infinite fluid. In the experimental papers for porous systems[52,53] the values of $\overline{\xi_0}=8.4$ and 17 Å are given for porous gold and $\overline{\xi_0}=93$ Å for vicor. The latter $\overline{\xi_0}$ data are based on the actual superfluid effective densities in the confined systems. In our analysis (Fig. 2) we use the bulk value for ξ_0.

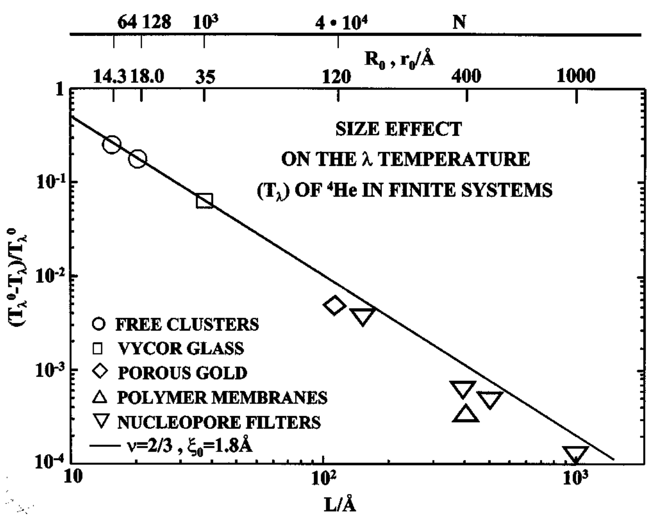

FIG. 2. Size scaling of the relative depression $\Delta T_\lambda/T_\lambda^0$ of the λ point of $(^4\text{He})_N$ in finite and in confined systems, according to Eqs. (17) and (18). (○) $(^4\text{He})_N$ clusters of radius R_0 (Ref. 30). (□) ^{4}He in vicor glass, pore radius $R_0=35$ Å (Ref. 52). (◇) ^{4}He in porous gold, pore radius $R_0=120$ Å (Ref. 53). (△) ^{4}He in cylindrical pores (radius $r_0=400$ Å) in polymer membrane (Ref. 52). (▽) ^{4}He in cylindrical pores (radius $r_0=150–1000$ Å) in nucleopore filters [Ref. 50(b)]. The confining dimension is $L=R_0$ for spherical clusters or pores, or r_0 for cylindrical pores. The solid line corresponds to the size scaling with $\xi_0=1.7$ Å and $\nu=2/3$.

From the foregoing analysis (Fig. 2) of simulation and experimental data we infer that the size scaling relation $\Delta T_\lambda\propto L^{-3/2}$ (where $L\simeq R_0$ for clusters and nearly spherical confined spaces and $L\sim r_0$ for cylinders) is obeyed over a wide size domain of $L\simeq14–400$ Å (i.e., $N=14–4\times10^4$ for clusters and nearly spherical confined spaces), and of $L\simeq150–1000$ Å for cylindrical channels. This broad range of size domain with the proper critical $\nu\simeq2/3$ exponents, indicates that it is unnecessary to replace T_λ^0 by a size independent reference temperature, as proposed[51] to account for a lower scaling component reported for (^{4}He) confined in polymer films over a narrow size domain.[50]

An important issue pertains to the broadening of the specific heat curve $C(T)$ in finite systems (Fig. 1). The region δT_λ of the rounding-off of the specific heat curve was determined from the available simulation data[30] and experimental data[50–53] by the $\frac{1}{2}$ (FWHM) of $C(T)$ for the range $T<T_\lambda$ for clusters and $T>T_\lambda$ for confined spaces (Table I). Following the Fisher theory[7] (Sec. I), one expects that the ratio $\delta T_\lambda/(\Delta T_\lambda/T_\lambda^0)=\text{const}$, being size independent. Indeed, this relation is reasonably well obeyed (within a numerical factor of 3 over the range $R_0=14$–400 Å) for the quantum simulations for small clusters, for porous gold and for the membrane polymer. However, a marked (one order of magnitude) deviation from this relation is exhibited for ^{4}He confined in vicor glass (Table I), which may be attributed to constrained randomness effects,[69,70] and which calls for further scrutiny.

IV. FINITE SIZE SCALING

The relation $\Delta T_\lambda \propto R_0^{-1/\nu}$ obtained from the Ginzburg–Pitaevskii–Sobaynin theory for a finite system is related to the theory of second-order phase transitions with the experimental critical parameter, $\nu=0.67$, for the superfluid fraction and for the correlation length scaling near the critical point of infinite systems.[69,71] This theory implies that the intensive properties of a system of size $L(=R_0)$ depend on the ratio $L/\xi(T)\sim Lt^\nu$, where $\xi(T)=\xi_0(T_\lambda^0-T)^{-\nu}$ is the bulk correlation length.

