

ROLE OF TEMPERATURE IN THE PHYSICS OF METALLIC CLUSTERS

Aurel BULGAC

Department of Physics, University of Washington,

P.O. Box 351560, Seattle, WA 98195–1560, USA

bulgac@phys.washington.edu, <http://www.phys.washington.edu/~bulgac/>

I review here a variety of effects induced on various properties of the metallic clusters by the finite temperature of the ionic degrees of freedom, such as: phase transitions, shape fluctuations, static and dynamic structure formfactors, electron single-particle spectra, optical response, $1/f$ -noise.

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It is fair to say that most of the experimental information we have acquired so far about metallic clusters in particular was gathered by probing the electronic degrees of freedom, with perhaps one exception, cluster abundances. However, even cluster abundances are interpreted routinely by considering the electronic properties of metallic clusters only. It should come as no surprise then that most of the theoretical studies performed so far have been focused on the role played by the electrons in determining metallic cluster properties, see e.g. Ref. [1]. Clusters are made however of both ionic cores and electrons, and reducing the role of the ions simply to that of “maintaining the charge neutrality” [2] should struck us as simplistic at least in this day and age. A simple comparison between the ionic density of states and the electronic density of states in a cluster at excitation energies of about a couple of eV’s [3], a typical excitation energy in cluster studies [4], shows that the former is astronomically large in comparison with the latter. In typical experiments clusters are “hot”, with an estimated temperature of a few hundreds Kelvin. In a gross approximation, the valence electrons in an alkali cluster can be assimilated

with a degenerate Fermi gas, as their Fermi energy $\varepsilon_F \approx 1.6 \dots 4.7$ eV (from Cs to Li respectively) is exceeding by about two orders of magnitude their temperature. Using the Dulong–Petit model one can estimate the ionic internal energy at ≈ 1.5 eV (see Ref. [5] for more accurate values) for a 20–atom cluster at 300 K, while the thermal excitation energy of the electrons pales by comparison.

One might legitimately ask: “Where are the ions?”. One can fairly often find in literature the statement that the ionic contribution is smooth as a function of particle number or temperature and thus can hardly be put in evidence. One can also argue that for relatively small clusters electronic quantum localization effects should play a dominant role in determining such cluster properties as: abundances, interaction with light, ionization, etc. [6]. If that would be the case the ions should behave like putty, or a jellium, or in more “physical” terms, the ions should be melted. As deforming a small Fermi droplet should be energetically costly, one should expect that the shape and size of small clusters should be well defined, which in particular would lead to rather sharp photo–absorption spectra and magic numbers should be well defined. There is more than enough experimental evidence to “convert” almost anybody to the jellium model [4]. However, there is a number of nagging “small details”. While experiment clearly indicates for example that $N = 40$ is a pretty good magic number, the jellium model argument does not look so convincing, and $N = 34$ looks often in theory as a much better candidate. The photo–absorption lines are not as sharp as one might have expected at relatively high temperatures [8] and moreover they have a rather strong temperature dependence [7], which cannot be explained within the jellium model, even by taking into account the bulk–like thermal expansion of the ionic background [5, 9]. They are sharp at very low temperatures, where the ions are most likely strongly localized [5, 9], as it is assumed to be in quantum chemistry calculations [10]. Jellium model makes perfect sense if the electron wavelength is much larger than the inter–atomic separation, which is clearly not the case for alkali clusters, where one has exactly one valence electron per atom

and this ratio is thus of order one and consequently the electrons experience all the ionic roughness. Moreover, how can one reconcile the jellium picture and the magic character of the (most likely) melted eight electron clusters with the photo–electron spectra measured by Bowen’s group [11], which show clear non–spherical single–particle levels.

One can turn the table around and go from one extreme to the other, and one has clearly several options. One can put in the ions explicitly, find their optimal arrangement and describe the electrons as well as one can do it. A cursory review of the available calculational approaches [10, 12, 13, 14] shows that the theory leads to greatly varying results, even in the case of identical theoretical calculational schemes, depending on the details of the implementation. Moreover, the ground state configuration is usually characterized by some point symmetry, but the particular symmetry often varies from one approach to another. The ground state configuration of Na_8 has a D_{2d} symmetry in LDA [12] and a T_d symmetry in CI [10] and DDTB [14]. In the case of Na_{20} the symmetry of the ground state configuration has two essentially degenerate shape isomers with C_s (lowest) and C_3 symmetries in LDA [12], while in the DDTB model, the C_3 –symmetry is most stable and the C_s structure is a shape isomer [14]. The Nilsson–Clemenger or jellium model predicts an exactly spherical shape for both clusters [4]. The energy differences and ordering of the shape isomers present even larger variations from one description to another. At the same time, the corrections to essentially any calculational scheme could be of the same order of magnitude or larger than the temperature effects.

There is enough theoretical evidence to conclude that the details of the electronic properties depend on the ionic configuration, not merely on the overall shape of the cluster. At almost any conceivable beam temperature, the ionic motion is significantly slower than the Fermi velocity of the electrons. Thus one can conclude that the electronic properties carry information about different static ionic configurations and are essentially insensitive to ionic dynamics. This is not quite so, as the electron–phonon interaction determines the conductivity/resistivity in the bulk for example. What one sees while

measuring cluster electronic properties is merely an incoherent superposition of electronic properties corresponding to all ionic configurations represented in the beam. At very low temperatures in most cases the ground state has a well defined structure and different shape isomers are sufficiently high in energy that their influence can be safely neglected. However, when the cluster melts, the ions change their relative positions and the shape of the cluster fluctuates significantly [5, 15, 18, 19]. The switching time from one shape isomer to another is rather long, from a few picoseconds at high temperatures, to hundreds of picoseconds and longer at low temperatures [19]. In order to describe correctly the statistical weight of various ionic configurations as a function of the cluster temperature a rather high level of theoretical accuracy is needed. First of all, for each shape isomer one needs to have a well defined local equilibrium ionic configuration and an accurate estimate of the potential stiffness towards various small amplitude deformations. The statistical weight of different isomers is controlled by the energy difference between different shape isomers. The height and width of potential barriers control the switching time between shape isomers.

