

ROLE OF TEMPERATURE IN THE PHYSICS OF METALLIC CLUSTERS

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Abstract

Since the density of states for the ionic degrees of freedom is enormous (when compared with the density of states for the electronic degrees of freedom) the cluster properties at temperatures typical for current experiments are in many respects dominated by ionic entropic effects. Structural properties can be understood in terms of phase transitions in finite systems. One can introduce several types of order parameters, so as to characterize whether a cluster has undergone a phase transition or not. Some parameters can be related to the geometrical properties of a cluster, others to particle correlations, e.g. generalized structure functions, while others can be related to energetic properties, such as specific heat. There are many surprises: melting occurs at significantly lower temperatures than in the bulk; fluctuations in clusters are significantly larger than the corresponding thermal fluctuations in the bulk as well and this is because of the prominent role of the surface effects; the electronic single particle properties and the response to external fields are changed in qualitative ways and the interplay between ionic and electronic degrees of freedom becomes a rather subtle issue. Depending on how one chooses to “look” at a phase transition, or in other words, depending on what quantity is measured, the phase transitions can appear either as rather wide, occurring over a “range of temperatures” or to be incredibly sharp. Surprisingly enough, clusters also show a very peculiar temporal behaviour, the so called $1/f$ -noise at times scale where in principle “nothing remarkable” should happen.

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 mainly 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. [2]. 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” [1] 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 $\epsilon_F \approx 1.6 \dots 4.7$ 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. At the same time, the ionic internal energy is comparable to the energy of the Mie resonace.

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 photoabsorption 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 in theory as a much better candidate. The photoabsorption 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 bulklike 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 assumed to be in quantum chemistry calculations [10]. Jellium model makes perfect sense if the electron wavelength is much larger than the interatomic 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 photoelectron spectra measured by Kit Bowen’s group [11], which show clear nonspherical 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 [10,12–14] 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. In Table I we quote results obtained by different authors for the geometry of ground state configuration of Na_4 , in order to illustrate this particular aspect of the present theoretical understanding. 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, theoretical corrections to essentially any calculational scheme could be of the same order of magnitude as the temperature effects. Thus one can hope for at most a semiquantitative agreement with experiment.

TABLES

TABLE I. Various properties of Na_4 in the ground state ionic configuration (rhombus) calculated in the Hartree-Fock (HF) and Local Density Approximation (LDA) as well as at the Configuration Interaction (CI) level. Calculations were performed with the all electrons (AE) or using pseudopotentials (PP) or effective core potentials (ECP). Results for the distance dependent tight binding model (DDTB) are also included. a is the small diagonal of the rhombus and b is half of the long diagonal of the rhombus in atomic units. ΔE is the energy difference between the ground state and first isomer. The initials of the authors, see Refs. [10,13,14], are indicated.

a (au)	b (au)	ΔE (meV)	Method	Authors
6.14	6.36	89	AE–HF	B–KFK
6.10	6.28	27	ECP–HF	B–KFK
6.23	6.12	140	ECP–CI	B–KFK
6.50	5.60		PP–CI	SP
5.50	5.56	150	PP–LDA	MBC
5.80	5.93		PP–LDA	MMRB
5.82	5.68		AE–LDA	GCKS
5.86	5.38	60	DDTB	PS

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 electronic properties carry information about different static ionic configurations and are essentially insensitive to ionic dynamics. What one sees while measuring 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 [5,14,20,18]. The switching time from one shape isomer to another is rather long, from a few picoseconds at high temperatures to hundreds of picoseconds at low temperatures [20]. 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 potential barriers between shape isomers control the switching time. This aspect becomes an issue in theory only when ionic configurations are followed in real time, as in molecular dynamics for example. This explains the usual need for relatively long trajectories of the order of a nanosecond or so, if one aims at a reliable description of the various statistical weights.