At this stage finite-size scaling theory[8,9] is applicable for the description of the specific heat maximum and of the onset of the superfluid density (see Sec. I), which characterize the rounded-off λ transition. The singular free energy density, *f*, of the finite system (in the absence of external fields) can be described in terms of a universal function ($Y(\,)$) in the form[9] $f=L^{-d}Y(KtL^{1/\nu})$, where K is a metric factor, which contains all the system-dependent aspects of the critical behavior and d is the dimensionality. Defining the parameter $y=KL^{1/\nu}t$, the free energy $f=L^{-d}Y(y)$ yields the specific heat $C=T(\partial^2 f/\partial T^2)$. Accordingly, $C\propto Y^{(2)}(y)$, being determined by the second derivative, $Y^{(2)}$, of Y. The maximum of the specific heat ($\partial C/\partial y=0$), which characterizes the smeared-out λ transition at T_λ, is located at $y=y_{\max}$, being manifested at $y^{(3)}(y_{\max})=0$, where $Y^{(3)}$ is the third derivative of Y. Accordingly, the rounded off λ transition is exhibited for $t_{\max}=y_{\max}K^{-1}L^{-1/\nu}$, with $t_{\max}=(T_\lambda^0-T_\lambda)/T_\lambda^0$, in accord with the results of the order parameter analysis of Sec. III. The broadening of the specific heat curve, characterized by the 1/2(FWHM) of C (at $T^{(1)}<T_\lambda$) is given by the 1/2(FWHM) of the $Y^{(2)}(y)$ function. These results in the width of the specific heat curve $\delta T=(T^{(1)}-T_\lambda)/T_\lambda^0\propto L^{-1/\nu}$, with the same finite size scaling of $t_{\max}$ and of Δt, are in accord with the analysis of Fisher,[8] which was adopted in Sec. IV.

The alternative description of T_λ is given in terms of the onset of the superfluid density. The superfluid fraction was expressed as[8,60–64] $\rho_s(t,L)\sim L^{-1}Q(L^{1/\nu}t)$, where the (unknown) analytic function $Q(\,)$ was linearized, i.e., $\rho_s(t,L)\sim L^{-1}(a+bL^{1/\nu}t)$, with a and b being constant, finite parameters. The λ transition in the finite system is characterized by $\rho_s(t,L)=0$ at $t=(T_\lambda^0-T_\lambda)/T_\lambda^0$, so that $T_\lambda^0-T_\lambda\sim a/bL^{1/\nu}$, i.e., $(T_\lambda^0-T_\lambda)\propto L^{-1/\nu}$, in accord with the phenomenological theory.

The finite size scaling analysis resulted in the identical finite size scaling $L^{-1/\nu}$ for the maximum of the specific heat and for the onset of the superfluid density. At the present stage we could only provide a proof that for both observables $T_\lambda<T_\lambda^0$ in a finite system, with identical $\Delta T_\lambda\propto L^{-1/\nu}$ scaling. However, we could not demonstrate that the numerical value of T_λ characterizing the two observables is nearly identical, as empirically indicated by the simulation and experimental data[30,52,53] (see Sec. I). The size effects considered herein correspond to large values of $\Delta T_\lambda/T_\lambda$ (0.3–0.15 K) for the small clusters ($R_0=14$–18 Å), while for larger pores ($R_0=35$–120 Å) the values of $\Delta T_\lambda/T_\lambda^0$ are smaller (6×10^{-2}–6×10^{-3}). In any case, the bulk correlation length at the corresponding temperature is small compared to the characteristic cluster size $L\sim R_0$.

V. CONCLUDING REMARKS

All thermodynamic phase transitions in finite systems, e.g., clusters, are rounded off.[8,9,72] The present analysis, based on the Ginzburg–Pataevskii–Sobaynin theory, attempted to elucidate some of the features of such rounded-off second-order phase transitions in clusters for the size dependence of T_λ, obtaining size equations which are in accord with the finite-size scaling theory. Several general issues regarding rounded-off second-order phase transitions in finite systems are of interest. For rounded-off first-order phase changes in finite systems the change of the thermodynamic properties in the transition region is different for the canonical and microcanonical ensemble,[73] as the thermodynamic limit is, of course, not realized in finite systems. While the present analysis is conducted for the canonical ensemble, it is interesting to establish the ensemble dependence for second-order transitions in finite systems. Another surprising result emerging from the simulations[30] and the present analysis is the clear manifestation of second-order phase transitions for rather small clusters ($N=64$, $R_0=14$ Å). An open, interesting, question pertains to the lower system's size limit for the exhibition of second-order phase transitions, such as the λ transition in ^{4}He clusters. A simple-minded argument will imply that the minimal cluster size $R_0^{\min}$ for the realization of superfluidity transition is $R_0^{\min}>\xi_0$. Making use of Eq. (19b), a lower limit for $R_0^{\min}$ will be manifested for $T_\lambda\to0$, whereupon $(\gamma/R_0^{\min})^{3/2}\sim1$ and $R_0^{\min}\sim\pi\xi_0$. Taking the short correlation length $\xi_0\simeq2$ Å, $R_0^{\min}\sim6$ Å, so that the smallest ^{4}He cluster will consist of a central atom and the first coordination layer.

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