With increasing temperature, clusters go first through a glassy/molten or fluctuating state (150–300 K) and eventually become totally liquid (above 300 K) [5]. In this temperature range they are almost incompressible, but highly deformable and show increasingly large size and shape fluctuations. At still higher temperatures (850–1000 K) they start boiling, vaporization sets in and they also become rather soft/compressible. In contradistinction with noble gas clusters [16], the melting and boiling do not seem to be a geometric or a particle number effect and the same behavior is observed for all the clusters we have studied [5, 9, 17, 18, 19, 20]. The thermal expansion properties of neutral clusters seem to be more pronounced when compared to the bulk and it is mostly due to an increased surface diffuseness and deformation of the cluster. Charged clusters are likely more stiff. The onset of the new phases can be observed in both thermodynamic and geometric properties of the clusters, which have a strong temperature dependence. The

relatively high ratio between the surface and the volume of a cluster is unquestionably at the origin of the large shape fluctuations, which also grow with temperature.

Besides melting and boiling in a quite different way than the bulk, sodium clusters seem to have also a rather distinct thermal expansion behavior. Since the experiments are likely performed with liquid clusters, their larger volume can easily serve as an argument in favor of a lower plasmon energy. The classical Mie plasmon frequency will change approximately as $\delta\omega_{Mie}/\omega_{Mie} = -3\delta r/2r$ when the radius of the cluster changes. At 400–600 K (the estimated temperature of the clusters in nozzle experiments) the linear dimensions of a cluster seem to be about 6...15% larger than at T=0 K, already of the right order of magnitude to explain the observed red shift of the Mie plasmon [5, 9]. The thermal shape and size fluctuations are of the same order of magnitude.

The features in measured photoelectron spectra of small alkali clusters [11] can also be understood within such a picture. At temperatures of about 100–150 K, the cluster has enough thermal energy to begin exploring higher energy isomers and the single-particle spectrum becomes bimodal. With increasing temperature the cluster spends more and more time in the higher energy shape isomers and above 300 K the “fingerprint” of the ground state shape is hardly visible. At low temperatures the single-particle energy level splittings are manifestly smaller than at higher temperatures. The single-particle energy level splittings increase monotonically with temperature up to about 150 K, where the distributions become bimodal, and the splittings stay essentially constant thereafter. As was established in Refs. [5, 15, 9, 18] above 100 K sodium clusters experience large quadrupole fluctuations. Due to the presence of significant thermal fluctuations, the clusters have, on average, a triaxial shape essentially irrespective of whether in their ground state these clusters are magic or not. The single-particle spectra are characterized by well defined peaks, which indicates that on average the deformation is larger than the size of its fluctuations in this temperature range.

Melting is accompanied also by the appearance of the flicker or $1/f$ -noise. The appear-

ance of a power law spectrum in the cluster dynamics in the very low frequency domain seems in some respects natural. Below the frequency $f \approx \omega_D/(2\pi N^{1/3}) = f_D/N^{1/3}$ (ω_D is the Debye frequency) there are no reasons to expect any cluster specific characteristic frequencies and the spectrum should attain an “universal” character. The normal modes of a cluster are located approximately in the frequency interval $(f_D/N^{1/3}, f_D)$. A power law spectrum is consistent with absence of any specific time scales and thus is “universal”. A white spectrum is a particular example of an “universal” power spectrum, that points to the absence of memory effects. On the other hand, the flicker or $1/f$ -noise is indicative of the presence of memory effects. The onset of the flicker noise is rather abrupt, and, after exceeding a rather narrow excitation energy region, the entire frequency domain below the characteristic cluster normal modes is filled with $1/f$ -noise. In the case of clusters, as in the case of other phenomena, the origin of the flicker noise seems however equally mysterious. Apparently, irrespective of the specifics of the theoretical model used, the flicker noise always emerges [19]. The rules governing the very long-time cluster dynamics are at least surprising, if not totally unexpected. The presence of the flicker noise should leave a strong imprint on a variety of cluster properties, for example on inelastic X-ray or neutron scattering and perhaps on the dynamic cluster properties studied with femtosecond pump and probe laser techniques.

We would like to add as a final comment a general observation, which seems to emerge from our work [5, 17, 20, 18, 19]. It seems to have been generally accepted that phase transitions in clusters are “wide” and not sharp as in the bulk. This however seems to depend on the “order parameter” chosen to gauge these phase transitions. One-body properties, such as different shape variables, and the specific heat mostly seem to behave this way. On the other hand quantities which depend in a direct way on the inter-particle distances, such as relative bond fluctuations, dynamic and static structure factors, individual atom coordination numbers and single-particle electron energies seem to experience relatively sharp changes at a well defined temperature, which in small

sodium clusters is approximately 140 K. A change in temperature from $T = 143$ K to $T = 145$ K leads to dramatic changes. The dynamical structure factor shows an even more pronounced variation. The single-particle spectrum we have discussed above changes its character also rather sharply in a small temperature interval. As the exact values of the single-particle energies depend on the ion relative positions, one can regard the single-particle spectrum as another type of measure of the ion-ion correlations. The fact that structural changes in a finite system can have such a sharp character is apparently a rather unexpected qualitative phenomenon, which certainly adds a new dimension to the cluster physics in particular.

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