Since the energy scale characteristic for the ionic degrees of freedom is relatively small, a huge phase space becomes available upon increasing the temperature of the cluster. These entropic effects show up in rather drastic structural changes and, without being extremely pedantic concerning the adequacy of the terminology, one can characterize these changes as phase transitions in finite systems.

With increasing temperature, the clusters go first through a glassy/molten or fluctuating state (1500–300 K) and eventually become totally liquid (above 300 K). 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 become rather soft/compressible. In contradistinction with noble gas clusters [16], the melting and boiling do not seem to be a geometric or particle number effect and the same behaviour is observed for all the clusters we have studied [5,9,17–19]. The thermal expansion properties of these 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. Thermally induced rotation is never fast enough to lead to any rotationally induced effects and in the temperature range studied, one can safely characterize these sodium clusters as rigid bodies with respect to rotational degrees of freedom. The onset of the new phases can be observed in both thermodynamic and geometric properties of the clusters, which have a strong temperature dependence.

These facts might play a quite significant role in explaining the red shift of the Mie plasmon in sodium clusters and its width [4,2,7]. In the jellium calculations, routinely used in describing the optical response of sodium clusters, the bulk density for the jellium is assumed. Besides melting and boiling in a quite different way than the bulk, sodium clusters seem to

have also a rather distinct thermal expansion behaviour. 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 (and significantly larger for higher temperatures), already of the right order of magnitude to explain the observed red shift of the Mie plasmon [5,9]. At the same time, at these temperatures the volume distribution of the clusters have a quite sizeable width $\Delta r/r \approx 0.04...0.07$ (and significantly larger at higher temperatures), which can explain at least part of the width of the plasmon [5,9].

The features in measured photoelectron spectra of small alkali clusters [11] and mentioned above can also be understood within such a picture. At temperatures of about 100K, the cluster has enough thermal energy to begin exploring higher energy isomers and the single-particle spectrum becomes bimodal. In Ref. [?] (and to some extent in Ref. [?]) the existence of shape isomers manifested itself at somewhat higher temperatures, around 140 K or so, which is due to a higher stiffness of the potential energy surface in that case. 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 and stay essentially constant thereafter. In Fig. 1 we present the single-particle electron energy density $\rho_i(\varepsilon)$ for each occupied single-particle level $i = 1, \dots, n/2$ (n is the number of electrons and $\int \rho_i(\varepsilon)d\varepsilon = 2$ where the factor 2 accounts for the spin degeneracy) in Na₈ and Na₂₀ respectively in the temperature range $T=100, \dots, 300$ K. For the temperature range when some of the single-particle levels show a bimodal pattern, around 150 K, the width of those distributions attain a maximum. As was established in Refs. [5,14,9,18] 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 fact that the single-particle spectra are characterized by well defined peaks is indicative of the fact that on average the deformation is larger than the size of its fluctuations in this temperature range, a quite nontrivial situation. Only at higher temperatures are these structures expected to be washed out by the thermal fluctuations.

If the excitation energy is sufficiently high, so as to allow isomer hopping, a cluster generally “melts”. This is accompanied almost immediately by the appearance of the flicker or $1/f$ -noise. The appearance of a power spectrum in the cluster dynamics in the very low frequency domain seems 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 [21]. 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. One is tempted to even call this onset a phase transition. The presence of the flicker noise thus only signals that a cluster has already “melted”, but cannot serve as a finer probe of the cluster configuration, e.g. cannot indicate what the temperature of the cluster is or what is the cluster structure. (At very high temperatures a cluster boils and eventually becomes a gas and thus as a matter of fact it does not exist anymore, except as a very rapidly decaying system. Such temperatures are less interesting from the point of view of cluster structure and we do not discuss them here.) The flicker noise is observed only when isomer hopping occurs. In the case of clusters thus, as in the case of other phenomena, the origin of the flicker noise seems equally mysterious [21]. 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 inelastic X-ray or neutron scattering [18] and most likely 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 [5,17,19,18,20]. 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, mostly seem to behave this way. On the other hand quantities which depend in a direct way on the interparticle 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.

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